
Calculated Infrared Spectra of Hydrogen-Bonded Methanol–Water, Water–Methanol, and Methanol–Methanol Complexes

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Received 5 January 2005; accepted 18 January 2005

Published online 15 April 2005 in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/qua.20585

ABSTRACT: Ab initio calculations at the B3LYP/aug-cc-pVDZ, B3PW91/aug-cc-pVDZ, MP2/aug-cc-pVDZ, B3LYP/6-311++G(2d,2p), B3PW91/6-311++G(2d,2p), and MP2/6-311++G(2d,2p) levels are performed for the IR spectra of isolated water and methanol molecules and hydrogen-bonded water–methanol, methanol–water, and methanol–methanol complexes. Frequency shifts and changes in intensities are obtained for the proton donor molecule and the results are compared with available experimental and theoretical results. Characteristic changes are discussed in all cases. For methanol we obtained considerable shifts in the OH group. The C–OH wag is calculated to blue shift and the OH stretch is calculated to red shift and increase in intensity is compared to the isolated methanol molecule. The magnitude of these shifts are obtained and discussed. For the methanol dimer the C–OH wag increases the frequency by $\sim 400\text{ cm}^{-1}$ and the OH stretch decreases the frequency by $\sim 170\text{ cm}^{-1}$, with an increase in intensity of nearly 15 times. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 104: 808–815, 2005

Key words: density functional theory; perturbation theory; infrared spectra; hydrogen bonds; methanol–water complexes

1. Introduction

Infrared spectroscopy is an important experimental technique widely used to characterize molecular clusters. For hydrogen-bonded systems

IR spectroscopy is useful in probing the properties of the molecular cluster from changes in vibration frequencies and intensities [1–4]. In this direction, alcohol–water mixtures are among the most important mixtures. Because alcohol and water are both proton donor and acceptor their aggregation yields two possible hydrogen-bonded structures. In one, the alcohol is the proton donor $\text{ROH} \cdots \text{OH}_2$ and in

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the other it is the proton acceptor $\text{RHO} \cdots \text{HOH}$. This dual relation allows alcohol and water to form two isomers. Recently, many studies have been devoted to these systems because of its great importance in physical chemistry [5–22]. Methanol–water is the most common example where both methanol and water can act as proton donor and proton acceptor of hydrogen bonds. Theoretical and experimental studies on the IR spectrum of methanol–water complexes have been reported [12, 17, 19, 20]. The methanol–methanol complex has been less studied than water–methanol complexes. The methanol–methanol system was studied both experimentally and theoretically [10, 14–16], but apparently there is no detailed study of the IR spectrum. Lovas et al. [21] have determined the microwave spectrum of the methanol dimer but no information of the infrared spectrum is given.

An important additional question on these isomers is the determination of which is more stable in gas phase. Early conflicting results [23–26] were solved with more recent calculations [7, 12, 15, 17, 22] that have shown that the isomer where the water molecule is the proton donor is more stable than the isomer where the water molecule is the proton acceptor, by less than 1.0 kcal/mol. These results have been confirmed by microwave rotation-tunneling spectroscopy [18].

In this work we use density functional theory (DFT) [27] and second-order many-body perturbation theory in the Møller–Plesset partitioning (MP2) [28] to determine the structure and IR spectrum of the complexes involving methanol and water. Three possible cases are considered: methanol–water, water–methanol, and methanol–methanol. The shifts in the most characteristic vibration frequencies of the proton donor molecules are determined as well as the IR ratio intensities after the hydrogen bond formation. We also present the results for the binding energy of the different complexes.

2. Calculation Details

Ab initio calculations were performed to obtain the structures, vibration frequencies, binding energies, and IR intensities of the complexes involving the water and methanol molecules: $\text{CH}_3\text{HO} \cdots \text{HOH}$ (WM), $\text{CH}_3\text{OH} \cdots \text{OH}_2$ (MW), $(\text{CH}_3\text{OH})_2$ (MM), and the isolated species. All binding energies reported are corrected against the BSSE using the counterpoise correction [29]. These complexes are shown in Figure 1. To ascertain the theoretical accuracy, six different the-

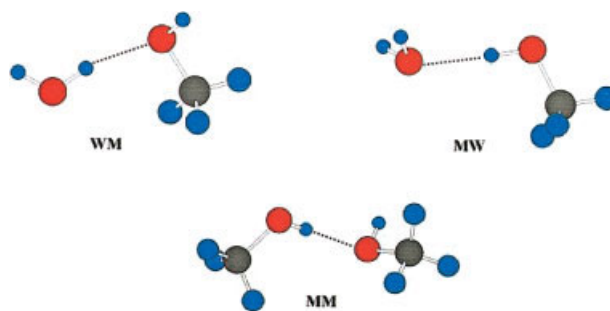


FIGURE 1. The structures of the complexes involving methanol and water: MW, where methanol is the proton donor; WM, where water is the proton donor; and the dimer complex methanol–methanol, MM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

oretical models have been used: B3LYP/aug-cc-pVDZ, B3PW91/aug-cc-pVDZ, MP2/aug-cc-pVDZ, B3LYP/6-311++G(2d,2p), B3PW91/6-311++G(2d,2p), MP2/6-311++G(2d,2p). The hybrid DFT functionals, and the corresponding acronyms, are explained in Ref. [30]. In the calculation of the binding energies single-point calculations are made up to the CCSD(T) level [28]. All calculations were carried out with the GAUSSIAN 03 ab initio package [31].

3. Results and Discussion

3.1. DISTANCES, BINDING ENERGIES AND DIPOLE MOMENTS

Vibration frequencies are obtained as the eigenvalues of the Hessian matrix determined at the corresponding equilibrium configurations. Therefore, we first performed full geometry optimizations for water–methanol (water is the proton donor, WM), methanol–water (methanol is the proton donor, MW), and methanol–methanol (MM) complexes as well as the isolated species water and methanol (Fig. 1). The equilibrium geometries have been obtained using all the six different theoretical models. The results are summarized in Table I and corroborate theoretical results obtained previously at the MP2/aug-cc-pVDZ level [22]. Overall, the hydrogen bond distances agree well with experimental results, when available [18, 21]. The dipole moments of the isolated molecules and the complexes are also given in Table I. The experimental dipole moments of isolated water and methanol, 1.86 and 1.70 D [32], are well reproduced at the

TABLE I

Calculated dipole (D) and $R_{O...O}$ and $R_{O...H}$ (Å) distances for the hydrogen-bonded complexes using six theoretical models.

		Aug-cc-pVDZ			6-311++G(2d,2p)		
		B3LYP	B3PW91	MP2	B3LYP	B3PW91	MP2
W	Dipole	1.850	1.864	1.879	1.960	1.956	1.975
M	Dipole	1.657	1.633	1.714	1.743	1.714	1.795
WM	$R_{O...O}$	2.875	2.880	2.844	2.884	2.886	2.860
	$R_{O...H}$	1.908	1.912	1.904	1.919	1.921	1.911
	Dipole	2.712	2.704	2.040	2.788	2.799	2.367
MW	$R_{O...O}$	2.920	2.913	2.912	2.927	2.920	2.911
	$R_{O...H}$	1.954	1.950	1.942	1.965	1.959	1.948
	Dipole	2.598	2.535	2.734	2.600	2.539	2.800
MM	$R_{O...O}$	2.882	2.882	2.846	2.893	2.890	2.852
	$R_{O...H}$	1.916	1.915	1.887	1.928	1.927	1.895
	Dipole	2.668	2.675	2.499	2.772	2.726	2.720

MP2/aug-cc-pVDZ level. Among the DFT methods, the best performance for the dipole moment of the isolated species is obtained with the B3PW91/aug-cc-pVDZ. Limited information is available for the dipole moment of the complexes. Experimentally, the value for the WM complex has been obtained as 2.66 D [18]. The theoretical results range between 2.04 and 2.80 D depending on the model used and, again, the B3PW91/aug-cc-pVDZ result of 2.70 D is in better agreement. It is conceivable that, in a binary mixture [5], two isomers, WM and MW, are present and the dipole moment should be obtained using the Boltzmann average. In this case, for instance, the MP2/aug-cc-pVDZ average result would be 2.55 D.

The hydrogen bond energies were also determined for the three complexes and are shown in Table II. The results for the MW and WM complexes are similar to those obtained before [22] and reiterate that the WM isomer is more strongly bound than MW by less than 1 kcal/mol [12, 17, 18, 22]. But it can be noted that the MM complex has the strongest binding energy. The value of 5.45 kcal/mol expected to be the basis-set limit of CCSD(T) [14] for the MM complex is in very good agreement with our B3PW91/aug-cc-pVDZ//CCSD(T) value of 5.40 kcal/mol, and is slightly higher than the B3LYP/aug-cc-pVDZ//CCSD(T) result of 5.16 kcal/mol and the MP2/aug-cc-pVDZ//CCSD(T) value of 5.11 kcal/mol. Among the DFT results we note a better performance using the B3PW91 geometry. The results of Table II permit a systematic analysis of the electron correlation

effects on the binding energy. The similarity of the CCSD(T) and MP2 results is noteworthy, suggesting that MP2 is a well-balanced model for obtaining binding energies of hydrogen bond complexes.

3.2. VIBRATION FREQUENCIES AND INFRARED INTENSITIES

Next we discuss the IR results for the three complexes with the six different theoretical models. For reference, we first consider the calculated vibration modes of the isolated molecules, water and methanol. Experimental results are available and are presented in Table III along with the theoretical results for the vibration frequencies and IR intensities of water and the most characteristic normal modes of the methanol molecule. Overall, the results are in fair agreement with experiment. The τ_{C-OH} is the low-frequency wag of the OH group of methanol; it is observed for methanol in argon matrix at 272 cm^{-1} . Our results for the isolated methanol molecule range between the lowest value of 286 cm^{-1} and the largest value of 311 cm^{-1} . Of particular interest is the ν_{OH} mode of methanol that is expected to suffer the largest shift after complex binding, when methanol is the proton donor (MW and MM). The largest differences between the computed and experimental frequencies are obtained for the $\nu_{\text{Methyl(asy)}}^{\text{Methyl(asy)}}$ and $\nu_{OH(\text{sym})}^{\text{OH(sym)}}$ modes of the methanol molecule at the MP2/6-311++G(2d,2p) level. The $\nu_{CO} + \delta_{COH}$ normal mode is described in very good agreement with the corresponding experimental frequency in all theoretical models. This

TABLE II
Calculated counterpoise corrected binding energies (kcal/mol) of the complexes.

Method	B3LYP Geometry					
	Aug-cc-pVDZ			6-311++G(2d,2p)		
	WM	MW	MM	WM	MW	MM
MP2	5.14	4.51	5.24	5.16	4.52	5.20
MP3	4.95	4.44	5.04	4.98	4.45	5.02
D-MP4	4.87	4.36	4.96	4.91	4.38	4.95
DQ-MP4	4.74	4.22	4.79	4.78	4.23	4.78
SDQ-MP4	4.81	4.27	4.88	4.83	4.27	4.85
MP4	5.04	4.48	5.18	5.04	4.47	5.12
CCSD	4.80	4.26	4.86	4.83	4.28	4.85
CCSD(T)	5.03	4.49	5.16	5.04	4.48	5.11
ΔZPE	1.89	1.54	1.27	1.91	1.64	1.27
Method	B3PW91 Geometry					
	WM	MW	MM	WM	MW	MM
	MP2	5.07	4.51	5.39	5.08	4.52
MP3	4.88	4.44	5.17	4.91	4.45	4.98
D-MP4	4.81	4.36	5.15	4.84	4.38	4.91
DQ-MP4	4.67	4.21	4.95	4.71	4.23	4.75
SDQ-MP4	4.74	4.27	5.07	4.76	4.27	4.82
MP4	4.97	4.48	5.42	4.96	4.47	5.08
CCSD	4.73	4.26	5.05	4.76	4.27	4.81
CCSD(T)	4.96	4.49	5.40	4.97	4.49	5.08
ΔZPE	1.88	1.60	1.25	1.89	1.65	1.31
Method	MP2 Geometry					
	WM	MW	MM	WM	MW	MM
	MP2	5.15	4.48	5.22	5.15	4.45
MP3	4.90	4.40	4.96	4.94	4.39	4.97
D-MP4	4.82	4.32	4.88	4.87	4.31	4.89
DQ-MP4	4.67	4.17	4.69	4.73	4.16	4.71
SDQ-MP4	4.76	4.22	4.80	4.79	4.20	4.79
MP4	5.04	4.44	5.14	5.02	4.40	5.08
CCSD	4.74	4.22	4.77	4.79	4.20	4.78
CCSD(T)	5.02	4.45	5.11	5.02	4.42	5.07
ΔZPE	1.94	1.58	1.29	1.92	1.72	1.34

DA stands for proton donor and proton acceptor, respectively. ΔZPE is the zero point energy difference between the complex and the separate parts.

mode is a combination of stretching of the CO covalent bond and the bending of the COH angle. The calculated infrared intensities are consistent in all methods. The CO stretch mode, $\nu_{CO} + \delta_{COH}$ of the methanol molecule, is calculated as the most intense normal mode.

For isolated water, agreement is also reasonable but we note that the calculated frequencies are sys-

tematically lower than the experimental results from Ref. [33] and higher than the experimental results of Ref. [35]. It is normally expected that calculated frequencies are slightly overestimated compared to experiment [36]. Regarding the shifts in vibration frequencies, when water is the proton donor (WM complex), the two stretching modes are expected to suffer a red shift and a concomitant

TABLE III

Calculated vibration frequencies (cm^{-1}) and infrared intensities (km/mol) for the isolated water and methanol molecules.

Description	Aug-cc-pVDZ						6-311++G(2d,2p)						Exp ^(a) ω
	B3LYP		B3PW91		MP2		B3LYP		B3PW91		MP2		
	ω	I	ω	I	ω	I	ω	I	ω	I	ω	I	
H₂O													
δ_{HOH}	1619	71.34	1625	70.60	1622	67.48	1639	71.08	1643	70.24	1661	65.50	1648 1590
$\nu_{\text{OH(sym)}}$	3795	4.02	3820	4.00	3804	4.14	3821	7.49	3852	7.87	3862	10.04	3832 3638
$\nu_{\text{OH(asym)}}$	3904	60.62	3931	58.94	3938	67.07	3923	61.71	3957	62.11	3982	73.47	3942 3733
CH₃OH													
$\tau_{\text{C-OH}}$	298	106.85	309	107.62	311	104.89	286	115.32	288	115.33	287	113.58	272
$\nu_{\text{CO}} + \delta_{\text{COH}}$	1041	115.83	1054	93.67	1043	112.10	1037	120.20	1053	118.55	1048	114.29	1034
δ_{COH}	1358	25.65	1362	25.92	1366	22.11	1371	24.84	1373	25.18	1386	21.45	1340
$\nu_{\text{Methyl(sym)}}$	3002	64.05	3003	65.70	3053	56.54	3004	62.41	3007	62.20	3069	53.27	2999
$\nu_{\text{Methyl(asym)}}$	3058	54.12	3066	55.02	3131	44.65	3050	54.67	3059	53.42	3138	42.74	2970
ν_{OH}	3830	29.68	3857	30.73	3841	34.37	3852	31.65	3884	33.50	3895	39.90	3682

The last column presents the experimental results for the frequencies.

^(a) Refs. [33, 34]. Values on the bottom are the frequencies of H₂O from Ref. [35].

increase in intensity, whereas the δ_{HOH} bending mode is expected to suffer a blue shift, after complexation. The IR intensity in water is the subject of considerable theoretical interest [37]. On the experimental side the relative intensities [38] are 1:14.5:21.5 for the $\nu_{\text{OH(sym)}}$, $\nu_{\text{OH(asym)}}$, and δ_{HOH} modes, respectively. On the theoretical side, these ratios are in reasonable agreement. For the B3LYP/aug-cc-pVDZ model, for instance, these ratios are 1:15.1:17.7.

Table IV reports the changes in vibration frequencies after hydrogen bonding for all complexes and all theoretical models considered here. The vibration frequencies of the proton acceptor molecules change little and are not reported. This is the case of water in MW and methanol in WM. In the case of MM, only the changes in the proton donor methanol are reported. We will comment on the small exceptions later in this section. To facilitate comparison, Table IV also gives the average result of the six theoretical models for the frequency shifts, some available experimental results and a previous theoretical study [17] of the MW complex. Another previous theoretical study of the WM and MW vibration frequencies was made by Kirschner and Woods [12], using the MP2/aug-cc-pVDZ. As this is one of the theoretical models employed here, their results are reproduced and are not discussed

separately. In comparing the theoretical results for the vibration shifts with the experimental values it should be kept in mind that the experimental values [19, 20] for WM and MW are in argon and nitrogen matrices, respectively.

For the vibration frequencies of water in WM we can note the expected qualitative result leading to intensity increase and red shift for the stretching modes. The numerical result of a shift of -150 cm^{-1} is in quite good accord with the experimental result of -169 cm^{-1} . For this OH stretching mode of the water molecule in the WM complex, the intensity is calculated as around 100 times the corresponding intensity in the isolated molecule when calculated with aug-cc-pVDZ basis set and 50 times when calculated with 6-311++G(2d,2p). For the bending mode, the expected blue shift is obtained but the value of 22 cm^{-1} is smaller than the experimentally inferred result of 48 cm^{-1} . The shift of approximately -35 cm^{-1} for the asymmetric OH stretching is considerably smaller than the experimental result of approximately -240 cm^{-1} , but is very close to the other experimental value of -29 cm^{-1} . We attribute this discrepancy partly to some dichotomy in the experimental results but also to the use of the harmonic approximation. Indeed, a calculation of the anharmonic frequency of the asymmetric OH stretching, using B3LYP/aug-cc-pVDZ, decreases

TABLE IV
Calculated vibration frequency shifts (cm^{-1}) and ratio of the infrared intensities (km/mol) for the proton donor molecule in water–methanol (WM), methanol–water (MW), and methanol–methanol (MM) complexes.

Description	Aug-cc-pVDZ						6-311++G(2d,2p)						Average Theor ^(a)		Exp ^(b,c)
	B3LYP		B3PW91		MP2		B3LYP		B3PW91		MP2		$\Delta\omega$	$\Delta\omega$	$\Delta\omega$
	$\Delta\omega$	I_{ratio}	$\Delta\omega$	I_{ratio}	$\Delta\omega$	I_{ratio}	$\Delta\omega$	I_{ratio}	$\Delta\omega$	I_{ratio}	$\Delta\omega$	I_{ratio}	$\Delta\omega$	$\Delta\omega$	
WM															
δ_{HOH}	20	0.6	19	0.6	24	0.7	22	0.62	22	0.63	23	0.63	22		48, 107
$\nu_{\text{OH(sym)}}$	-156	106.3	-160	105.8	-146	82.1	-147	55.60	-157	53.11	-136	35.37	-150		-169, -99
$\nu_{\text{OH(asym)}}$	-32	1.4	-28	1.4	-38	1.6	-31	1.38	-32	1.34	-36	1.48	-33		-238, -29
MW															
$\tau_{\text{C-OH}}$	373	1.5	373	1.4	371	1.5	389	1.8	398	1.7	410	1.9	386	408	336
$\nu_{\text{CO}} + \delta_{\text{COH}}$	22	0.9	32	1.2	20	0.9	19	0.9	27	1.0	19	0.8	23	20	14
δ_{COH}	52	1.5	51	1.5	58	1.3	53	1.6	53	1.6	61	1.5	55	56	40
$\nu_{\text{Methyl(sym)}}$	-16	1.3	-13	1.3	-13	1.2	-14	1.2	-12	1.2	-13	1.2	-14	-19	-17
$\nu_{\text{Methyl(asym)}}$	-24	1.2	-20	1.2	-19	1.2	-20	1.2	-18	1.2	-18	1.2	-20	-15	—
ν_{OH}	-137	14.4	-153	14.2	-119	11.8	-127	13.0	-148	12.7	-109	10.1	-132	-122	-156
MM															
$\tau_{\text{C-OH}}$	382	0.7	375	0.7	397	0.9	390	0.7	395	0.6	417	0.9	393	—	—
$\nu_{\text{CO}} + \delta_{\text{COH}}$	23	1.2	34	1.0	20	0.8	20	0.8	29	0.6	20	0.8	24	—	—
δ_{COH}	59	1.6	57	1.5	70	1.3	59	1.5	57	1.5	69	1.4	62	—	—
$\nu_{\text{Methyl(sym)}}$	-18	1.3	-15	1.3	-16	1.3	-15	1.3	-14	1.3	-16	1.3	-16	—	—
$\nu_{\text{Methyl(asym)}}$	82	0.8	86	0.7	71	1.2	84	0.8	52	0.7	74	1.2	75	—	—
ν_{OH}	-170	17.7	-183	17.2	-166	14.0	-157	15.9	-175	15.3	-150	12.1	-167	—	—

^(a) Theoretical results using B3LYP/6-311+G(d,p) from Ref. [17].

^(b) Frequency shifts from Refs. [19, 20, 33, 34]. Results for WM and MW are in argon and nitrogen matrices, respectively.

^(c) Values on the right-hand side are obtained using the H_2O frequencies from Ref. [35].

this vibration mode of water in WM by 190 cm^{-1} , leading to a final result of about -220 cm^{-1} , now in good accord with one experimental value. The anharmonic correction for the symmetric OH stretching is also sizable. In this case, including the anharmonicity would lead to a red shift much larger than experiment.

The B3PW91 method provided the smaller shifts while the MP2 provided larger shifts with B3LYP standing in an intermediate place. For instance, the most intense red shift of the water molecule in the WM complex varied from -160 cm^{-1} using the B3PW91/aug-cc-pVDZ model to -136 cm^{-1} with the MP2/6-311++G(2d,2p) model. Now, fixing the method and observing the influence of the basis set we can note that this influence is generally small. For instance, in the case of the MP2 method the difference due to the basis set in the shift for the OH stretching mode of water is 10 cm^{-1} . The blue shift of HOH bending mode was found in a range between 19 cm^{-1} and 24 cm^{-1} (in B3PW91/aug-cc-pVDZ and MP2/aug-cc-pVDZ, respectively). The shifts associated to the methanol molecule in WM

are small, because in this case it is the proton acceptor. However, we note that the $\nu_{\text{Methyl(sym)}}$ and $\nu_{\text{Methyl(asym)}}$ modes associated with the methyl group present a slight blue shift in the range of 25 cm^{-1} , depending on theoretical model considered.

Table IV also shows the results for the frequency shifts of the methanol molecule in the MW complex. The largest shift is seen to occur for the OH wag, the $\tau_{\text{C-OH}}$ mode, of the methanol donor. A calculated blue shift with an average value of $\sim 386 \text{ cm}^{-1}$ is obtained. This compares favorably with the experimentally inferred value of 336 cm^{-1} and the previous theoretical result [17] of 408 cm^{-1} . The largest intensity variation upon complex formation is, as expected, associated to the stretching ν_{OH} of the methanol molecule. This mode presents an average red shift of -132 cm^{-1} . The separate results range between -109 cm^{-1} using MP2/6-311++G(2d,2p) and -153 cm^{-1} using B3PW91/aug-cc-pVDZ level. This is the same qualitative picture discussed for the water molecule in the WM complex. The δ_{COH} mode has a significant blue shift with an average of 55 cm^{-1} . The $\nu_{\text{CO}} + \delta_{\text{COH}}$ mode

suffers an average blue shift of 23 cm^{-1} . These results agree well with the experimentally inferred results and the previous theoretical result [17]. In general, these shifts have similar values, not depending strongly on the different theoretical models. The $\nu_{\text{Methyl(asy)}}^{\text{Methyl(asy)}}$ mode presents an average red shift of -20 cm^{-1} , similar but with opposite sign compared to the same mode in the WM complex. Hence this $\nu_{\text{Methyl(asy)}}^{\text{Methyl(asy)}}$ mode suffers a blue shift in the case of methanol as the proton acceptor and a red shift in the case of methanol as the proton donor. Regarding the intensity changes, the only mode that suffers a strong intensity change compared to the isolated molecule is the ν_{OH} mode which is found here to change by a factor of ~ 14 using the DFT methods and ~ 10 using the MP2 methods.

We now discuss the interesting case of the MM dimer, also shown in Table IV, for which there is a lack of previous systematic results for comparison. For all modes shown for methanol donor the shifts are significant. It is expected that a red shift will appear for the OH stretch mode and a blue shift will appear for the OH wag. The large shift for this complex is seen to occur for the OH wag, the $\tau_{\text{C-OH}}$ mode, of the methanol donor. A calculated blue shift ranging between 375 cm^{-1} and 417 cm^{-1} , with an average value of $\sim 400\text{ cm}^{-1}$ is obtained. The stretching ν_{OH} mode presents a large intensity increase and a red shift in the range of -183 cm^{-1} and -150 cm^{-1} , with an average value of approximately -170 cm^{-1} . Note that this shift is larger than the corresponding shift ($\sim 130\text{ cm}^{-1}$) in MW. This agrees with the larger binding energy and smaller hydrogen bond distance of MM compared to MW, as discussed above. The $\nu_{\text{Methyl(sym)}}^{\text{Methyl(sym)}}$ mode presents a slight red shift with an average value of -16 cm^{-1} . The other modes of the proton donor methanol molecule in MM present a blue shift. In the case of $\nu_{\text{Methyl(asy)}}^{\text{Methyl(asy)}}$, this blue shift has a calculated average value of 75 cm^{-1} . Summarizing, the MM IR spectrum, compared to the isolated methanol molecule, is characterized by a strong blue shift of the OH wag mode and a strong red shift, with intensity increase, of the OH stretch modes of the proton donor methanol molecule.

Figure 2 summarizes the calculated vibration spectra for the three complexes as obtained using the B3LYP/aug-cc-pVDZ model. Some interesting features can be seen. The most prominent aspect is the very intense transition in the region of $3600\text{--}3700\text{ cm}^{-1}$. This transition corresponds to the OH stretch in the complexes that has low intensity in

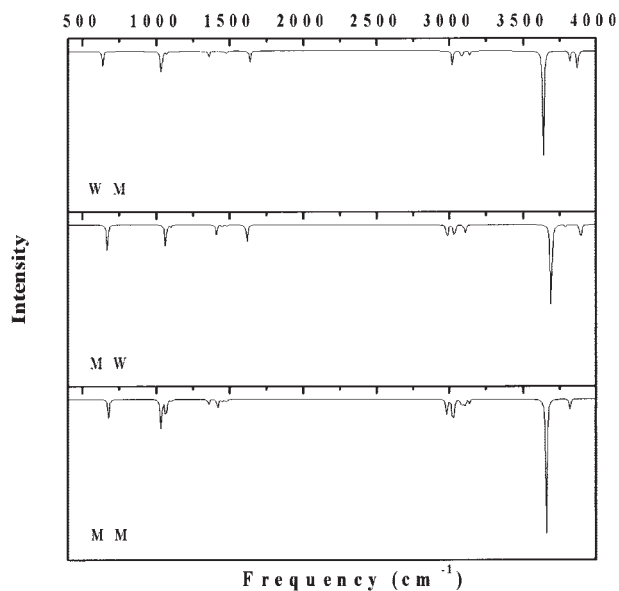


FIGURE 2. The convoluted spectra showing the calculated vibration frequencies and relative intensities for the hydrogen-bonded complexes MW, WM, and MM. This illustration uses the B3LYP/aug-cc-pVDZ model.

the isolated molecules. For the proton donor molecule, it suffers a considerable increase in the intensity (Table IV). For WM, this transition is the OH stretch of H_2O that has a considerable intensity increase. For MW, the water is the proton acceptor and the corresponding transition has low intensity. In turn the OH stretch of methanol gains intensity and appears located at 3693 cm^{-1} . For the MM dimer, this frequency is the OH stretch of the proton donor methanol. Another interesting feature, shown in Figure 2 is the $\nu_{\text{CO}} + \delta_{\text{COH}}$ frequency of methanol, seen as a single transition in the WM and MW complexes, around 1060 cm^{-1} , and doubled in the MM complex. The bend δ_{HOH} frequency of water can also be seen located slightly above 1620 cm^{-1} in both WM and MW complexes, but absent in the MM complexes.

4. Summary and Conclusions

The IR spectra of the hydrogen-bonded complexes formed by the combination of methanol and water have been analyzed theoretically using six theoretical models composed of two hybrid density functionals and the second-order Møller–Plesset perturbation theory, in two extensive sets of Gaussian-type functions. We calculated the vibrational

modes of the isolated methanol and water molecules and compared with the corresponding modes of the three complexes formed, i.e., water-methanol, methanol-water, and the methanol dimer. In every case, we obtained the vibration shifts of the proton donor molecules resulting from the complex formation. Whenever possible, the results were compared with available experimental results and were found to be in good agreement. For the methanol case we obtained considerable shifts in the OH group. The C—OH wag is calculated to blue shift and the OH stretch is calculated to red shift and increase in intensity compared to the isolated methanol molecule. The magnitude of these shifts are obtained and discussed. For the methanol dimer the C—OH wag increases the frequency by $\sim 400\text{ cm}^{-1}$ and the OH stretch decreases the frequency by $\sim 170\text{ cm}^{-1}$, with an increase in intensity of nearly 15 times.

ACKNOWLEDGMENT

This work was partially supported by CNPq and FAPESP (Brazil).

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