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# Ab initio prediction of the vibrational spectrum of the hydrogen-bonded compex $H_2CO$...HOCN

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## Abstract

The vibrational features characterising the hydrogen-bonded interaction between $H_2CO$ and $HOC{\equiv}N$ have been studied. The vibrational frequencies, IR intensities and Raman activities for free and complexed $H_2CO$ and $HOC{\equiv}N$ have been predicted by ab initio calculations with the 6-31G basis set. It was established that the complexation leads to changes in the vibrational characteristics for the stretching and deformation vibrations. The most sensitive vibrations to the complexation are the stretching O–H and C=O vibrations, involved in the hydrogen bonding. Their frequencies are shifted to lower wavenumbers. The changes in the vibrational characteristics for stretching O–H vibration are larger than the corresponding changes for the stretching C=O vibration. The remaining vibrations (stretching and deformation) are less sensitive to the hydrogen bonding. Their vibrational characteristics are changed with smaller magnitude.

*Keywords:* Ab initio calculations; Vibrational spectra; Hydrogen-bonded compex

## 1. Introduction

The structure and dynamics of weakly bound molecular complexes has become of greater and greater interest to chemists in a variety of fields, partly because of an interest in the physical nature of the interaction.

Hydrogen bonding, for example is the key to understanding how molecules align themselves, both in crystal and in the gas phase. Numerous workers have demonstrated that matrix isolation spectroscopy is a particularly effective means for studying hydrogen-bonded complexes [1–4] and provides vibrational information to complement the gas-phase rotational data.

It is known that the carbonyl group of aldehyde and ketones forms weak hydrogen bonds with proton donors. The simplest member of this family is formaldehyde, $CH_2O$, and it might be expected to show similar behaviour. However, formaldehyde is a very weak Lewis base, with a proton affinity [5] of only 166 kcal $mol^{-1}$, and should form quite weak hydrogen bonds.

The elucidation of the structure and energetic of the complexes pertains to the understanding of intramolecular interactions and a concerted application of experimental and theoretical methods

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can be used to obtain a clear picture of hydrogen bonding structures. A large number of theoretical studies, employing ab initio calculations have been undertaken in recent years for the hydrogen-bonded systems [6–12].

In our previous studies [13–15] the hydrogen-bonded complexes, involving formaldehyde and a series of proton donors of varying strengths: $H_2O$, $CH_2CHOH$, NH=CHOH and HOC≡N have been investigated at different levels of ab initio MO theory and configuration interaction (CI) calculations. The most stable structures of the complexes studied have been established. The nature of the hydrogen bonding in the complexes have been studied. The solvent shift for singlet and triplet $n \rightarrow \pi^*$ transitions was determined in CI calculations for the complexes studied.

In recent years the ab initio calculations have been widely employed in order to elucidate the vibrational spectra for a large number of molecules, ions and complexes [16–24]. The ab initio predicted values of the vibrational characteristics are not expected to be accurate, but they give useful qualitative values and correct trends going from the monomer to the complex.

The changes in the infrared characteristics from an isolated acetonitrile to acetonitrile co-ordinated with metal cations ($Li^+$ and $Na^+$) have been evaluated by ab initio calculations with the 6-31G and 6-31G** basis sets [18].

In a previous paper [25] the vibrational spectra of the hydrogen-bonded formaldehyde–water complexes have been predicted by ab initio calculations with the 6-31G** basis set. It was established that the hydrogen bonding leads to changes in the vibrational characteristics (vibrational frequencies, infrared intensities and Raman activities). The predicted changes are in good agreement with the experimental data.

The object of the present study is the binary complex formed from $H_2CO$ and HOC≡N. The aim of the study is first, to predict the vibrational spectra for the monomers ($H_2CO$ and HOC≡N) and for the hydrogen-bonded complex $H_2CO$...HOC≡N, and secondly, to estimate the changes in the vibrational characteristics (vibrational frequencies, infrared intensities and Raman activities) from free monomers to a complex employing ab initio calculations at the 6-31G basis set.

## 2. Results and discussion

### 2.1. Molecular structure

In a previous study [14] the most stable structure for the binary complex formed between $H_2CO$ and HOC≡N has been established by ab initio calculations with various basis sets (6-31G/SCF, 6-31G/MP2, 6-31G**/SCF, 6-31G**/MP2, 6-311G(2d,2p)/SCF and 6-311G(2d,2p)/MP2) employing the GAUSSIAN 90 series of programs [26]. The optimised structural parameters obtained from SCF calculations with the 6-31G basis set for the monomers ($H_2CO$ and HOC≡N) and for the complex are shown in Table 1. The optimised structure for the complex $H_2CO$...HOC≡N is shown on Fig. 1.

Table 1
Optimised geometries for free and complexed $H_2CO$ and HOCN, calculated with the 6-31G basis set

| Parameter | Monomer[a] | Complex[b] | Change of the parameter |
|---|---|---|---|
| Bond length[a] | | | |
| $r(C_1O_2)$ | 1.210 | 1.215 | 0.005 |
| $r(C_1H_3)$ | 1.082 | 1.079 | −0.003 |
| $r(C_1H_4)$ | 1.082 | 1.079 | −0.003 |
| $r(H_5O_6)$ | 0.955 | 0.968 | 0.013 |
| $r(O_6C_7)$ | 1.304 | 1.296 | −0.008 |
| $r(C_7N_8)$ | 1.146 | 1.148 | 0.002 |
| $r(O...H)$ | — | 1.786 | — |
| Angle[c] | | | |
| $H_3C_1O_2$ | 121.7 | 121.6 | −0.1 |
| $H_3C_1H_4$ | 116.6 | 117.5 | 0.9 |
| $H_5O_6C_7$ | 116.6 | 115.0 | −1.6 |
| $O_6C_7N_8$ | 177.3 | 181.4 | 4.1 |
| $O_2O_6C_7$ | — | 102.6 | — |
| $C_1O_2O_6$ | — | 135.8 | — |
| $E^{tot.}$ (a.u.) | −113.80837[d]<br>−167.63472[e] | −281.46300 | |

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

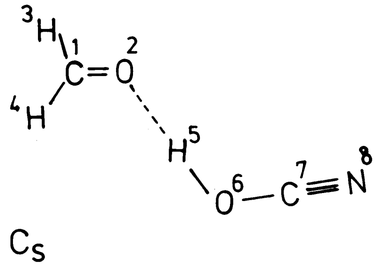

Fig. 1. Optimised structure for the binary complex formed between $H_2CO$ and HOC≡N.

The changes of the parameters from monomers to a complex are defined. As can be seen from the results in Table 1, the bond lengths and angles for the binary complex $H_2CO$...HOC≡N are slightly perturbed from their values in the monomers.

In the present study the Mulliken population analyses is used to investigate the charge rearrangement upon hydrogen bonding. The computed atomic charges ($q_i$) at the 6-31G level for the monomers and for the complex, and the changes in the atomic charges ($\Delta q_i$) from free monomers to a complex are listed in Table 2.

The data for $\Delta q_i$ show, that the complexation between $H_2CO$ and HOC≡N leads to a charge rearrangement. The negativity of the atoms $O_2$ (from $H_2CO$) and $N_8$ (from HOC≡N) increases significantly in the complex, while the negativity of the $O_6$ increases at a lower rate. It can seen that as a result of the hydrogen bonding the atoms $O_2$ and $N_8$ act as an acceptor of electric charge and the hydrogen atoms ($H_3$, $H_4$ and $H_5$) release positive charge.

Table 2
Mulliken charges ($q_i$) at the 6-31G/SCF level for free and complexed $H_2CO$ and HOCN

| No. | Atom | Monomers | Complex | $\Delta q_i$ |
|---|---|---|---|---|
| 1 | C | 0.1589 | 0.2006 | 0.0417 |
| 2 | O | −0.4543 | −0.5353 | −0.0810 |
| 3 | H | 0.1477 | 0.1840 | 0.0363 |
| 4 | H | 0.1477 | 0.1840 | 0.0363 |
| 5 | H | 0.4709 | 0.5282 | 0.0573 |
| 6 | O | −0.7139 | −0.7516 | −0.0377 |
| 7 | C | 0.4457 | 0.4324 | −0.0133 |
| 8 | N | −0.2027 | −0.2430 | −0.0403 |

See Fig. 1 for numbering of atoms.
$\Delta q_i = q_i^{\text{complex}} - q_i^{\text{monomer}}$.

## 2.2. Vibrational spectra

The vibrational characteristics (vibrational frequencies, infrared intensities and Raman activities) for the free monomers ($H_2CO$ and HOC≡N) and for the binary complex studied (see Fig. 1) have been predicted by ab initio calculations with the 6-31G basis set.

It is important to note, that in the interacting system, i.e. hydrogen-bonded system, the geometrical symmetry of the monomers often changes under perturbation [27]. The vibrational mixing, derived by a perturbation approach, is the counterpart of the orbital mixing.

In addition, the ab initio calculations show errors in harmonic frequencies of order of 10% [16,28]. In order to increase the accuracy of the ab initio prediction of harmonic frequencies the scaling procedures are used [17,29,30].

In the present study, the vibrational frequencies, IR intensities and Raman activities for free and complexed $H_2CO$ and HOC≡N are predicted with the 6-31G basis set, using the GAUSSIAN 90 series of programs [26]. The calculated values of the above vibrational characteristics are listed in Table 3. The shifts in the vibrational frequencies ($\Delta\nu^{\text{scal}}$) of $H_2CO$ and HOC≡N arising from the hydrogen bonding are calculated with the 6-31G basis set and are scaled by using a scale factor 0.89 for all frequencies. The scale factor 0.89 is taken from the calibration of the 6-31G results for $H_2CO$ with the experimental frequencies, observed by Nelander [31].

As can be seen from the data in Table 3, the hydrogen bonding between $H_2CO$ and HOC≡N leads to changes of the vibrational frequencies ($\Delta\nu^{\text{scal}}$), infrared intensities (ΔIR int.) and Raman activities ($\Delta R.a.$) of the stretching and deformation vibrations. Fig. 2A–CFig. 3A–C illustrate the spectral results, obtained by ab initio calculations at the 6-31G basis set for free and complexed $H_2CO$ and HOC≡N. Fig. 2 displays a comparison between the theoretical non-scaled 6-31G IR spectra of the monomers: $H_2CO$ (Fig. 2A), HOC≡N (Fig. 2B) and of the complex

Table 3
Vibrational frequencies ($\nu$), infrared intensities ($IR_{int.}$) and Raman activities ($R_a$) calculated at the 6-31G level for free and complexed $H_2CO$ and HOCN

| Mode | Approximate description (PED)[a] | $\nu$ ($cm^{-1}$) |  | $\Delta\nu_{(scal)}$ | $IR_{int.}$ (km $mol^{-1}$) |  | $\Delta IR_{int.}$ | $R_a$ ($A^4$ $amu^{-1}$) |  | $\Delta R_a$ |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Monomers | Complex |  | Monomers | Complex |  | Monomers | Complex |  |
| $\nu_1$ | C=O str(78), $CH_2$(21) | 1909.9 | 1892.3 | −15.6 | 90.5 | 131.0 | 40.5 | 7.0 | 8.3 | 1.3 |
| $\nu_2$ | CH sstr(63), CH asstr(37) | 3207.9 | 3239.2 | 27.9 | 23.0 | 16.8 | −6.2 | 136.0 | 113.5 | −22.5 |
| $\nu_3$ | CH asstr(63), CH sstr(37) | 3298.9 | 3347.7 | 43.4 | 95.4 | 44.2 | −51.2 | 54.2 | 53.4 | −0.8 |
| $\nu_4$ | $CH_2$ def(78), C=O str(22) | 1673.6 | 1665.2 | −7.5 | 24.3 | 46.1 | 21.8 | 17.1 | 15.9 | −1.2 |
| $\nu_5$ | $CH_2$ rot(99) | 1373.7 | 1371.4 | −2.0 | 17.8 | 16.1 | −1.7 | 5.0 | 3.5 | −1.5 |
| $\nu_6$ | $CH_2$ wag(99) | 1329.2 | 1348.1 | 16.8 | 6.0 | 5.6 | −0.4 | 0.1 | 0.1 | 0 |
| $\nu_7$ | CH str(84), C–O str(16) | 2572.3 | 2554.3 | −16.0 | 120.9 | 152.8 | 31.9 | 27.8 | 27.5 | −0.3 |
| $\nu_8$ | H–O str(99) | 3980.0 | 3720.8 | −230.7 | 204.3 | 997.2 | 792.9 | 82.9 | 91.1 | 8.2 |
| $\nu_9$ | HOC bend (97) | 1322.2 | 1442.6 | 107.2 | 149.8 | 200.6 | 50.8 | 6.6 | 11.2 | 4.6 |
| $\nu_{10}$ | O–C str(84), CN str(14) | 1130.1 | 1149.1 | 16.9 | 86.8 | 61.3 | −25.5 | 5.9 | 6.8 | 0.9 |
| $\nu_{11}$ | OCN t(99) | 496.9 | 503.7 | 6.1 | 10.8 | 12.0 | 1.2 | 4.7 | 4.4 | −0.3 |
| $\nu_{12}$ | OCN b(90) | 453.4 | 484.6 | 27.8 | 22.2 | 12.1 | −10.1 | 6.2 | 5.2 | 1.0 |
| $\nu_{13}$ | OH…O t(99) | — | 706.1 | — | — | 300.5 | — | — | 3.4 | — |
| $\nu_{14}$ | H…O str(100) | — | 232.2 | — | — | 34.3 | — | — | 2.2 | — |

str, stretch; s, symmetric; as, antisymmetric; def, deformation; rot, rotation; wag, wagging; b, bend; t, torsion.
$\Delta\nu_{(scal)} = k(\nu^{complex} \sim \nu^{monomer})$; $k = 0.89$.
[a] PED, potential energy distribution (%). Only those contributions ≥10% are shown.

$H_2CO…HOC{\equiv}N$ (Fig. 2C). Fig. 3 displays a comparison between the theoretical non-scaled 6-31G Raman spectra of the monomers (Fig. 3A,B) and of the complex (Fig. 3C).

In a previous IR study [32] it was established, that for most hydrogen-bonded systems the most intense infrared absorption is the hydrogen stretching mode of the proton donor in the complex. This mode is usually observed shifted to lower energies due to a broadening of the potential function and often intensified 10–100 times relative to the free acid.

In the present work, the ab initio calculations show, that the most intense absorption for the complex $H_2CO…HOC{\equiv}N$ is the OH-stretching vibration ($\nu_8$ mode).

The mode $\nu_8$ is shifted to lower frequency by 230.7 $cm^{-1}$, compared with the monomer value. The magnitude of the wavenumber shift is indicative of relatively strong OH…O hydrogen-bonded interaction. The calculated values of the binding energy with various basis sets, corrected for the basis set superposition errors (BSSE) and MP2 correlation contribution for the complex $H_2CO…HOC{\equiv}N$ confirm also relatively strong hydrogen-bonded interaction [14].

The ab initio calculations show that the complexation leads to a strong increase in the IR intensity of the stretching OH vibration ($\nu_8$) about five times and an increase in the Raman activity about 10%.

The second monomer bond involved in the hydrogen bonding is the C=O bond (see Fig. 1). The changes in the vibrational characteristics of the stretching C=O vibration ($\nu_1$) from free monomer to a complex are defined. The magnitude of the shift of the carbonyl stretching mode in the complex is relatively small compared with

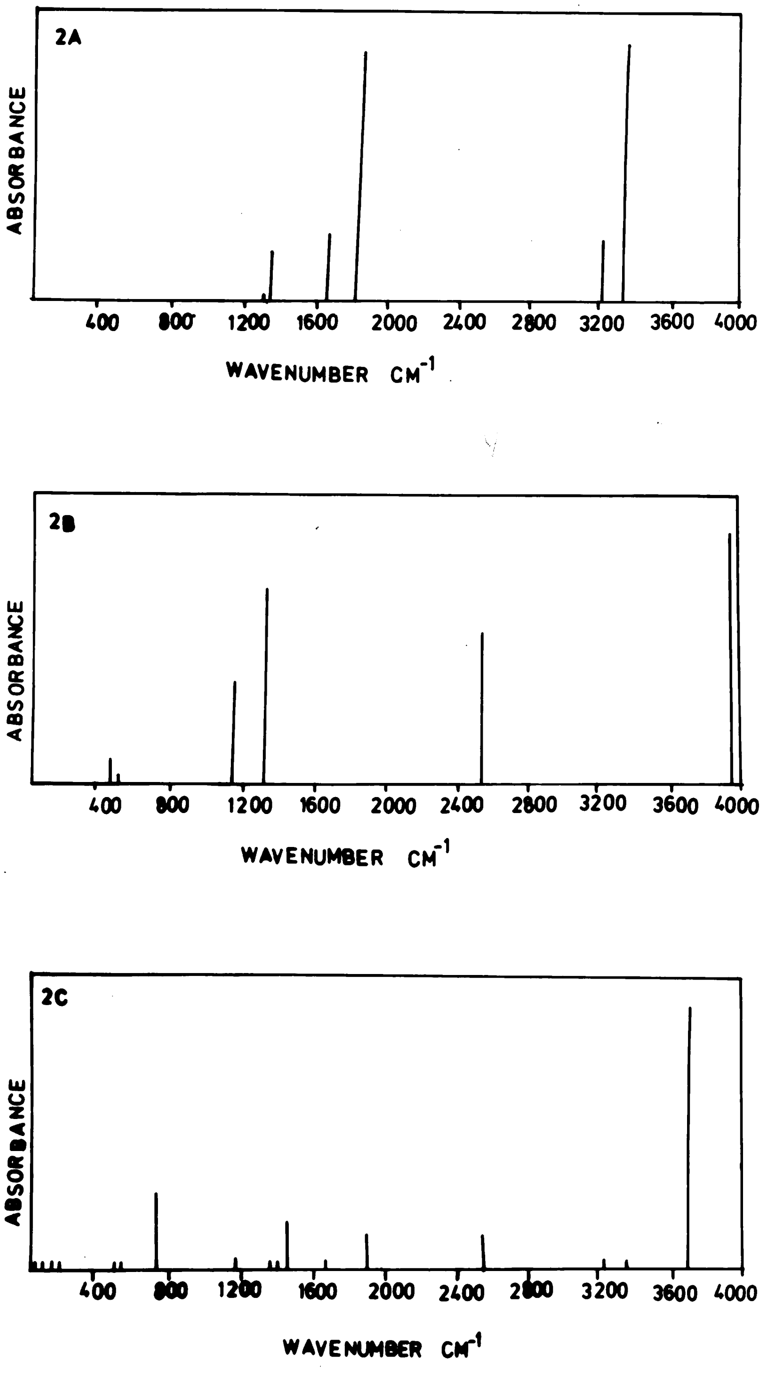

Fig. 2. Theoretical non-scaled 6-31G IR spectra of: $H_2CO$ (A), HOC≡N (B) and $H_2CO$...HOC≡N (C).

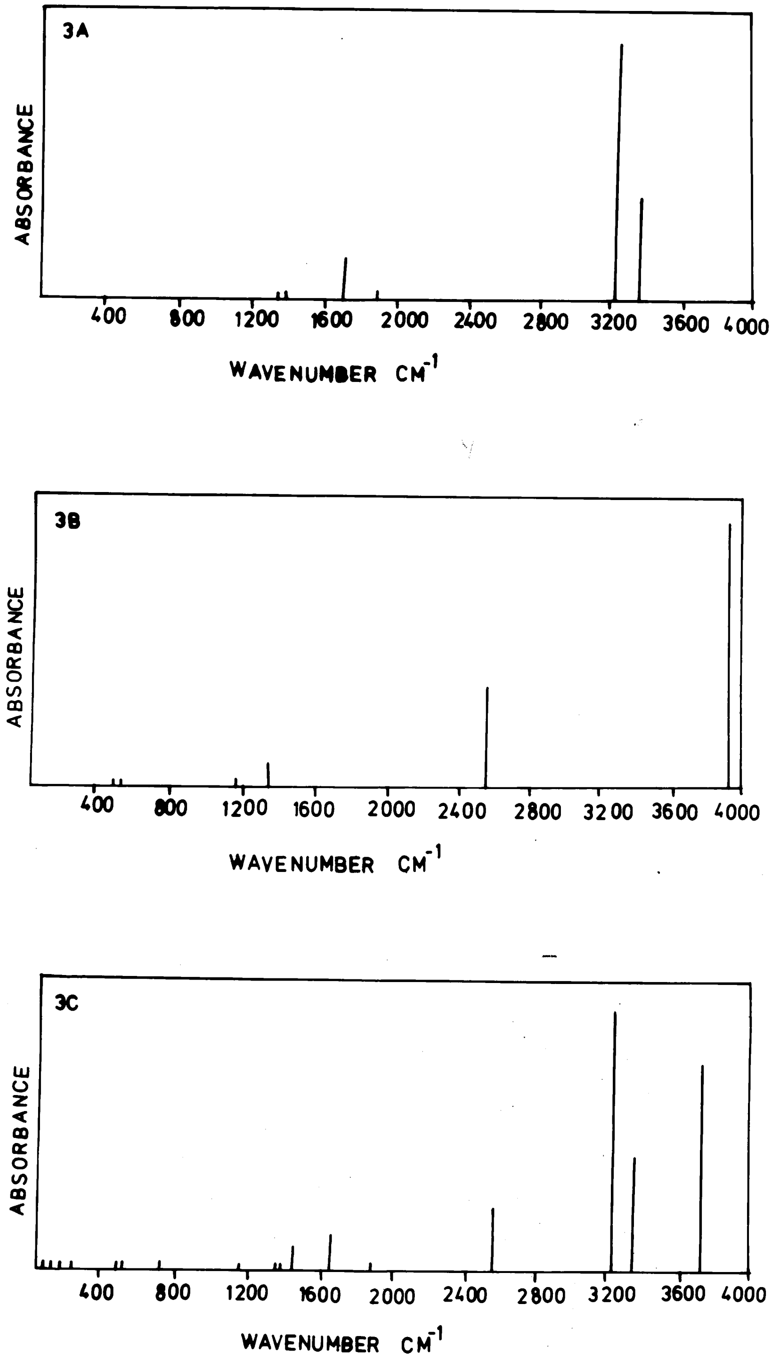

Fig. 3. Theoretical non-scaled 6-31G Raman spectra of: $H_2CO$ (A), HOC≡N (B) and $H_2CO$...HOC≡N (C).

the shift, for example, of the OH-stretching vibration. The predicted frequency shift for the mode $\nu_1$ is $-15.6$ cm. The IR intensity of the $\nu_{CO}$ vibration increases significantly in the complex (by about 50%), while the Raman activity of the same mode increases by about 18%.

The stretching C≡N vibration ($\nu_7$) is also sensitive to a complexation. The predicted frequency $\nu_{CN}$ in the complex is shifted to lower frequency, corresponding to bond weaking, namely $\Delta\nu^{scal}$ is $-16.0$ cm$^{-1}$. At the same time, the IR intensity of the mode $\nu_7$ increases by about 40%, while the Raman activity changes negligibly upon hydrogen bonding. The changes in the vibrational characteristics of the stretching C≡N vibration arising from the complexation can be explained with the charge rearrangement. As a result of the hydrogen bonding the nitrogen atom (see Table 2) acts as an acceptor of electric charge and its negativity increases significantly in the complex.

The data presented in Table 3 show that the complexation between $H_2CO$ and HOC≡N leads to frequency shifts of the rest stretching vibrations in the complex studied: $\nu_{CH}^{sym}$ ($\nu_2$), $\nu_{CH}^{as}$ ($\nu_3$) and $\nu_{OC}$ ($\nu_{10}$). The calculated frequencies in the complex are shifted to higher frequencies in comparison with the corresponding values for the monomers. At the same time the predicted IR intensities of these vibrations are lower in the complex, while their Raman activities change negligibly.

It is important to note that the complexation leads to some changes of the vibrational characteristics of the deformation vibrations. The ab initio calculations predict small changes in the vibrational frequencies, IR intensities and Raman activities for the deformation vibrations $\nu_4$, $\nu_5$ and $\nu_6$.

As can be seen from the calculated values presented in Table 3, the most sensitive to the hydrogen bonding is the deformation HOC vibration ($\nu_9$). Its frequency is shifted to higher wavenumbers, namely $\Delta\nu^{scal}$ is 107.2 cm. The IR intensity of this vibration increases by about 34%, while the Raman activity remains low.

The ab initio calculations predict small changes of the vibrational characteristics of the deformation vibrations ($\nu_{11}$ and $\nu_{12}$ of HOC≡N in the complex. These vibrations are shifted to higher frequencies.

Two additional modes are predicted for the hydrogen-bonded complex between $H_2CO$ and HOC≡N (see Table 3): the deformation OH...O vibration ($\nu_{13}$) and the stretching H...O vibration ($\nu_{14}$). The ab initio calculations predict high IR intensity and low Raman activity of the deformation OH...O vibration. The stretching H...O vibration has low IR intensity and Raman activity.

## 3. Conclusions

In the present study the influence of the hydrogen bonding on the vibrational characteristics for the binary complex formed between $H_2CO$ and HOC≡N has been investigated using ab initio calculations at the 6-31G basis set. The main results can be summarised as follows:

(1) The complexation between $H_2CO$ and HOC≡N results in essential changes of the vibrational characteristics of the stretching vibrations: $\nu_{O-H}$ and $\nu_{C=O}$ for both monomer bonds involved in hydrogen bonding. The frequency of the $\nu_{O-H}$ is shifted to a lower wavenumber by 230.7 cm$^{-1}$ and its IR intensity increases about five times. The magnitude of the frequency shift of the $\nu_{C=O}$ is relatively small compared with shift of the $\nu_{O-H}$.

(2) The ab initio calculations show that the remaining vibrations (stretching and deformation) are less sensitive to the complexation. Their vibrational characteristics are changed with lower magnitudes.

(3) The ab initio calculations predict high IR intensity and low Raman activity for the deformation OH...O vibration, while the stretching H...O vibration has low IR intensity and Raman activity.

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