Solvent effects on vibrational spectra of hydrogen-bonded complexes of formaldehyde and water: an ab initio study

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Abstract

The vibrational spectrum of the system H_2CO + H_2O has been predicted by ab initio calculations employing the 6-31G** basis set. The changes in the vibrational characteristics (vibrational frequencies, infrared intensities and Raman activities) from free monomer to a complex have been evaluated. In agreement with experiment, the ab initio calculations show that the stretching C = O and O–H vibrations involved in hydrogen bonding are shifted to lower frequency, corresponding to bond weakening. It was established that for the asymmetric $H_2CO...H_2O$ structure the ab initio solvent shifts show the best agreement with the experimentally measured shifts.

Keywords: Ab initio; Solvent effect; Formaldehyde–water complex

1. Introduction

Hydrogen bonding is of fundamental importance in chemistry, physics and biology. Hydrogen bonding, for example, is the key to understanding how molecules align themselves, both in crystals and in the gas phase.

In many organic and biological systems the carbonyl group is by far the most important proton acceptor. The carbonyl group is the most common base forming a hydrogen bond with a proton donor such as the OH or NH group. For this reason, a large number of theoretical studies using ab initio procedures have been undertaken in recent years for the simplest carbonyl–hydroxyl interaction, H_2CO + H_2O [1–9].

Hydrogen-bonded formaldehyde–water complexes have been investigated by means of ab initio and configuration interaction (CI) calculations [6]. The influence of water molecules on the properties of a carbonyl group, in particular the effect of one molecule at different sites relative to the C = O group, and the influence of two and three water molecules, have been investigated.

Hydrogen-bonded complexes involving formaldehyde and a series of proton donors of varying strengths, N = COH, NH = CHOH, CH_2CHOH and H_2O, have been investigated at different levels of ab initio MO theory and with CI calculations [7,8]. The most stable structures of the complexes studied have been established. The nature of the hydrogen bonding in the complexes and the influence of one and two proton-donor molecules of varying strengths have been studied.

It may be possible to identify experimentally some of the intramolecular vibrations for the complexes and thus to determine the changes in vibrational frequencies that occur upon hydrogen bonding [10–13]. The values of the frequency shifts can be related to the
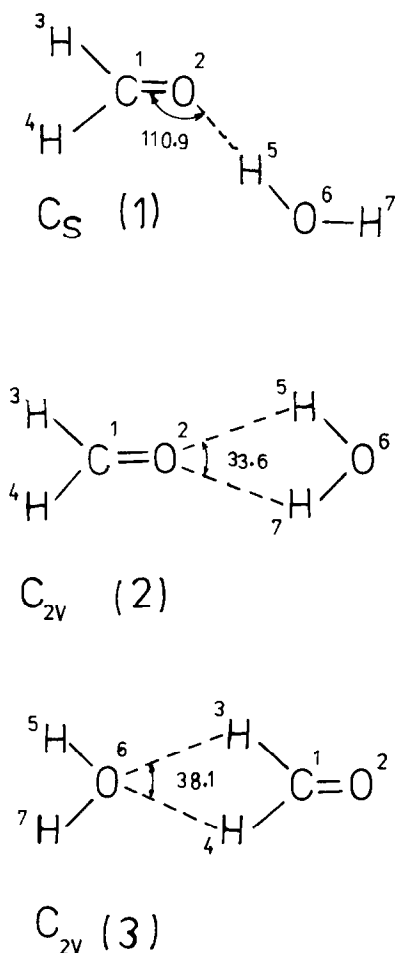
Fig. 1. Optimized structures of the complexes of formaldehyde with one water molecule (complexes 1, 2 and 3).

monomers (H_2CO and H_2O) and of the complexes studied 1–3 (see Fig. 1). The second is to estimate the changes in the vibrational characteristics (vibrational frequencies, IR intensities and Raman activities) for hydrogen-bonded formaldehyde–water complexes upon hydrogen bonding.

2. Results and discussion

2.1. Geometries and stabilities

In a previous study [6] the structure of the complexes studied was established employing the GAUSSIAN 90 series of programs [16]. The nature of hydrogen bonding in the complexes was studied; the geometry of the formaldehyde–water complexes was optimized with the 6-31G** basis set.

In Fig. 1 and Table 1 are shown the optimum values of the total energy and the equilibrium geometries for the complexes studied, at the 6-31G** basis set. The complex 1 has the optimum geometry for H...O distance 2.077 Å. The hydrogen bonds for complexes 2 and 3 are weaker and longer than the hydrogen bond for complex 1. As can be seen from the data in Table 1, the most stable structure is the first, with the deepest minimum in the total energy and the strongest hydrogen bond.

It is found that for the formaldehyde–water complexes the bond lengths and angles are slightly perturbed from their values in the monomers. The asymmetric $H_2CO...H_2O$ structure 1 is found to be the most stable by about 0.6 kcal mol^{-1} after consideration of the zero-point vibrations and the BSSE error; structures 2 and 3 are less stable but almost isoenergetic [6].

2.2. Charge distribution

In the present study, Mulliken population analysis is used to investigate the charge distribution in the hydrogen-bonded formaldehyde–water complexes 1–3. Table 2 gives the computed atomic charges (q_i) with the 6-31G** basis set for the monomers (H_2CO and H_2O) and for the complexes 1–3. The changes in the atomic charges (Δq_i) upon hydrogen bonding for the complexes studied are also determined.

strength of the hydrogen bond [14,15]. That is a difficult quantity to determine directly from the experiment, but it may provide an indirect way of measuring the hydrogen bond strength.

In a previous IR study [12], the IR spectra of the formaldehyde–water complex in argon and nitrogen matrices have been obtained. The shifts in the vibrational fundamentals give clear evidence for the existence of a hydrogen-bonded complex.

The aim of the present study is to investigate the vibrational features that characterize the interaction between formaldehyde and water by ab initio calculations employing the 6-31G** basis set. The first step in the study is to predict the vibrational spectra of the

Table 1
Optimized geometry for the hydrogen-bonded formaldehyde–water complexes **1–3** obtained from SCF calculations employing the 6-31G** basis set

Parameter	Complex[a]			Monomers[a]
	1	2	3	
Bond length[b]				
$r(C_1O_2)$	1.185	1.186	1.186	1.184
$r(C_1H_3)$	1.095	1.092	1.091	1.093
$r(C_1H_4)$	1.095	1.092	1.091	1.093
$r(H_5O_6)$	0.948	0.943	0.943	0.943
$r(H_7O_6)$	0.928	0.943	0.943	0.943
$r(O \cdots H)$	2.077	2.567	2.805	–
Angle[c]				
$H_3C_1O_2$	121.0	122.0	122.5	122.1
$H_3C_1H_4$	118.0	116.0	115.0	115.7
$H_4C_1O_2$	121.0	122.0	122.5	122.1
$H_5O_6H_7$	113.3	103.7	106.1	106.0
$E^{tot.}$ (a.u.)	– 189.900 83	– 189.898 64	– 189.897 63	– 113.869 74[d]
				– 76.023 61[e]

[a] See Fig. 1 for numbering of atoms.
[b] In angstroms.
[c] In degrees.
[d] $E^{tot.}$ for H_2CO.
[e] $E^{tot.}$ for H_2O.

As can be seen from the data in Table 2, the negativity of the oxygen atoms O_2 and O_6 increases in complexes **1**, **2** and **3** in comparison with the corresponding values in the monomers. As a result of hydrogen bonding between formaldehyde and water, the oxygen atoms O_2 (from H_2CO) and O_6 (from H_2O) act as an acceptor of electric charge and the hydrogen atoms release positive charges. It can be concluded that the mechanism of complexation does indeed cause a charge rearrangement.

The calculated values for Δq_i show that the charge rearrangement is greatest in the most stable structure **1**. These charge transfers demonstrate how the oxygen atoms act as an electron acceptor in the process of forming the complexes.

In addition, a linear relationship is found between the complex net charges $q(O_2)$ and $q(O_6)$ and the optimum value of hydrogen bond distance, calculated with the 6-31G** basis set (see Fig. 2).

Table 2
Mulliken charges (q_i) for the hydrogen-bonded formaldehyde–water complexes **1–3**, obtained from SCF calculations with the 6-31G** basis set

No.[a]	Atom	$q_i/\Delta q_i$ [b]			
		Complex **1**	Complex **2**	Complex **3**	Monomers
1	C	0.2500/0.0050	0.2524/0.0074	0.2501/0.0051	0.2450
2	O	– 0.4559/ – 0.0245	– 0.4533/ – 0.0219	– 0.4494/ – 0.0180	– 0.4314
3	H	0.1145/0.0213	0.1038/0.0106	0.0960/0.0028	0.0932
4	H	0.1145/0.0213	0.1038/0.0106	0.0960/0.0028	0.0932
5	H	0.3593/0.0240	0.3419/0.0066	0.3421/0.0068	0.3353
6	O	– 0.7063/ – 0.0357	– 0.6906/ – 0.0200	– 0.6769/ – 0.0063	– 0.6706
7	H	0.3437/0.0084	0.3419/0.0066	0.3421/0.0068	0.3353

[a] See Fig. 1 for numbering of atoms.
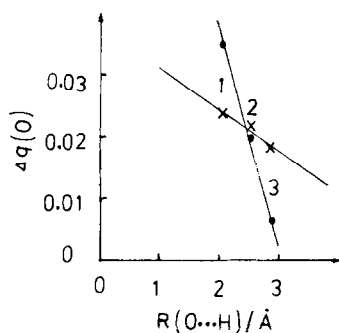[b] $\Delta q_i = q_i^{complex} - q_i^{monomer}$

Fig. 2. Plot of calculated hydrogen-bond distance $(R_{O \cdots H})$ vs calculated complex net charges $\Delta q(O_2)$ (x) and $\Delta q(O_6)$ (●) for the hydrogen-bonded complexes **1–3**.

2.3. Vibrational frequencies and intensities

In recent years the prediction of vibrational characteristics by ab initio calculations has become widely employed in order to elucidate spectra for a large number of molecules, ions and complexes [17–25]. It is known that certain ab initio predicted values of vibrational frequencies and IR intensities are not

expected to be accurate, but they are known to give useful qualitative values and to give correct trends in going from the monomer to the complex [19]. In order to investigate the vibrational frequencies, infrared intensities and Raman activities that characterize the interaction between H_2CO and H_2O, ab initio calculations with the 6-31G** basis set with the GAUSSIAN 90 series of programs [16] have been performed.

The infrared frequencies of free and complexed H_2CO and H_2O observed by Nelander [12] in Ar matrix are shown in Table 3. The complex shifts in the vibrational fundamentals $(\Delta \nu)$ clearly show that water forms a hydrogen bond with formaldehyde. As can be seen from the experimental data in Table 3, the stretching frequencies for both monomer bonds involved in hydrogen bonding $(\nu_1, \nu_7$ and $\nu_8)$ are shifted to lower frequency, corresponding to bond weakening. The remaining frequencies are either unchanged or shifted to higher frequency.

The vibrational characteristics for all modes in the monomers have been calculated with the 6-31G** basis set and the calculated values compared with

Table 3
Experimental (Ar matrix) and calculated (6-31G**) data of the vibrational frequencies (ν, cm^{-1}), infrared intensities (IR int., km mol^{-1}) and Raman activities (R.a., Å^4 amu^{-1}) for free and complexed H_2CO and H_2O

No.	Mode[a]	$\nu^{exp.}$ [12]		$\Delta \nu^{exp.\ b}$	Monomers[c]	
		Monomers[c]	Complex[d]		$\nu^{calc.}$ Scale factor	IR int.$^{calc.}$ R.a.$^{calc.}$
ν_1	(C = O str)	1742.2	1737.0	− 5.2	2025.1	147.1
					0.8603	8.4
ν_2	(C–H as str)	2864.7	2881.5	16.8	3195.8	132.8
					0.8964	58.7
ν_3	(C–H sym str)	2798.4	2816.0	17.6	3120.8	49.0
					0.8967	138.1
ν_4	(CH$_2$ def)	1499.0	1499.0	0.0	1668.2	10.0
					0.8986	12.4
ν_5	(CH$_2$ rot)	1245.2	1245.7	0.5	1376.7	22.9
					0.9045	4.2
ν_6	(CH$_2$ wag)	1168.6	1173.9	5.3	1335.5	0.6
					0.8750	0.7
ν_7	(O–H as str)	3734.3	3709.3	− 25.0	4266.9	58.0
					0.8751	36.4
ν_8	(O–H sym str)	3638.0	3582.8	− 55.2	4149.8	16.3
					0.8767	74.5
ν_9	(OH$_2$ def)	1589.1	1610.7	21.6	1769.1	104.6
					0.8982	5.5

[a] as, asymmetrical; sym, symmetrical; str, stretching; def, deformation; rot, rotation; wag, wagging.
[b] $\Delta \nu_i^{exp.} = \nu_i^{complex} - \nu_i^{monomer}$.
[c] H_2CO and H_2O.
[d] $H_2CO.HOH$.

Table 4
Vibrational frequencies (ν, cm^{-1}), infrared intensities (IR int., km mol^{-1}) and Raman activities (R.a., Å^4 amu^{-1}) for the formaldehyde–water complexes 1–3 calculated with the 6-31G** basis set

No.[a]	Complex 1[b] ν/IR int./R.a. $\Delta\nu^{scal}$/ΔIR int./ΔR.a.	Complex 2[b] ν/IR int./R.a. $\Delta\nu^{scal}$/ΔIR int./ΔR.a.	Complex 3[b] ν/IR int./R.a. $\Delta\nu^{scal}$/ΔIR int./ΔR.a.
ν_1	2014.4/169.1/9.2	2019.7/155.3/10.0	2019.4/157.5/8.6
	– 9.2/22.0/0.8	– 4.6/8.1/1.6	– 4.9/10.4/0.2
ν_2	3206.1/90.5/61.9	3217.1/108.9/60.3	3226.8/118.9/53.1
	9.2/ – 42.3/3.2	19.1/ – 23.9/1.6	27.8/ – 13.9/ – 5.6
ν_3	3131.9/43.4/126.6	3135.8/47.4/131.4	3145.5/48.4/123.7
	9.9/ – 5.6/ – 11.5	13.4/ – 1.6/ – 6.7	22.1/ – 0.6/ – 14.4
ν_4	1667.9/15.6/12.1	1667.3/10.1/12.7	1653.0/20.2/15.1
	– 0.3/5.6/ – 0.3	– 0.8/0.1/0.3	– 13.6/10.2/2.7
ν_5	1380.7/19.3/3.9	1376.0/23.1/3.6	1361.0/26.7/2.8
	3.6/ – 3.6/ – 0.3	– 0.6/0.2/ – 0.6	– 14.2/3.8/ – 1.4
ν_6	1346.5/1.1/0.6	1340.4/0.7/0.7	1342.4/0.6/0.6
	9.6/0.5/ – 0.1	4.3/0.1/0.0	6.0/0.0/ – 0.1
ν_7	4237.3/59.1/52.7	4257.6/60.9/35.0	4260.9/72.9/40.0
	– 25.9/1.1/16.3	– 8.1/2.9/ – 1.4	– 5.2/14.9/3.6
ν_8	4106.7/21.6/90.2	4161.5/27.5/70.2	4146.2/25.2/71.3
	– 37.8/5.3/15.7	10.8/11.2/ – 4.3	– 3.1/8.9/ – 3.2
ν_9	1806.8/188.8/5.6	1787.7/233.7/11.7	1771.9/199.5/6.1
	33.8/84.2/0.1	16.7/129.1/6.2	2.5/94.9/0.6
ν_{10}	522.2/212.4/3.1	369.6/329.9/3.49	155.1/197.3/0.3
	—	—	—
ν_{11}	266.8/2.9/8.2	121.3/1.0/0.1	125.3/1.9/5.0
	—	—	—

[a] See Table 3 for characterization of vibrations ν_1–ν_9; ν_{10} is ν(OH...O def) and ν_{11} is ν(H...O str).
[b] $\Delta\nu^{scal}$ = $k(\nu^{complex} - \nu^{monomer})$, where k is a scale factor.
ΔIR int. = IR int.^{complex} – IR int.^{monomer}.
ΔR.a. = R.a.^{complex} – R.a.^{monomer}.

the corresponding experimental data. The results are shown in Table 3.

It is known that ab initio calculations show errors in harmonic frequencies of the order of 10% [17,26]. The accuracy of ab initio prediction of harmonic frequencies can be increased by the utilization of scaling procedures [18,27,28]. In the present study the 'optimal' scale factors for the stretching and bending vibrations of the monomers are determined using the ratio ν^{exp}/ν^{calc} in order to improve the estimates of the frequency shifts. Scale factors for the stretching and bending vibrations of the monomers are shown in Table 3.

As can be seen from the results in Table 3, the water O–H stretching modes are characterized by scale factors noticeably smaller than the uniform factor 0.9.

The calculated vibrational frequencies, IR intensities and Raman activities for complexes 1–3 are listed in Table 4.

The shifts in the vibrational frequencies ($\Delta\nu^{scal}$) of formaldehyde and water upon formation of the hydrogen-bonded complex have been calculated with the 6-31G** basis set and scaled by using the corresponding scale factors from Table 3. For each vibration the predicted frequency shift is

$$\Delta\nu_i^{scal} = k_i(\nu_i^{complex} - \nu_i^{monomer}),$$

where k_i is the corresponding 'optimal' scale factor.

The data in Table 4 show that the hydrogen bonding between H_2CO and H_2O leads to changes of the vibrational frequencies, IR intensities and Raman activities of the stretching and deformation vibrations. In agreement with experiment [12], the ab initio calculations with the 6-31G** basis set show that the most sensitive parameters to the complexation are the stretching vibrations for both monomer bonds involved in hydrogen bonding (ν_1, ν_7 and ν_8).

The predicted frequency for the stretching ν_{CO}

vibration of structures **1**, **2** and **3** is shifted to low frequency corresponding to bond weakening. $\Delta\nu^{scal}$ for complex **1** is $-9.2\ cm^{-1}$, for complex **2** it is $-4.6\ cm^{-1}$, and for complex **3** it is $-4.9\ cm^{-1}$; the corresponding experimental value is $-5.2\ cm^{-1}$. Obviously, for the most stable structure, **1**, the predicted frequency shift $\Delta\nu_{CO}$ is largest.

The ab initio calculations predict high IR intensity of the stretching ν_{CO} vibration (ν_1) for the complexes studied here, which is in agreement with the experimentally observed strong band at $1737\ cm^{-1}$ for the complex $H_2CO.H_2O$ [12]. The predicted IR intensity of the mode ν_1 is highest for the most stable structure, **1** (see Table 4). The Raman activity of the same mode for the complexes studied is lower.

The ab initio predicted shifts of the OH-stretching vibrations ($\Delta\nu_7$ and $\Delta\nu_8$) for complex **1** are largest and are of the correct sign with regard to the corresponding experimental values (see Tables 3 and 4).

The ab initio calculations show that the dimer modes ν_7 and ν_8 have intermediate IR intensities and Raman activities (see Table 4). Mode ν_7 has higher IR intensity than mode ν_8, while Raman activity for mode ν_8 is about twice as high as for mode ν_7

As can be seen from the results in Table 4, the stretching vibrations ν_{C-H}^{as} (ν_2) and ν_{C-H}^{sym} (ν_3) are sensitive to the complexation. In agreement with the experimental data [12], the calculated values of the stretching C–H vibrations for complexes **1–3** are shifted to higher frequencies in comparison with the corresponding values for the monomer.

At the same time, the IR intensity of mode ν_2 is about twice as high as the IR intensity of mode ν_3 in the hydrogen-bonded complexes **1–3**. The predicted Raman activities of these vibrations in the complexes studied are in opposite dependence, namely R.a.(ν_3) / R.a.$(\nu_2) \simeq 2$.

In connection with the frequency shifts of the stretching CH vibrations ($\Delta\nu_2$ and $\Delta\nu_3$), it should also be noticed that for structure **3** (see Fig. 1), which supposes involvement of the CH bonds in the hydrogen bonding, the calculated frequency shifts $\Delta\nu_2$ and $\Delta\nu_3$ are largest.

The calculated frequencies of the deformation ν_4, ν_5, ν_6 and ν_9 vibrations in the complexes are either unchanged or shifted to higher frequencies. The predicted frequency shifts for complex **1** show the best agreement with the experimentally observed shifts [12].

The ab initio calculations show that the deformation OH_2 vibration (ν_9) is very sensitive to complexation. The largest frequency shift, in good agreement with experiment, is calculated for complex **1**.

The predicted IR intensity of the deformation OH_2 vibration is higher for the hydrogen-bonded complexes **1–3** in comparison with the corresponding value in the monomer (H_2O), in some cases by more than a factor of 2. At the same time, the Raman activity of this vibration is low.

The calculated frequency shift $(\Delta\nu_9)$ is negligible for complex 3, only $2.5\ cm^{-1}$, a value which is not in good agreement with the experimentally measured one. This fact can be explained by the structure of complex **3**, namely that the hydrogen bond for this complex is formed between the oxygen atom from H_2O and the hydrogen atoms from H_2CO (see Fig. 1.).

Two new vibrations appear for the complexes: the deformation OH...O vibration (ν_{10}) and the stretching H...O vibration (ν_{11}) (see Table 4). The ab initio calculations predict high IR intensity and low Raman activity of the deformation OH...O vibration, whereas the stretching H...O vibration has low IR intensity and Raman activity.

The most consistent agreement between the computed values of the frequency shifts for complex **1** and those experimentally observed by Nelander [12] suggests that complex **1** is the preferred structure. This observation, taken together with the earlier ab initio and CI study [6] for this species, convinces us that the most likely structure of the formaldehyde–water system is the asymmetric, C_s, $H_2CO...H_2O$ hydrogen-bonded structure **1** (see Fig. 1).

3. Conclusions

The vibrational features characterizing the interaction between formaldehyde and water have been investigated by ab initio calculations employing the 6-31G** basis set. The main results of the present study indicate the following:

1. Hydrogen bonding between H_2CO and H_2O leads to changes of the vibrational frequencies, infrared intensities and Raman activities of the stretching and deformation vibrations. The parameters most sensitive to the complexation are the stretching

vibrations for both monomer bonds involved in hydrogen bonding. These vibrations are shifted to lower frequency, corresponding to bond weakening. The vibrational characteristics of the remaining vibrations are less sensitive to hydrogen bonding. The frequencies of these vibrations are either unchanged or shifted to higher frequency.

2. The best agreement between the ab initio predicted and experimentally observed frequency shifts is for the asymmetric $H_2CO...H_2O$ structure, **1**, which suggests that it is the most likely one to have been observed.

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