

Calculations of vibrational frequencies, Raman activities and degrees of depolarization for complexes involving water, methanol and ethanol

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Abstract

Raman activities and degrees of depolarization are reported for 14 complexes involving methanol, ethanol and water using the MP2/aug-cc-pVDZ model. For ethanol both *trans* and *gauche* isomers are considered. The red-shifts of the OH stretching and the blue shifts of the bending $\tau_{\text{CO-OH}}$ mode were analyzed for the proton-donor molecules upon hydrogen bond. The shift of the ν_{CO} stretching mode of the alcohol molecules are also analyzed and found to be specific giving characterization of the amphoteric relation, being positive for the proton-acceptor and negative for the proton-donor molecule.

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1. Introduction

Alcohol–water and alcohol–alcohol mixtures are very important systems exhibiting physico-chemical properties that are of great interest. In particular alcohol–water mixtures and its anomalous thermodynamics properties have motivated a large number of experimental and theoretical studies [1–22]. Most, if not all, interesting properties are derived from the great ability alcohol and water has of forming hydrogen bonds. Because of this hydrogen-bonded complexes have been widely studied allowing a microscopic vision of the different phenomena, including solvation [14,15]. In fact, the organization and structural arrangement of the hydrogen bonds network formed by alcohol and water are related to the amphoteric relation, where they can be both proton-donor and proton-acceptor. Alcohol and water can have two hydrogen-bonded structures corresponding to the two possible heterodimers, where a molecule can be proton-acceptor or proton-donor. Theoretical studies involving amphoteric systems have used dif-

ferent models such as density-functional theory [6], second-order Møller–Plesset (MP2) [1–4,7,12] and higher-order MP and coupled-cluster [1,7,12].

The amphoteric relation has motivated the study of the dual hydrogen-bonded complexes to characterize the structure and the intermolecular interactions. Spectroscopic characterization has been largely used, in special infrared spectroscopy associated with theoretical calculations. However, there have been only very few reports of *ab initio* studies of Raman spectra and intensities on hydrogen-bonded complexes [5,18]. In fact most of the previous works treat only isolated molecules [23–28]. A detailed theoretical Raman characterization seems to be missing. Raman spectra can be very useful in the possible characterization of these complexes. Opposite to the case of elastic (Rayleigh) scattering the depolarization in the Raman case is specific for each vibrational mode and thus becomes convenient to probe the changes upon hydrogen bond formation. This is the subject of this Letter. To fill the gap we report *ab initio* results for Raman activities (vibration frequencies and intensities) and degrees of light depolarization for 14 dimers and heterodimers complexes involving water (W), methanol (M) and ethanol molecules, with this latter considered in both *trans* (E_t) and *gauche* (E_g) forms. There

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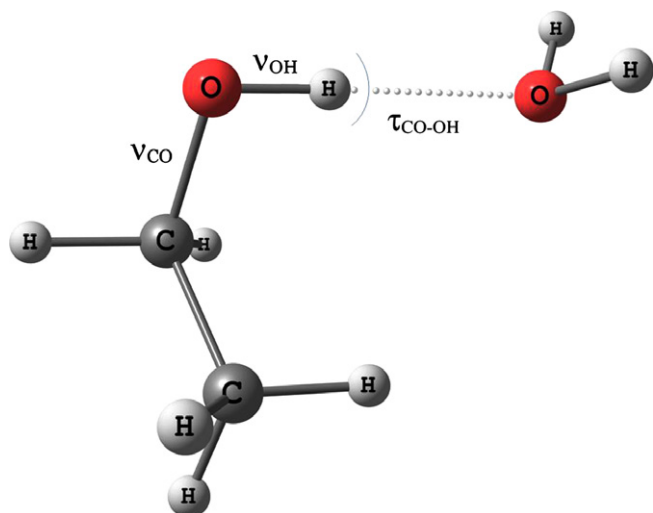


Fig. 1. Illustration of the three vibrational modes associated to the OH (ν_{OH}) stretching, the OH torsion mode, ($\tau_{\text{CO-OH}}$) and the CO (ν_{CO}) stretching of the RCOH proton-donor molecule.

are of course a large number of vibration frequencies for these complexes, making an extensive amount of data. Here we are interested in characterizing the influence of hydrogen bond formation on these modes to obtain a useful characteristic for the amphoteric relation. Therefore, we will report only the modes that are mostly influenced by the hydrogen bonds. These are the OH (ν_{OH}) stretching, the OH bending, or torsion mode, ($\tau_{\text{CO-OH}}$) and the CO (ν_{CO}) stretching of the RCOH proton-donor molecule (Fig. 1). We also present the frequency shifts upon complexation and analyze these in terms of the amphoteric character of the hydrogen-bonded systems.

2. Methodology

Full geometry optimizations were made for all systems using the MP2/aug-cc-pVDZ theoretical method implemented in the GAUSSIAN 03 program [29] with the CHEM-CRAFT program [30] serving as the graphical interface. Previous applications have shown that the MP2 method is a good compromise giving accurate results with a relatively low computational cost [1–4,7,12,21,31–33]. In total 18 systems were considered, corresponding to the four isolated molecules and 14 hydrogen-bonded complexes. Vibrational frequencies were calculated for all molecules and complexes. The vibration analysis also serves the purpose of ensuring that all the optimized geometries are true energy minima. The 14 complexes studied are the dimers (H_2O)₂, (CH_3OH)₂ and ($\text{CH}_3\text{CH}_2\text{OH}$)₂, and the heterodimers $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$, $\text{CH}_3\text{OH}\cdots\text{OH}_2$, $\text{CH}_3\text{CH}_2\text{HO}\cdots\text{H}_2\text{O}$, $\text{CH}_3\text{CH}_2\text{OH}\cdots\text{OH}_2$, $\text{CH}_3\text{CH}_2\text{HO}\cdots\text{HOCH}_3$ and $\text{CH}_3\text{CH}_2\text{OH}\cdots\text{OHCH}_3$, where the ethanol molecule is considered in the *trans* and *gauche* forms. The two forms of the ethanol can lead to a large variety of conformers [1,5,12,18,21]. In fact, there are several possible combinations [12,18] of two ethanol molecules to form the ethanol dimer. Explicit consideration of all possi-

ble conformers of the ethanol dimer would depart us from the present focus of interest. In the following we consider the four best-known ethanol dimers. In the following we use the acronym DA where the first letter stands for the proton-donor and the second for the proton-acceptor molecule.

3. Results

Table 1 present the calculated values for the vibrational frequencies, unscaled (ω) and scaled (ω_{scaled}), infrared intensities (I_0), Raman activities (A_0) and degrees of depolarization (ρ_{p0} and ρ_{n0}) for the three selected vibrational modes of each isolated molecule. ρ_{p0} and ρ_{n0} stand for the depolarization of planar and natural incident light, respectively. For water, all modes are given while for alcohol molecules we have selected only the modes involved in the hydrogen bond, where the changes in the infrared intensities and/or Raman activities are sizeable. The infrared spectrum for the isolated molecules was analyzed previously [1,2] so here we discuss only the properties of the Raman spectra. For the water molecule the experimental values [24] of the Raman activities are 0.9 ± 2 , 108 ± 14 and 19.2 ± 2.1 [25] $\text{\AA}^4 \text{uma}$, respectively for δ_{HOH} , $\nu_{\text{OH(sym)}}$ and $\nu_{\text{OH(asym)}}$ modes. Previous theoretical values obtained at the CCSD [26] level are 1, 111 and $26 \text{\AA}^4 \text{uma}$, in good agreement. The results of 2, 104 and $24 \text{\AA}^4 \text{uma}$ obtained in this work are in good agreement with both the experimental and previous theoretical results, giving credence to the present calculated results. For the δ_{HOH} and $\nu_{\text{OH(sym)}}$ modes, the depolarization values of 0.63 and 0.04 obtained here are also in good agreement with the CCSD theoretical results of 0.71 and 0.04 [26] and the experimental results of 0.74 and 0.03 [24].

Table 1

Calculated vibrational frequency (cm^{-1}), infrared intensities (km/mol), Raman activities ($\text{\AA}^4 \text{uma}$) and degrees of depolarization for polarized and unpolarized light for the isolated species

Mode	ω	ω_{scaled}	I_0	A_0	ρ_{p0}	ρ_{n0}
<i>Water</i>						
δ_{HOH}	1622	1558	67	2	0.63	0.77
$\nu_{\text{OH(sym)}}$	3803	3652	4	104	0.04	0.08
$\nu_{\text{OH(asym)}}$	3937	3781	67	24	0.75 ^a	0.86 ^a
<i>Methanol</i>						
$\tau_{\text{CO-OH}}$	311	299	105	1	0.75 ^a	0.86 ^a
ν_{CO}	1043	1002	112	4	0.19	0.32
ν_{OH}	3841	3689	34	71	0.16	0.27
<i>Ethanol-t</i>						
$\tau_{\text{CO-OH}}$	307	295	86	1	0.75 ^a	0.86 ^a
ν_{CO}	1099	1055	42	6	0.46	0.63
ν_{OH}	3829	3677	32	100	0.19	0.32
<i>Ethanol-g</i>						
$\tau_{\text{CO-OH}}$	280	269	68	1	0.62	0.76
ν_{CO}	1092	1049	58	5	0.68	0.81
ν_{OH}	3822	3671	26	68	0.14	0.25

A scaling factor of 0.9604 was taken from Ref. [35].

^a These are the exact values of 3/4 and 6/7, respectively. See text.

For the alcohol molecules we report only the three modes that are involved in the hydrogen bond. For the methanol molecule, the larger Raman active among these modes is for ν_{OH} . The Raman activity of 71 \AA^4 uma obtained is comparable to the previous CCSD(T) result of 65 \AA^4 uma [34]. The degree of depolarization ρ_p calculated here is 0.16 while the CCSD(T) value is 0.25 [34]. For ethanol molecule ν_{OH} is again the most Raman active and the values obtained here for ρ_p were 100 and 68 \AA^4 uma, respectively for E_t and E_g . No previous result was found for ethanol. The depolarizations of $\nu_{\text{OH(asy)}} of water and $\tau_{\text{CO-OH}}$ of methanol and ethanol-*trans* take the maximum possible value of (3/4 for ρ_p and 6/7 for ρ_n) because there is no variation of the dipole polarizability with respect to these vibration modes. In the case of ethanol-*gauche*, however, the depolarization is slightly lower but still very large.$

We now analyze the hydrogen-bonded systems. Tables 2–4 present the frequency shifts and the increase (or decrease) factor, after hydrogen bond formation, in relation to the isolated molecule, of the infrared intensity (I/I_0) Raman activity (A/A_0) and degrees of depolarization (ρ_p/ρ_{p0} and ρ_n/ρ_{n0}). Table 2 presents the results for ν_{OH}

Table 2

Calculated vibrational frequency shifts (cm^{-1}), ratio of infrared intensities, ratio of Raman activities and ratio of degrees of depolarization for polarized and unpolarized light for all complexes for the ν_{OH} mode

ν_{OH} mode	$\Delta\omega$	I/I_0	A/A_0	ρ_p/ρ_{p0}	ρ_n/ρ_{n0}
WM	-145	82.0	1.5	3.5	3.2
MW	-120	11.8	2.1	1.1	1.1
E_tW	-159	81.3	1.4	3.6	3.3
E_tW	-117	13.7	2.0	1.1	1.1
E_gW	-161	82.4	1.4	3.6	3.3
E_gW	-113	13.2	2.1	1.2	1.1
ME_t	-181	13.3	1.8	1.4	1.3
E_tM	-161	15.1	1.8	1.2	1.2
ME_g	-184	13.8	1.9	1.4	1.4
E_gM	-157	15.0	1.9	1.4	1.3
WW	-98	68.0	1.6	2.6	2.5
MM	-166	14.0	2.0	1.4	1.3
E_tE_t	-179	15.4	1.7	1.2	1.2
E_gE_g	-174	14.8	1.7	1.4	1.4

Table 3

Calculated vibrational frequency shifts (cm^{-1}), ratio of infrared intensities, ratio of Raman activities and ratio of degrees of depolarization for polarized and unpolarized light for all complexes for the $\tau_{\text{CO-OH}}$ mode

$\tau_{\text{CO-OH}}$ mode	$\Delta\omega$	I/I_0	A/A_0	ρ_n/ρ_{n0}	ρ_p/ρ_{p0}
MW	371	1.0	0.4	1.0	1.0
E_tW	377	1.1	0.5	1.0	1.0
E_gW	388	1.4	0.7	1.1	1.0
ME_t	404	1.0	0.6	1.0	1.0
E_tM	390	1.2	1.0	1.0	1.0
ME_g	398	0.8	0.8	1.0	1.0
E_gM	410	1.4	1.0	1.1	1.0
MM	397	1.0	0.6	1.0	1.0
E_tE_t	409	1.3	0.7	1.0	1.0
E_gE_g	421	1.4	1.0	1.0	1.0

Table 4

Calculated vibrational frequency shifts (cm^{-1}), ratio of infrared intensities, ratio of Raman activities and ratio of degrees of depolarization for both polarized and unpolarized light for all complexes for the ν_{CO} mode

ν_{CO} mode	$\Delta\omega$	I/I_0	A/A_0	ρ_p/ρ_{p0}	ρ_n/ρ_{n0}
WM	-15	0.9	1.6	0.8	0.8
MW	20	0.8	1.6	1.1	1.1
E_tW	12	0.9	0.9	0.8	0.9
WE_t	-17	0.8	0.9	0.8	0.9
E_gW	4	1.8	0.6	1.1	1.1
WE_g	-12	0.5	1.0	1.1	1.0
ME_t	19 (-16)	0.8 (0.8)	1.5 (1.0)	1.1 (0.7)	1.1 (0.7)
E_tM	12 (-14)	1.0 (1.0)	0.9 (1.7)	0.8 (0.6)	0.8 (0.6)
ME_g	19 (-13)	0.6 (0.4)	2.2 (1.0)	1.2 (1.1)	1.2 (1.0)
E_gM	6 (-16)	1.6 (1.0)	0.5 (1.5)	0.8 (0.7)	0.9 (0.8)
MM	20 (-14)	0.8 (1.0)	1.7 (1.6)	1.1 (0.8)	1.1 (0.8)
E_tE_t	12 (-16)	0.9 (0.6)	0.8 (0.7)	0.7 (1.4)	0.8 (1.2)
E_gE_g	5 (-13)	1.7 (0.4)	0.5 (0.9)	0.7 (1.1)	0.8 (1.0)

In the cases of alcohol–alcohol complexes the values in parenthesis are related to the proton-acceptor molecule.

mode of the proton-donor molecule. A large red-shift in the frequency varying from -98 cm^{-1} (for WW) to -184 cm^{-1} (for ME_g) is obtained. This red-shift is consistent with the increase of the O–H bond of the proton-donor molecule, as shown in Table 5. The increasing factor of the infrared intensity is around 80 for the complexes where water is the proton-donor molecule. For the other complexes, where water is the proton-acceptor there is a dramatic change and the increasing factor is reduced lying in the range of 11–16. The Raman activity for this mode also increases after complexation. For complexes where water is the proton-donor this increase is systematically around 40% but when water is the proton-acceptor this increase is around 100%. In the cases of alcohol–alcohol complexes the increase is around 80%. In the case of the degrees of depolarization we obtain a large increase for all complexes where the water molecule is the proton-donor. However the increase refers to a very small reference value of the isolated molecule (see Table 2). For the other complexes the increase of the degrees of depolarization varies from *ca.* 10% to 50%.

The results for the $\tau_{\text{CO-OH}}$ mode of the proton-donor molecule are given in Table 4. This mode presents a large and characteristic blue-shift (around 400 cm^{-1}). All Raman activities for the isolated molecule are small ($\sim 1 \text{ \AA}^4$ uma) and in general decrease upon complexation. The degrees of depolarization are not significantly influenced by the hydrogen bond.

Table 4 presents the results for the ν_{CO} mode. This mode is present only for alcohol. We have analyzed this mode both for the proton-acceptor and proton-donor molecules of the alcohol–alcohol complexes. First, we note, for the complexes where the water is proton-donor, a red-shift of -12 to -17 cm^{-1} is calculated for the proton-acceptor alcohol system. For the case of water as a proton-acceptor the calculated blue-shift is small varying from 4 to 20 cm^{-1} . For the alcohol–alcohol complexes the results indicate systematically that the proton-donor molecules present a blue-

Table 5

Calculated distances R_{O-H} and R_{C-O} at proton-donor and R_{C-O} at proton-acceptor molecule (Å) for all complexes obtained from MP2/aug-cc-pVDZ theoretical level

	$R_{O...O}$	R_{O-H}	$R_{C-O(acceptor)}$	$R_{C-O(donor)}$	μ	α	$\Delta\alpha$
<i>Monomers</i>							
W	–	0.966	–	–	1.88	9.30	1.03
M	–	0.966	–	–	1.71	21.22	3.35
E_t	–	0.966	–	–	1.62	33.58	3.46
E_g	–	0.967	–	–	1.75	33.55	4.38
<i>Homodimers</i>							
WW ^a	2.918	0.973	–	–	2.64	19.10	3.57
MM ^a	2.846	0.974	1.444	1.429	2.50	42.77	5.55
$E_tE_t^a$	2.850	0.975	1.451	1.433	2.59	67.41	8.04
E_gE_g	2.845	0.975	1.449	1.433	2.26	67.00	8.99
<i>Heterodimers</i>							
MW ^a	2.912	0.972	–	1.429	2.73	31.19	4.04
WM ^a	2.844	0.975	1.444	–	2.04	30.67	4.43
E_tW	2.914	0.972	–	1.434	2.49	43.71	6.41
WE_t	2.843	0.976	1.452	–	1.94	42.90	5.25
E_gW	2.922	0.973	–	1.433	2.84	43.51	4.28
WE_g	2.834	0.976	1.449	–	2.04	42.86	4.52
ME_t	2.888	0.974	1.450	1.429	3.32	54.83	6.04
E_tM	2.853	0.974	1.443	1.433	2.66	55.15	7.42
ME_g	2.830	0.975	1.449	1.430	2.13	55.11	7.34
E_gM	2.860	0.975	1.444	1.433	2.55	54.86	8.67

The values for R_{C-O} distance of the isolated species are 1.435; 1.440 and 1.437 Å for methanol, ethanol-t and ethanol-g, respectively. The R_{O-H} distance is 0.966 Å for all isolated molecules. Dipole moments (D) and the average and anisotropic dipole polarizabilities (in au) of the hydrogen-bonded species are also given for completeness.

^a Obtained in Ref. [1], except the dipole polarizabilities.

shift and for proton-acceptor molecule a red-shift. This result is consistent with the fact that the R_{C-O} distance increases for the proton-acceptor and decreases for the proton-donor molecule, as can be seen in Table 5. The Raman activities for this mode in the isolated molecules are 4.2, 6.0 and 5.2 Å⁴ uma for methanol, ethanol-*trans* and ethanol-*gauche* respectively. Overall the Raman activity does not suffer appreciable modification upon complexation. The increase factor for the degrees of depolarization varies only from 0.6 to 1.2. For completeness Table 5 also gives the calculated average and anisotropic dipole polarizabilities for all 14 systems considered here.

4. Conclusion

We present results of MP2/aug-ccpVDZ calculations of the vibrational frequencies, Raman activities and degrees of depolarization for 14 complexes involving alcohol and water. Comparison between the calculated results and the available experimental values for the Raman activities and degrees of depolarization of the isolated molecules is made and are found to be in good agreement. For the hydrogen-bonded systems three normal modes, mostly influenced by the hydrogen bond formation, were analyzed. One is the OH stretch ν_{OH} , where the usually large red-shift and the characteristic increase of the infrared intensity are obtained. The Raman activity and depolarization are analyzed for the OH (ν_{OH}) stretching, the OH torsion mode, (τ_{CO-OH}) and the CO (ν_{CO}) stretching of the

RCOH proton-donor molecule. The larger increase of the Raman activity occurs for the complexes where water is the proton-acceptor molecule. For τ_{CO-OH} a large blue-shift was calculated for all complexes. The Raman activities associated to the torsion mode τ_{CO-OH} decrease upon complexation and the depolarization is essentially the same. For the ν_{CO} stretch mode, however, it was found that for the proton-donor molecule it presents a blue-shift while for the proton-acceptor molecule it presents a red-shift. This result can be useful to distinguish between donor and acceptor molecule giving some additional insight to the amphoteric relation.

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