Effect of Inert Matrices on C$_2$H$_2$ and CO$_2$ Molecules

V.1 Introduction

Understanding the nature of weak intermolecular interaction involved in molecular recognition still remains a challenging problem. Such weak interactions can be explored experimentally by a variety of spectroscopic techniques. Even then there are experimental limitation in generating and studying large neutral clusters. A brief review on experimental methods for exploring clusters is furnished in Section 1.4. The two techniques generally used for generating cold, isolated molecules for the spectroscopic studies are the effusive and the supersonic jet expansion [1-4]. The samples thus prepared can be probed by any of the spectroscopic techniques such as infrared (IR) spectroscopy [5, 6], UV-visible absorption, laser induced fluorescence [7], electron spin resonance [8-10] and Mössbauer spectroscopy (cf. Chapter I).

In spite of several advantages of the matrix isolation (MI) technique over the gas phase technique [11], the interaction of the solid matrix medium with the probe molecule cannot, in general, be neglected and sometimes it can create serious problems in interpreting the spectra of the probe molecule. The present Chapter addresses this well known problem in the literature called the matrix effect. This weak matrix-probe molecule interaction drags the spectral peak either to red or blue regions relative to free molecular frequency mode depending on the nature and strength of interaction. Also, in none of the above spectroscopic techniques, special attention is paid to the effect of matrix on the spectra. Sheppard [12] suggested that this frequency shift, $\Delta \nu$ is constant for a particular matrix. But the experimental observation seems to be much more dependent on the nature of both the matrix as well as the probing molecule. Kirkwood [13] formulated an equation connecting $\Delta \nu$ and the dielectric constant of the matrix medium. Sambursky and Wolfsohn [14] discussed the effect of fluorescence of anthracene in terms of Onsanger’s dielectric theory. There have been attempts for correlating $\Delta \nu$ with oscillator strength by employing a modified equation. Breit et al. [15] tried to correlate $\Delta \nu$ with the absorption coefficient in the case of IR spectra. Earlier works aiming at the quantification of the magnitude of $\Delta \nu$ due to the solvent effects were based on macromolecular or thermodynamic parameters,
which include the refractive indices of the solvent [16], dielectric constants [17-19],
solubility parameters [20] or Taft parameters [21], pair potential of the matrix and host
molecule [16], the interaction energy [22] or the square root of matrix critical temperature
[23]. Even though there are attempts to quantify the frequency shifts due to matrix effect, a
reliable quantum mechanical study of these matrixes on the spectra is conspicuous by its
absence from the literature.

Thus there is a genuine need to quantify the effect of matrix on the IR spectra. The
magnitude of frequency shift or the experimental half-band width provides a method to
distinguish between dispersion and hydrogen bonding interaction. The solvent effect
produced due to the hydrogen bonding interaction on the combination band is typically 25
times larger than that due to van der Waals interactions [24, 25]. The qualitative
understanding and quantification studies on the effect of matrix on the spectra [26] would
firstly help in segregating the effect of matrix on the experimental spectrum and secondly,
it may assist in obtaining more realistic empirical parameters for molecular simulations.

This Chapter presents a systematic quantitative study on the effect of inert matrices on
carbon dioxide and acetylene molecules. Spectroscopic studies on CO$_2$-Ar complex began
with the microwave work of Steed et al. [27] and the geometric parameters were found to
be in good agreement with the T-shaped CO$_2$-Rg clusters. Later Sharpe et al. [28] and
Randall et al. [29] studied the periodic trends in the $v_4$ ro-vibrational band of the complex,
still preserving the T-shaped geometry for these kinds of complexes of CO$_2$ with Ne, Ar,
Kr, Xe. Fraser et al. [30] studied the sub-Doppler IR spectra of CO$_2$-Ar in the Fermi-diad
region of CO$_2$, viz. 3613- 3715 cm$^{-1}$ using opto-thermal molecular beam color-center laser
spectrometer. Microwave spectra of CO$_2$-Rg (Rg = Ne, Ar, Kr, Xe) complexes show that
the lower Fermi components are free of perturbation, whereas the upper components are
perturbed and the reported geometry is consistent with T-shaped complex. CO$_2$-Ar clusters
show a red shift (1.1cm$^{-1}$) relative to the free CO$_2$ in the band origin. Studies on these
systems enabled the development of empirical potential for clusters viz. Hough and Howard
potential [31]. A theoretical and experimental investigation on the vibrational relaxation
and excitation in CO$_2$-Ar has also been reported and the results are in agreement with the
earlier studies, validating the predominant existence of T-type of CO$_2$-Ar complexes [30].

A preliminary qualitative and quantitative understanding on these smaller CO$_2$-Ar
clusters has directed the attention of theoreticians as well as experimentalists towards larger
clusters. Xu et al. [32] reported a microwave study on larger clusters showing a T-shaped
CO$_2$(Ar)$_2$. Sperhac et al. [33] studied CO$_2$(Ar)$_2$ complexes using direct absorption supersonic IR spectroscopy and also with dynamics simulations. Their calculations revealed that these of complexes show a red shift in the $v_3$ region of the CO$_2$ molecule. CO$_2$(Ar)$_n$ complexes preferentially form a T-shaped geometry to show binding to the central carbon atom and the corresponding site gets saturated with five argon atoms around it. Similarly, the frequency shifts is also show saturation. Further, their calculations show that the primary solvation sphere will be completed with 17-Ar atoms surrounding CO$_2$ molecules. Recently Vigasin et al. [34] tried to comprehend all the Raman and IR spectroscopic experimental works on Rg-CO$_2$ complexes and tried to offer an explanation of the frequency shifts on the basis of the matrix critical temperature. It was reported that the CO$_2$-Ar, CO$_2$-Kr, CO$_2$-Xe complexes show bathochromic (red) shifts, while the CO$_2$-He, CO$_2$-Ne and CO$_2$-N$_2$, CO$_2$-CO$_2$ complexes show hypsochromic (blue) shift. Considering the above, an *ab initio* investigation on the effect of inert argon matrix seems worthwhile.

Theoretical investigations and experimental MI studies on acetylene show that it can act as a hydrogen bond acceptor and as well as donor. *Ab initio* as well as MI studies have revealed situations in which acetylene acts as a hydrogen bond acceptor through its $\pi$ bond *i.e.* with ($\pi$...H-X interactions), *viz.* for H-X = HCl [35], H$_2$O [36], CHCl$_3$[37], C$_2$H$_4$[38], C$_6$H$_6$ [39]. Acetylene acts also as a hydrogen bond donor through C-H...$\pi$ interaction with C$_2$H$_2$ [36], C$_2$H$_4$ [38] and C$_6$H$_6$ [39]. Hence understanding theoretically and experimentally the effect of inert argon and nitrogen matrices on this molecule is worthwhile.

This Chapter reports a combination of our theoretical works with the detailed experimental investigations from the research group of Dr. K.S. Viswanathan at IGCAR, Kalpakkam of the effect of matrix on the CO$_2$ and C$_2$H$_2$ molecules, as well as the hydrogen bonded acetylene-methanol complex. In view of this, the present Chapter firstly focuses on such a study of the structure and energetics of CO$_2$ (Ar)$_m$, C$_2$H$_2$ (Ar)$_n$ and C$_2$H$_2$ (N$_2$)$_m$ clusters along with a comparison with experiment. Secondly, *ab initio* studies on the geometry and energetics of clusters along with the effect of inert argon matrix on the CO$_2$ and C$_2$H$_2$ probe molecules *via* the asymmetric stretching frequency shifts are explored. Also, the presentation attempts to address the questions such as: How strong is the interaction of a matrix with a molecule? Could the experimentally observed IR shifts be
quantified theoretically? Can a particular matrix play a role in stabilizing a complex than some other?

V.2 Computational Method

The geometry optimizations of $C_2H_2(\text{Ar})_n$ and $C_2H_2(N_2)_m$ clusters have been carried out at the B3LYP and MP2 levels of theory with analytical gradients, using a 6-31++G(d) basis-set. The $CO_2(\text{Ar})_n$ clusters were optimized at MPWB1K level of theory using 6-31++G(2d) basis set to obtain energy minima corresponding to a variety of complexes. One of the most widely used hybrid density functional in the literature for exploring structure, energetics and properties of weakly interacting species is B3LYP. Moreover, the MPWB1K functional is recommended in the literature for exploring thermochemistry, thermochemical kinetics, hydrogen bonding and weak interactions [40]. The vibrational frequencies were calculated at these respective level and basis set and none of the computed harmonic vibrational frequencies were found to be imaginary. The normal frequencies were visualized by using the in-house developed package [41] UNIVIS-2000. The basis set superposition error (BSSE) for the stabilization energy was corrected by the Boys-Bernardi [42] counterpoise method. The MESP topographical analysis carried out to locate the critical points. The MESP minimum is a signature of the basicity of a species [43]. The acidity of a species can be interpreted in terms of the MESP minimum on the zero flux surface of the corresponding conjugate base [43].

The effect of increasing the number of matrix molecules or atoms complexed with a probe molecule is studied with a view to investigate how the probe bending and stretching frequencies are shifted. Furthermore the MESP minimum of the complexes is calculated for appraising the effect of matrix on the basicity of probe molecule because the deepest MESP minimum is a quantitative measure of the basicity. In the following sections, first we discuss the experimental spectra of CO$_2$ in argon matrix, and $C_2H_2$ in (i) argon, (ii) a mixture of argon and nitrogen, and (iii) nitrogen matrices. Further a comparison of the CO$_2$ and $C_2H_2$ asymmetric stretching ($v_3$) and bending ($v_5$) regions of $C_2H_2$ spectra is performed between the gas phase and the theoretical ones. Secondly, we explore how the MESP minimum of acetylene is affected by the matrix viz. in $C_2H_2(\text{Ar})_n$ and $C_2H_2(\text{N}_2)_m$ complexes and how this enables in stabilizing H-π acetylene-methanol complex in $N_2$ matrix but not in Ar matrix.
V.3 The Effect of Argon Matrix on Carbon Dioxide Molecule

In order to quantify the effect of inert argon matrix on the probe CO$_2$ molecule, the frequency shifts in the asymmetric stretching region of the later are explored. Hence a large number of CO$_2$(Ar)$_m$ clusters with $m = 1$ to 12 were generated and optimized at MPWB1K/6-31++G(2d) level of theory. We have performed these calculations only at this level of theory to tackle large CO$_2$(Ar)$_m$ clusters and its frequency evaluations.

![Figure V.1 Geometries of CO$_2$(Ar)$_m$ with $m=1, 2, 4, 5, 6, 8, 8$ and $12$ at MPWB1K/6-31++G(2d) level of theory with the distances are in Å. See text for more details.](image)

The most stable complexes are depicted in Fig. V.1, typical nearest C...Ar distances being 3.7 Å. The most stable CO$_2$(Ar)$_5$ complex geometry at the MPWB1K level is in agreement with the MD simulation reported by Severson et al. [45] The interaction energy at MPWB1K level of theory shows that, in CO$_2$(Ar)$_m$ clusters, argon atoms preferably has a predominant interaction with carbon over oxygen atom of CO$_2$ molecule. This is supported by the experimental observations of Steed et al. [27] and MD simulations reported by Severson et al. [45]. The reported CO$_2$-Ar structural parameters of this complex are defined in terms of $R$, the distance between carbon and argon atoms and $\theta$ is the $\angle O = C \cdots O$. Steed et al. [27] reported the following geometrical parameters, $R = 3.5$ and $\theta = 82.5^\circ$ and
the geometry belongs to $C_{2v}$ point group. The corresponding values, at MPWB1K level of
theory, these structural parameters are $R = 3.7$ and $\theta = 90.0^\circ$. Even though the geometries
of smaller $\text{CO}_2\text{(Ar)}_m$ clusters with $m = 1$ and $2$ are in agreement with the current
observations at MPWB1K level of theory, the higher clusters reported by Boyukata, [44]
with $m = 3$ to $7$ show a preferential interaction of the argon atoms with the oxygen atom of
$\text{CO}_2$ molecule. This disagreement in the geometries may be due to the empirical model
potential employed in the MD simulation. The BSSE counterpoise correction does not
seem to alter the relative trend in interaction energies of $\text{CO}_2\text{(Ar)}_m$ clusters. The BSSE
correction for $\text{CO}_2\text{(Ar)}_2$ and $\text{CO}_2\text{(Ar)}_4$ respectively are 0.09 and 0.60 kcal/mol, which does
not alter the trends in the interaction energies. To check the consistency of these results at
this DFT functional, we have performed these calculations again at MPW1B95/6-31++G(2d)
level of theory. Both these functionals show similar trends in structure and
energetics. Even though the interaction energy at DFT functionals are small compared to
that at MP2 level, the BSSE corrected MP2 ones are comparable with the former.
Moreover, the trends in interaction energies and frequency shifts at MP2 are consistent with
MPWB1K level of theory.

Table V.1 The $\text{CO}_2\text{(Ar)}_m$ clusters with $m = 1$ through $8$ at MPWB1K/6-31++G(2d) level of theory,
geometry, energy (in a. u.), interaction energy ($\Delta$E) (in kcal/mol), unscaled C-O frequencies, $\nu$ (in
$\text{cm}^{-1}$) and the corresponding intensities (in $\text{km} \text{ mol}^{-1}$) are given in parentheses. See text for more
details.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Energy ($\Delta$E)</th>
<th>$\nu$ (Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2\text{(Ar)}$ [M-I]</td>
<td>-716.10288 (-0.20)</td>
<td>2495.3 (742.6)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_2$ [M-II]</td>
<td>-1243.68280 (-0.41)</td>
<td>2494.5 (705.8)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_3$ [M-III]</td>
<td>-1771.26280 (-0.67)</td>
<td>2492.2 (678.4)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_4$ [M-IV]</td>
<td>-2298.84289 (-0.99)</td>
<td>2494.2 (626.8)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_5$ [M-V]</td>
<td>-2826.42330 (-1.51)</td>
<td>2495.5 (614.2)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_6$ [M-VI]</td>
<td>-3354.00300 (-1.59)</td>
<td>2490.3 (591.4)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_7$ [M-VII]</td>
<td>-4409.16417 (-2.85)</td>
<td>2490.1 (676.4)</td>
</tr>
<tr>
<td>$\text{CO}_2\text{(Ar)}_8$ [M-VIII]</td>
<td>-4409.16324 (-2.27)</td>
<td>2493.7 (850.7)</td>
</tr>
</tbody>
</table>

It has been observed that, with an increase in the percentage of argon in the matrix,
the asymmetric stretching frequency shifts to a lower wave number region [45]. The graph
of number of Ar atom vs frequency shift [45] of $\text{CO}_2\text{(Ar)}_m$ clusters reaches a saturation
region beyond $m \leq 5$, it corresponds to a saturation of the central carbon atom of $\text{CO}_2$
molecule. The interaction energy of \( \text{CO}_2(\text{Ar})_3 \) at MPWB1K level is -1.51 kcal/mol and that of \( \text{CO}_2(\text{Ar})_6 \) is -1.59 kcal/mol. The corresponding calculated frequencies are reported in Table V.1 also shows a saturation in frequency shift in \( \text{CO}_2(\text{Ar})_m \) clusters with \( m \geq 5 \). Fig. V.5 displays the geometries of most stable \( \text{CO}_2(\text{Ar})_m \) with \( m = 1 \) to 12. Table V.1 reports the frequencies of the \( \text{CO}_2(\text{Ar})_m \) clusters through \( m = 1 \) to 8 and the values show an increasing red frequency shifts from 0.7 through 5.6 cm\(^{-1}\) with number of argon atoms. This direction of shifts are in agreement with the earlier dynamics studies of Severson [45, 44] and direct supersonic FTIR experimental studies of Thiévin et al. [46].

The present \textit{ab initio} geometries and frequency shifts of the most stable \( \text{CO}_2(\text{Ar})_m \) clusters with \( m = 6 \) through 8 show a good agreement in MD simulation [45,44]. This red shifted asymmetric C-O stretching frequency in \( \text{CO}_2(\text{Ar})_m \) clusters can be justified on the basis of MED values at the C-O BCP. This BCP in \( \text{CO}_2(\text{Ar})_m \) clusters shows a slight decrease in MED with increasing number of argon atoms. The respective values for \( m = 6 \) and 8 are 0.47520 and 0.47519 a. u. and for \( \text{CO}_2 \) molecule is 0.47524 a. u. This decrease (~0.00004 a.u.) in MED, however small, indicates a weakening of both C-O bond strength and hence a red shift in frequency. These geometries show that beyond the saturation of the central carbon atom, the rest of the argon atoms cluster around the oxygen atom. MD simulation shows that the 17-argon atoms will saturate the first interaction or solvation sphere of the probe \( \text{CO}_2 \) molecule [45, 44]. This observation is indeed in agreement with calculations at MPWB1K level of theory.

V.4 Effect of Argon and Nitrogen Matrices on Acetylene Molecule

The first subsection discusses the experimental spectrum of acetylene in different proportions of matrices and is followed by the theoretical structure, frequencies at MPWB1K level of theory and a comparison with experiment.

V.4.1 Experimental Spectrum of Acetylene in Inert Matrices

The experimental spectra of acetylene (C\(_2\)H\(_2\)) in different proportions of matrices were carried out as a part of collaborative work with Drs. Sundararajan and Viswanathan, at IGCAR Kalpakkam. A brief description of this matrix isolation infrared (MI-IR) experiment [38] has been presented in Section I.4.5. Fig. V.2 shows the matrix-isolated spectrum of C\(_2\)H\(_2\) that was deposited in varying amounts of Ar and N\(_2\) matrices over the
regions 3312-3262 cm\(^{-1}\) (Block I) and 780-720 cm\(^{-1}\) (Block II), which correspond to the C-H asymmetric stretching \(v_3\) and bending \(v_5\) regions of acetylene submolecule. Fig. V.2A and Fig. V.2D show the spectra obtained in pre-annealed pure Ar and N\(_2\) matrices respectively (i.e. soon after deposition). On the other hand Fig. V.2B through D shows the spectra as the N\(_2\) concentration in Ar were varied progressively from 0.001% to 0.05%. Fig. V.2A (Block I) shows two strong absorptions of C\(_2\)H\(_2\) in the Ar matrix at 3288.9 and 3302.8 cm\(^{-1}\), which have been assigned to the components of a Fermi diad involving the \(v_3\) mode and a combination band \((v_2+v_4+v_5)\) respectively [47-50]. The Fermi resonance is a general name given to the strong interaction between any overtone or combination mode with the fundamental one. This may happen when two vibrational excitations result in states with same symmetry. Moreover, this has an effect on the intensities of both the transitions. The weak over tones borrows intensity from the strong fundamental mode. This phenomenon is first explained by Enrico Fermi in the vibrational spectrum of carbon dioxide and is known in his name.

Table V.2 Experimental frequencies (in cm\(^{-1}\)) of the upper and lower Fermi diad as well as the bending mode of C\(_2\)H\(_2\) in the gas phase \(v_3\) [see Ref. 44], in argon matrix \(v_{Ar}\), and in nitrogen matrix \(v_{N_2}\). The corresponding frequency shifts with respect to the gaseous phase are given in the last column. Here \(^*\)UFD (Upper Fermi Diad) and \(^*\)LFD (Lower Fermi Diad).

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>Gas Phase (v_3)</th>
<th>Ar matrix (v_{Ar})</th>
<th>N(<em>2) matrix (v</em>{N_2})</th>
<th>(\Delta v_{Ar}) = ((v_{Ar} - v_3))</th>
<th>(\Delta v_{N_2}) = ((v_{N_2} - v_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_3)</td>
<td>3294.8424</td>
<td>3302.80</td>
<td>3311.00</td>
<td>8.00</td>
<td>16.20</td>
</tr>
<tr>
<td></td>
<td>3281.9048</td>
<td>3288.90</td>
<td>3282.60</td>
<td>7.00</td>
<td>0.70</td>
</tr>
<tr>
<td>(v_2 + v_4 + v_5) (^{*})</td>
<td>730.3314</td>
<td>736.80</td>
<td>742.10, 747.40</td>
<td>6.50</td>
<td>11.80, 17.10</td>
</tr>
</tbody>
</table>

Table V.2 gives, in a nutshell, the frequencies of \(v_3\) and \(v_2 + v_4 + v_5\) mode of C\(_2\)H\(_2\) in the gas phase, Ar and N\(_2\) matrices, and the corresponding frequency shifts with reference to the gas phase value. A comparison of these diads in the Ar matrix with the gas phase values indicates blue shifts of 8.0 cm\(^{-1}\) for the upper and 7.0 cm\(^{-1}\) for the lower Fermi diads. As the concentration of N\(_2\) is increased in the Ar matrix, as shown in Fig.V.2B through V.2D, Block I, the diads featuring at 3288.9 and 3302.8 cm\(^{-1}\) are slightly red shifted to 3286.5 and 3300.9 cm\(^{-1}\) (Fig. V.2C, Block I), with the corresponding magnitudes of frequency shifts
are being 2.4 and 2.0 cm\(^{-1}\) respectively. Fig. V.2D, Block I shows the asymmetric stretching mode of the \(\text{C}_2\text{H}_2\) in pure \(\text{N}_2\) matrix with the lower Fermi diad at 3282.6 cm\(^{-1}\) and the upper Fermi diad vanishing completely. The former is red shifted by 6.30 cm\(^{-1}\) with reference to that in \(\text{Ar}\) matrix.

\[ \begin{align*}
\text{Block I} & \quad \text{Block II} \\
3300.9 & \quad 747.4 \\
3287.9 & \quad 742.1 \\
3282.6 & \quad 736.3 \\
3312 & \quad 736.8 \\
3286.5 & \quad 742.1
\end{align*} \]

Figure V.2 The experimental spectrum: (Block I) asymmetric stretching mode (Block II) bending mode of acetylene with increasing percentage of \(\text{N}_2\) in the matrix (A through D).

In Fig. V.2A, Block II shows the \(\nu_5\) bending mode of \(\text{C}_2\text{H}_2\) in \(\text{Ar}\), which occurs as a single sharp feature at 736.8 cm\(^{-1}\), that is blue shifted by 6.5 cm\(^{-1}\) with respect to gas phase \(\nu_5\) mode of \(\text{C}_2\text{H}_2\). As the concentration of \(\text{N}_2\) is increased (in Fig. V.2C and D, Block II), the doubly degenerate bending mode at 736.8 cm\(^{-1}\) splits into 736.3 and 742.1 cm\(^{-1}\). In pure nitrogen matrix, (Fig. V.2D, Block II) shows the lifting of degeneracy and the doublet peaks occurs at 742.1 and 747.4 cm\(^{-1}\) and is blue shifted by 11.8 and 17.1 cm\(^{-1}\) from the gas phase frequency (cf. Table V.1). In the \(\text{N}_2\) matrix, experimental spectrum shows that the double degeneracy of the \(\nu_5\) bending mode is being lifted up. The feature is again blue-shifted in this matrix with the shift being larger than that observed in the \(\text{Ar}\) matrix when compared with the gas phase frequency.
V.4.2 Theoretical Structures and Energetics of Complexes

In order to understand the behavior of the IR spectra of acetylene separately in Ar, N₂ matrices as well as in Ar/N₂ mixed matrices, calculations are carried out at MP2/6-31++g(d) level of theory for C₂H₂ as well as C₂H₂(Ar)ₙ, C₂H₂(N₂)ₙ and C₂H₂(N₂)ₙ⁻ (Ar)ₙ complexes. The MP2 level of theory is chosen because of the small size of the systems. For setting up the initial geometries, it is found useful to utilize the electrostatic properties of individual molecules. The MESP CP’s of C₂H₂ appear as a degenerate ring around the C≡C bond. The nitrogen molecule shows a two-lobed negative isosurface, corresponding to the lone pairs of nitrogen molecule. This MESP picture leads to two kinds of possible acetylene–nitrogen complexes, one with the negative MESP cloud of N₂ interacting with the positive hydrogen of acetylene and the second one with the negative acetylene degenerate ring interacting with the N≡N region of nitrogen. Based on this electrostatic picture, a large number of starting geometries of C₂H₂(N₂)ₙ complexes have been generated and subjected to ab initio geometry optimization. The MP2/6-31++g(d) level optimized structures show both types of complexes, preferentially the former one. The corresponding optimized geometries of C₂H₂(N₂)ₙ are displayed in Fig. V.3[X, XIII, XV].

Figure V.3 The geometries of C₂H₂(Ar)ₙ [VI and II], C₂H₂(N₂)₂ (Ar)ₙ₁₀ [IX] and C₂H₂(N₂)₂₆ [X, XIII and XV] complexes optimized at MP2/6-31++G(d) level. All distances are in Ångstroms. See Table V.3 for corresponding frequencies and energies.
Table V.3 reports the stabilization energies, the vibrational frequencies along with the corresponding intensities for the $C_2H_2(Ar)_n$, $C_2H_2(N_2)_m$ and $C_2H_2(Ar)_n(N_2)_m$ complexes. It is clear from this Table that with the increasing number of $N_2$ molecules in the complex, the stabilization energy also increases. The MESP around the argon atom is spherically symmetric and previous potential energy surface (PES) studies of $C_2H_2(Ar)_m$ complexes [50] indicate that an angular approach of the argon atom towards the hydrogen atom of $C_2H_2$ is preferred over the $T$-configuration [49]. Based on this information, several initial geometries of the $C_2H_2(Ar)_m$ complexes were generated and subjected to \textit{ab initio} level geometry optimization. The nature of the MP2/6-31++G(d) level optimized complexes also corroborates the above mentioned PES studies. The corresponding optimized geometries of $C_2H_2(Ar)_m$ are displayed in Fig. V.3[VI and II]. The geometries show linear- as well as angular approach of the argon atoms towards the hydrogen of acetylene molecule. The stabilization energy indicates that the more polarizable nitrogen molecule interacts preferentially with the acetylene hydrogen than the less polarizable argon atom. Hence in a mixture of both argon and nitrogen matrix, the nitrogen preferentially binds to the acetylene linearly and argon atoms then adopts an angular configuration. Fig. V.3[IX] displays the geometry of a mixture of $N_2$ and $Ar$ atoms complex with acetylene. From Fig. V.3 and Table V.3, it is clear that argon atoms show a preferential binding towards the hydrogen of $C_2H_2$, which is in agreement with the PES studies of $C_2H_2(Ar)$ complex [44].

**V.4.3 Comparison of Experimental and Theoretical Spectra**

Inert gases are known to crystallize in a face-centered cubic lattice. The guest molecules are normally trapped in substitutional sites, except the very small molecules or atoms, which can be trapped in interstitial sites. When the guest is trapped in a substitutional site, it may be trapped in a single substitutional site, provided the cavity produced is large enough to accommodate the guest molecule. In such a case, the guest would have twelve nearest neighbors. However, a larger number of molecules may need to be accommodated in substitutional sites involving the removal of two or more host atoms, in which case there is a progressive increase in the number of nearest neighbors. The picture is further complicated if one notes that often times the guest may be trapped in dislocation sites. Even in a single substitutional site, the number of nearest neighbors (\textit{i.e.}
12) could be quite large for accurately modeling the interactions between the guest and the host, using *ab initio* procedures. In the present work, the matrix environment is reasonably well mimicked and the calculations are performed on the clusters of size close to the first co-ordination sphere of the acetylene molecule, *viz* up to 10 argon atoms and 8 nitrogen molecules. Thus, it is expected that the present work sheds light on the nature of interactions existing between the guest and the host and offers explanation for the experimental observations. The scaling factor for each mode can be calculated by comparing the experimental and theoretically equivalent clusters. The clusters we dealt in our calculations are almost near to the first co-ordination sphere. In view of this, we avoid using scale factors and report unscaled theoretical IR frequencies. The relative trends in magnitude of the frequencies are more meaningful in the present work than their absolute values.

**Table V.3** The theoretical stabilization energies (in kcal/mol); $v_1$ and $v_5$ normal mode frequencies (in cm$^{-1}$) and the corresponding intensities (in D$^2$/u Å$^2$) of C$_2$H$_2$ in C$_2$H$_2$ molecule [I], C$_2$H$_2$ (Ar)$_n$ [II to VI], C$_2$H$_2$(N$_2$)$_2$ (Ar)$_p$ [VII to IX] and C$_2$H$_2$ (N$_2$)$_m$ complexes [X to XV] at MP2/6-31++G(d) level of theory. Energies in a. u. at MP2/6-31++G(d) level of theory; C$_2$H$_2$ = -77.07330, Ar = -526.91310 and N$_2$ = -109.26190.

<table>
<thead>
<tr>
<th>Formula [Structure Number]</th>
<th>$\Delta E$ (kcal/mol)</th>
<th>$v_1$ (cm$^{-1}$) (Intensity)</th>
<th>$v_5$ (cm$^{-1}$) (Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_2$ [I]</td>
<td>0.00</td>
<td>3461.1 (1.96)</td>
<td>734.1 (2.83), 734.2 (2.83)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (Ar)$_2$ [II]</td>
<td>-1.08</td>
<td>3468.5 (3.01)</td>
<td>759.8 (2.57), 759.9 (2.57)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (Ar)$_4$ [III]</td>
<td>-2.22</td>
<td>3472.3 (3.03)</td>
<td>762.0 (2.65), 760.6 (2.40)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (Ar)$_6$ [IV]</td>
<td>-3.70</td>
<td>3474.1 (3.04)</td>
<td>764.5 (2.22), 767.2 (2.73)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (Ar)$_8$ [V]</td>
<td>-5.80</td>
<td>3472.4 (2.11)</td>
<td>707.1 (2.83), 715.5 (2.79)</td>
</tr>
<tr>
<td>C$_2$H$<em>2$ (Ar)$</em>{10}$ [VI]</td>
<td>-9.80</td>
<td>3487.3 (3.27)</td>
<td>769.2 (2.23), 776.7 (2.44)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_2$ (Ar)$_6$ [VII]</td>
<td>-12.21</td>
<td>3464.6 (2.39)</td>
<td>734.9 (2.76), 740.8 (2.77)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_2$ (Ar)$_8$ [VIII]</td>
<td>-15.31</td>
<td>3468.1 (4.43)</td>
<td>769.6 (2.33), 777.3 (2.70)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$<em>2$ (Ar)$</em>{10}$ [IX]</td>
<td>-19.05</td>
<td>3475.3 (4.67)</td>
<td>786.2 (2.45), 786.4 (2.42)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_4$ [X]</td>
<td>-2.65</td>
<td>3458.1 (4.41)</td>
<td>766.2 (2.57), 766.3 (2.57)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_4$ [XI]</td>
<td>-7.47</td>
<td>3454.8 (2.27)</td>
<td>733.7 (3.40), 742.3 (2.35)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_4$ [XII]</td>
<td>-7.43</td>
<td>3449.9 (4.61)</td>
<td>767.2 (2.70), 773.5 (2.32)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_4$ [XIII]</td>
<td>-12.75</td>
<td>3450.8 (3.96)</td>
<td>754.9 (2.83), 765.8 (2.36)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_4$ [XIV]</td>
<td>-17.82</td>
<td>3449.2 (4.57)</td>
<td>757.8 (2.94), 765.6 (2.50)</td>
</tr>
<tr>
<td>C$_2$H$_2$ (N$_2$)$_4$ [XV]</td>
<td>-10.23</td>
<td>3443.9 (4.67)</td>
<td>767.7 (2.67), 768.5 (2.68)</td>
</tr>
</tbody>
</table>
Acetylene in Argon matrix: Table V.3 reports the theoretical $v_3$ stretching frequency of $C_2H_2(Ar)_n$ complexes [II through VI], with $n$ going from 2 to 10. The computation does not include anharmonicity effects due to which the Fermi diads observed in the experiment could not be modeled. To this extent, the computed asymmetric stretching frequency under harmonic approximation can at best be taken to be a good approximation to the experimental lower Fermi diad ($v_3$). Notwithstanding this limitation, relative trends in the changes of the theoretical and experimental vibrational frequencies of $C_2H_2$ as a result of interactions with Ar and N$_2$ matrices can still be compared. The theoretical $v_3$ frequencies of $C_2H_2(Ar)_n$ complexes [II through VI] in Table V.3 show a progressive blue shift from 7.4 cm$^{-1}$ to 26.2 cm$^{-1}$ for sizes 2 to 10, relative to the $C_2H_2$.

In a typical matrix experiment, it is difficult to estimate the number of Ar atoms directly coordinated or surrounded to the acetylene molecule, to make any quantitative comparison with the computations. However, it is reassuring to observe from the Table V.3, the computations reproduce the direction of shifts correctly i.e. blue shift irrespective of the number of Ar atoms that are coordinated. This is in agreement with the experimental observation in Fig. V.2(Block I). The calculated frequencies of $C_2H_2 (Ar)_n$ complexes show non-degenerate $v_5$ modes and the most intense peak shows a blue shift of 35.81 and 42.61 cm$^{-1}$ when $n$ goes from 2 to 10 when compared with the $v_5$ mode of $C_2H_2$ molecule. The experimental spectrum depicted in Fig. V.2(Block II), though the $v_5$ mode is seen to split, but the magnitude of splitting is very small in argon matrices.

Acetylene in Nitrogen matrix: Table V.3 reports the calculated $v_3$ stretching frequency of $(C_2H_2) (N_2)_m$ complexes [X through XV] and the respective frequency shift is from 3.00 to 11.9 cm$^{-1}$ when $m$ goes from 2 to 8. When compared with the gas phase $C_2H_2$ spectrum with that in nitrogen matrix there is a blue shift of only 0.7 cm$^{-1}$. In the $v_5$ bending region the doubly degenerate mode is lifted with increasing nitrogen molecules. This is similar to what we observe experimentally. The difference in the magnitude of the degeneracy lifted in the bending frequencies increases progressively as 0.16, 1.46, 2.77 and 8.38 cm$^{-1}$ for $n = 2, 4, 6$ and 8 respectively in $C_2H_2(Ar)_n$ complexes and these magnitudes are less than those for the corresponding $C_2H_2(N_2)_n$ [0.08, 8.63, 10.85, 7.88 cm$^{-1}$] complexes. This observation is also borne out by experiments if one notes that the experimentally observed splitting in degenerate mode is greater in the case of N$_2$ than with
Ar. Furthermore, while the splitting of the degenerate mode (in Fig. V.2A, Block II) is not very explicit and probably just manifests as a tail in the Ar matrix, the lifting of the degeneracy in the N$_2$ matrix is pronounced and the doublet is clearly discernible.

**Acetylene in Ar/N$_2$ Mixed Matrices**: Table V.3 displays the calculated $v_3$ frequency in the C$_2$H$_2$(N$_2$)$_2$(Ar)$_p$ complexes [VII through IX] for $p = 6$, 8 and 10. As the number of argon atoms goes from 6 through 10, there is an increase in blue shift in the $v_3$ mode frequency by 3.50 to 14.23 cm$^{-1}$ with respect to acetylene. In other words, the introduction of N$_2$ in the C$_2$H$_2$(N$_2$)$_2$(Ar)$_p$ cage, there is a red shift in the frequency of the C$_2$H$_2$ mode; i.e. the frequency of C$_2$H$_2$ is to longer wavelengths in the C$_2$H$_2$(N$_2$)$_2$(Ar)$_p$ cage compared with the C$_2$H$_2$(Ar)$_p$ system for the same ‘n’. This is also borne out by experiments, where with increasing concentration of N$_2$ in the mixed Ar/N$_2$ matrixes, there is a progressive red shift in the C$_2$H$_2$ asymmetric stretching feature. Table V.3 [VII through XV] gives the geometry of the complexes and which shows a preferential binding of argon atoms around the hydrogen of C$_2$H$_2$, which is in agreement with the PES of C$_2$H$_2$(Ar)$_n$ complex [50]. The bending modes also show an increase in the blue shift in $v_3$ mode frequency. The most intense peaks of these clusters show an increasing blue shift of magnitude 6.63 cm$^{-1}$, 43.12 cm$^{-1}$ as $p$ increases from 6, 8 to 10. However, an increase in the percentage of nitrogen molecule in the cluster shows a numerically higher difference in the magnitude of degeneracy lifted $v_3$ modes. Thus is in general agreement with the experimental observation (in Fig. V.2B through 1D, Block II) of two non-degenerate experimental peaks in N$_2$ matrix.

**V.5 MBAC on CO$_2$(Ar)$_m$, C$_2$H$_2$(N$_2$)$_m$ and C$_2$H$_2$(Ar)$_n$ Clusters**

Many body analyses on CO$_2$(Ar)$_m$, C$_2$H$_2$(N$_2$)$_m$ and C$_2$H$_2$(Ar)$_n$ clusters were carried with a view to partition the total interaction energy into two-, three- etc. body contributions, based on the partitioning scheme of Xantheas et al. [51] and to get a better molecular level understanding. Section IV.3.2 presents a brief description on the MBAC equations and analysis. Table V.4 gives a glimpse of the MBAC calculations on CO$_2$(Ar)$_m$ cluster at MPWB1K/6-31++g(2d) level of theory. In all these complexes, the total two-body contribution to the total interaction energy goes on increasing with the cluster size. Moreover, this total two-body contribution is higher compared to that of total three-body
and total higher-body ones. The maximum two-body contribution with increasing number of argon atoms in the matrix is almost constant at (-0.20 kcal/mol). Out of all these clusters, the CO$_2$(Ar)$_5$ cluster is seen to have the highest two-body contribution. The total three-body contribution is becoming more positive with cluster size because the number of unfavorable Ar...Ar interactions are increasing with cluster size. Majority of the Ar...Ar interactions are positive and only the three-body terms involving the CO$_2$ molecule is prudentially favorable. The total two-body contribution is remaining steady and three-body contribution is becoming positive, this indicates that the higher-body contributions are becoming more prominent with cluster size.

Table V.4 Many-body analysis of clusters (MBAC) partitioning of the interaction energy of CO$_2$(Ar)$_m$ clusters at MPWB1K/6-31++g(2d) level of theory. The reported values are in kcal/mol. See text for details.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Total ΔE</th>
<th>Max Two-body</th>
<th>Total Two-body</th>
<th>Max Three-body</th>
<th>Total Three-body</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$(Ar)</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$(Ar)$_2$</td>
<td>-0.41</td>
<td>-0.19</td>
<td>-0.38</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>CO$_2$(Ar)$_4$</td>
<td>-0.99</td>
<td>-0.19</td>
<td>-0.90</td>
<td>-0.20</td>
<td>-0.45</td>
</tr>
<tr>
<td>CO$_2$(Ar)$_5$</td>
<td>-1.51</td>
<td>-0.21</td>
<td>-1.41</td>
<td>-0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>CO$_2$(Ar)$_6$</td>
<td>-1.59</td>
<td>-0.20</td>
<td>-1.48</td>
<td>-0.02</td>
<td>0.96</td>
</tr>
<tr>
<td>CO$_2$(Ar)$_8$</td>
<td>-2.85</td>
<td>-0.21</td>
<td>-2.30</td>
<td>-0.10</td>
<td>-2.40</td>
</tr>
</tbody>
</table>

When the CO$_2$-CO$_2$ interaction in CO$_2$ clusters (cf. Section IV.3.2) is compared with that in CO$_2$-Ar, the former is nearly -0.95 kcal/mol, which is approximately 4.8 times that in later (−0.20 kcal/mol). This may be the reason for a higher frequency shift in CO$_2$ clusters than in CO$_2$(Ar)$_m$ clusters. But the average contribution of each body to the total interaction energy goes on decreasing with the number of molecules, meaning that the individual body in higher clusters looses interaction energy compared to that in the lower one. In the case of CO$_2$(Ar)$_8$ clusters, the three-body contributions is highly favorable because the argon atoms arrange around the oxygen atom as well and the distance between argon atoms are higher. But the three-body contribution will reduce with increase in the number of argon atoms because this will result in increasing number of energetically unfavorable interactions. Even though the interaction between the argon and CO$_2$ probe molecule is negligibly small, there is a definite frequency shift in the CO$_2$(Ar)$_m$ clusters, with respect to free CO$_2$ molecule.
The results of MBAC are presented in Table V.5, throwing light on the dominant interactions in C₂H₂(N₂)ₙ(Ar)ᵢ clusters. A look at this Table reveals that the strongest C₂H₂(N₂) interaction energy (ΔE) is typically -1.10 kcal/mol. We use the symbol ΔE for indicating the two-body, three-body, etc. interactions whereas (E denotes the total interaction energy. The sum of all two-body C₂H₂(N₂) ΔE is -7.60 and -6.00 kcal/mol for C₂H₂(N₂)₈ and C₂H₂(N₂)₁₀ complexes, respectively. A noteworthy feature is that for the pure C₂H₂-N₂ complexes, all the T-type interactions between the nitrogen matrix molecules taken together contribute substantially to the ΔE. These contributions for the first two complexes are, respectively, -8.20 and -5.90 kcal/mol. The strongest matrix molecule two-body ΔE for these two complexes is typically -0.70 kcal/mol.

### Table V.5 Many-body analysis of clusters (MBAC) partitioning of the interaction energy of C₂H₂(N₂)ₙ(Ar)ᵢ clusters at MP2/6-31++G(d) level of theory. The reported values are in kcal/mol. See text for details.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Total ΔE</th>
<th>Max two-body</th>
<th>Total three-body</th>
<th>Max three-body</th>
<th>Total three-body</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₂(N₂)₈</td>
<td>-17.82</td>
<td>-1.09</td>
<td>-15.79</td>
<td>-0.27</td>
<td>-1.99</td>
</tr>
<tr>
<td>C₂H₂(N₂)₁₀</td>
<td>-12.75</td>
<td>-1.12</td>
<td>-11.89</td>
<td>-0.22</td>
<td>-0.82</td>
</tr>
<tr>
<td>C₂H₂(N₂)₂(Ar)₁₀</td>
<td>-19.05</td>
<td>-1.10</td>
<td>-11.91</td>
<td>-0.13</td>
<td>-4.03</td>
</tr>
<tr>
<td>C₂H₂(N₂)₃(Ar)₁₀</td>
<td>-15.31</td>
<td>-1.17</td>
<td>-9.52</td>
<td>-0.11</td>
<td>-2.80</td>
</tr>
<tr>
<td>C₂H₂(N₂)₄(Ar)₁₀</td>
<td>-12.21</td>
<td>-1.15</td>
<td>-7.56</td>
<td>-0.12</td>
<td>-1.62</td>
</tr>
<tr>
<td>C₂H₂(Ar)₆</td>
<td>-5.80</td>
<td>-0.32</td>
<td>-4.36</td>
<td>-0.10</td>
<td>-1.07</td>
</tr>
<tr>
<td>C₂H₂(Ar)₁₀</td>
<td>-9.14</td>
<td>-0.48</td>
<td>-6.73</td>
<td>-0.10</td>
<td>-1.50</td>
</tr>
</tbody>
</table>

However, it is the preponderance of these interactions (the number of interactions being 8×7/2=28 and 6×5/2=15 for the first two complexes, respectively) that contributes to the matrix contribution to the two-body ΔE. Three-body ΔEs are typically less than 15% (and much smaller for complexes containing argon atoms) for all the complexes reported in Table V.5. In C₂H₂(Ar) binary complexes, the ΔEs are numerically much smaller compared to those in complexes involving N₂ molecules. The ΔE between two Ar atoms is substantially smaller than that between C₂H₂ and Ar atoms. In the C₂H₂-mixed matrix complexes, there is interplay between the matrix-matrix and the C₂H₂-matrix interactions. As the number of Ar atoms increases, the relative contribution of the total two-body ΔE increases with respect to the two-body contribution of the complexes incorporating C₂H₂.
This is, of course, due to the increasing number of the former type of interactions as the number of Ar atoms increases.

V.6 The Effect of Inert Matrix on Basicity of Acetylene-methanol complexes

Sundararajan et al. [52] in an earlier work on acetylene-methanol complex, observed the H-π C_{2}H_{2}(MeOH) complex only in the N_{2} matrix whereas the n-σ C_{2}H_{2}(MeOH) complex was evidenced in both argon and nitrogen matrices. In this work [52], they could not give any concrete reason why the H-π C_{2}H_{2}(MeOH) complex was observed only in the N_{2} matrix. In the present work an attempt is made to address this problem on the basis of MESP distribution. The deepest MESP minimum point (Y) of C_{2}H_{2} molecule and the variation of this minimum on complex formation with two argon atoms and two nitrogen molecules are displayed in Fig. V.4. The values of V_{min} correspond to the π region of the acetylene molecule. The deepest MESP point of acetylene molecule is -0.0353 a. u. and this value becomes substantially deeper in C_{2}H_{2}(N_{2})_{4} to -0.0383 a. u. than that in the C_{2}H_{2}(Ar)_{2} complex (-0.0361 a. u.).

In other words, acetylene becomes more basic when attached to nitrogen rather than to argon. This deepening of MESP minimum in C_{2}H_{2}(N_{2})_{n} complexes, is thus the cause for the acetylene molecule to act as a better hydrogen bond acceptor as compared to the free C_{2}H_{2}.
and the C\textsubscript{2}H\textsubscript{2} (Ar)\textsubscript{n} complexes. Hence one may anticipate the formation of weak H-\(\pi\) C\textsubscript{2}H\textsubscript{2}(MeOH) complex in nitrogen as compared to that in argon matrix. The MESP topographical analysis of methanol molecule shows two (3, +3) minima near the oxygen atom with a function value -0.096 a. u., deeper than the minimum for the C\textsubscript{2}H\textsubscript{2} molecule. Hence, methanol is a more potent hydrogen bond acceptor. The MESP considerations predict the favorable existence of two kinds of C\textsubscript{2}H\textsubscript{2}-MeOH complexes, one in which acetylene acts as hydrogen bond donor to methanol oxygen \textit{i.e.} n-\(\sigma\) C\textsubscript{2}H\textsubscript{2}(MeOH) and another one, wherein it acts as a hydrogen bond acceptor through its \(\pi\) bond \textit{i.e.} H-\(\pi\) C\textsubscript{2}H\textsubscript{2}(MeOH) complexes. The strength of such intermolecular hydrogen bonding can be predicted in terms of the ‘length-strength relationship’ [53] of the MESP. This relationship states that “hydrogen bond (HB) strength” is inversely proportional to the sum of the ‘hydrogen bond radius’ of HB donor functional group and the distance of the MESP minimum from the nearest HB acceptor atom. This relation predicts that the n-\(\sigma\) C\textsubscript{2}H\textsubscript{2}(MeOH) complex is more stable than H-\(\pi\) C\textsubscript{2}H\textsubscript{2}(MeOH) complex.

Table V.6 Formula of the complexes, stabilization energies/ BSSE corrected energies\textsuperscript{g} (in kcal /mol) and \(\nu_3\) and \(\nu_5\) normal mode frequencies (in cm\(^{-1}\)) and the corresponding intensities (in D\textsuperscript{2}/\textmu\text{A}\(^2\)) of acetylene in C\textsubscript{2}H\textsubscript{2}-MeOH [XVI and XVII], C\textsubscript{2}H\textsubscript{2}(MeOH) (Ar\textsubscript{2}) [XVIII and XIX] and C\textsubscript{2}H\textsubscript{2}(MeOH) (N\textsubscript{2})\textsubscript{2} complexes [XX and XXI] optimized at MP2/6-31++G(d) level of theory. See text for details.

<table>
<thead>
<tr>
<th>Formula</th>
<th>(\Delta E / \Delta E_{\text{BSSE}}) (kcal/mol)</th>
<th>(\nu_3) (cm(^{-1}))</th>
<th>(\nu_5) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-(\sigma) C\textsubscript{2}H\textsubscript{2}(MeOH) [XVI]</td>
<td>-4.66/-2.89</td>
<td>3414.1 (6.75)</td>
<td>865.6 (2.43), 890.7 (1.91)</td>
</tr>
<tr>
<td>H-(\pi) C\textsubscript{2}H\textsubscript{2}(MeOH) [XVII]</td>
<td>-3.53/-1.83</td>
<td>3451.2 (2.30)</td>
<td>734.1 (2.40), 743.5 (2.99)</td>
</tr>
<tr>
<td>n-(\sigma) C\textsubscript{2}H\textsubscript{2}(MeOH)(Ar\textsubscript{2}) [XVIII]</td>
<td>-5.14/-2.79</td>
<td>3414.3 (7.59)</td>
<td>867.6 (2.38), 898.9 (1.94)</td>
</tr>
<tr>
<td>H-(\pi) C\textsubscript{2}H\textsubscript{2}(MeOH)(Ar\textsubscript{2})[XIX]</td>
<td>-3.78/-1.91</td>
<td>3460.4 (3.65)</td>
<td>762.0 (2.15), 770.4 (2.69)</td>
</tr>
<tr>
<td>n-(\sigma) C\textsubscript{2}H\textsubscript{2}(MeOH)(N\textsubscript{2})\textsubscript{2} [XX]</td>
<td>-5.54/-3.52</td>
<td>3382.3 (8.18)</td>
<td>866.3 (2.55), 885.2 (1.98)</td>
</tr>
<tr>
<td>H-(\pi) C\textsubscript{2}H\textsubscript{2}(MeOH)(N\textsubscript{2})\textsubscript{2}[XXI]</td>
<td>-4.82/-2.51</td>
<td>3447.5 (4.30)</td>
<td>764.8 (2.20), 769.6 (3.02)</td>
</tr>
</tbody>
</table>

Energies (in a. u.) of MeOH= -115.35830, C\textsubscript{2}H\textsubscript{2}= -77.07330, Ar = -526.91310 and N\textsubscript{2} = -109.26190.

It may be noticed that these calculations yield two minima in PES, one in which acetylene acts as a hydrogen bond donor to methanol \textit{viz.} n-\(\sigma\) C\textsubscript{2}H\textsubscript{2}(MeOH), with a raw stabilization energy -4.66 kcal/mol. There is yet another complex in which acetylene acts as a hydrogen bond acceptor through its \(\pi\) bond \textit{viz.} H-\(\pi\) C\textsubscript{2}H\textsubscript{2}(MeOH), with raw stabilization
energy -3.53 kcal/mol. The more stable n-σ C2H2(MeOH) complex shows a red shift with respect to acetylene molecule by 44.64 cm⁻¹ in ν₁ mode and the corresponding H-π C2H2(MeOH) complex shows a red shift of 9.41 cm⁻¹.

Table V.6 also reports the BSSE-corrected stabilization energies at MP2/6-31++G (d) level for both the complexes. Incorporation of BSSE correction does not change the trend in the interaction energies of the complexes. However, on complexation with nitrogen, the n-σ and H-π stabilization energy values turn out to be comparable, viz. -5.54, -4.82 kcal/mol respectively. Furthermore the stabilization energy of the same complexes when complexed with argon turns out to be: -5.14 and -3.78 kcal/mol (cf. Table V.6). The difference in stabilization energy of the H-π and the n-σ complexes is much less when C2H2-MeOH complexed with N₂ (-0.71 kcal/mol) as compared to the bare C2H2-MeOH complex (-1.13 kcal/mol) and complexed with Ar atoms (-1.36 kcal/mol). This stabilization of H-π complex in nitrogen compared to that in argon matrix might be attributed to increased basicity of acetylene as revealed by the deepening of C2H2 minimum in nitrogen than in argon complexes. This offers a probable reasoning for observing experimentally the weak H-π C2H2(MeOH) complex in N₂ matrix rather than in argon matrix.

V.7 Concluding Remarks

The present Chapter reports the theoretical studies on the effect of a matrix (argon) on carbon dioxide and (nitrogen and argon) on acetylene IR spectra. The results are compared with experimental investigations by Viswanathan and Sundararajan. Hence we have studied the structure, energetics of the CO₂(Ar)ₙ clusters at MPWB1K/6-31++G(2d). The effect of inert matrix on the CO₂ molecule asymmetric stretching frequency is quantified and the frequency shifts shows a red shift of 0.73 to 5.9 cm⁻¹ on increasing the number of argon atoms in the cluster from m = 1 to 8 and this observation is indeed in good agreement with experiments.

In the experimental spectrum, the acetylenic C-H stretching mode in nitrogen as well as argon matrices shows a blue shift with reference to pure acetylene. This blue shift (3 cm⁻¹ to 11.9 cm⁻¹) is less in C2H2(N₂)ₙ complexes as compared to that (7.4 to 26.2 cm⁻¹) in C₂H₂(Ar)ₙ ones. This feature of relative blue shift in argon matrix with reference to nitrogen one is borne out by theoretical studies at MP2/6-31++G(d) level. The theoretical calculations at MP2/6-31++G(d) for different C₂H₂(N₂)ₙ and C₂H₂(Ar)ₙ show a large blue
shift for the C$_2$H$_2$(Ar)$_n$ complexes and red shift for the C$_2$H$_2$(N$_2$)$_m$ complexes with reference to the theoretical acetylene frequency. The trends in calculated frequency and the direction of shift are in fair agreement with the experiments in asymmetric stretching and bending regions. Similar observations have been made for the C-H bending region for the acetylene. It is not only the frequency shifts which reflect the matrix interaction, but also the lifting of the degenerate bending mode in nitrogen matrix (compared to argon matrix) sheds light on the behavior of different modes in different environment. Attempts are also made to simulate the argon/nitrogen mixed matrices with small clusters. Here too the trends in the frequency shifts for the stretching and bending acetylenic modes are in good qualitative agreement with the experiment.

Electrostatic considerations and *ab initio* calculations at MP2/6-31++g(d) level of theory reveal two types of acetylene-methanol complexes, one in which acetylene acts as hydrogen bond acceptor and another as hydrogen bond donor viz. H-π and n-σ C$_2$H$_2$(MeOH) complexes respectively. Calculations show the deepening of MESP minimum of acetylene in (C$_2$H$_2$)(N$_2$)$_m$ as compared to that in the (C$_2$H$_2$)(Ar)$_n$ complexes as well as in pure acetylene. In other words, the presence of nitrogen molecule around acetylene makes the later more basic, which in turn favors the H-π complex stabilization. Experimentally also a weak H-π complex has been observed in N$_2$ matrix whereas the same is not seen in the argon matrix. This agreement between the theoretical and experimental spectra is indeed gratifying. We trust that the present work opens new avenues for understanding and quantifying the matrix effects on the IR spectra of a variety of molecules.

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References


