

EFFECT OF ARGON ENVIRONMENT ON VIBRATIONAL SPECTRA OF ETHANOL

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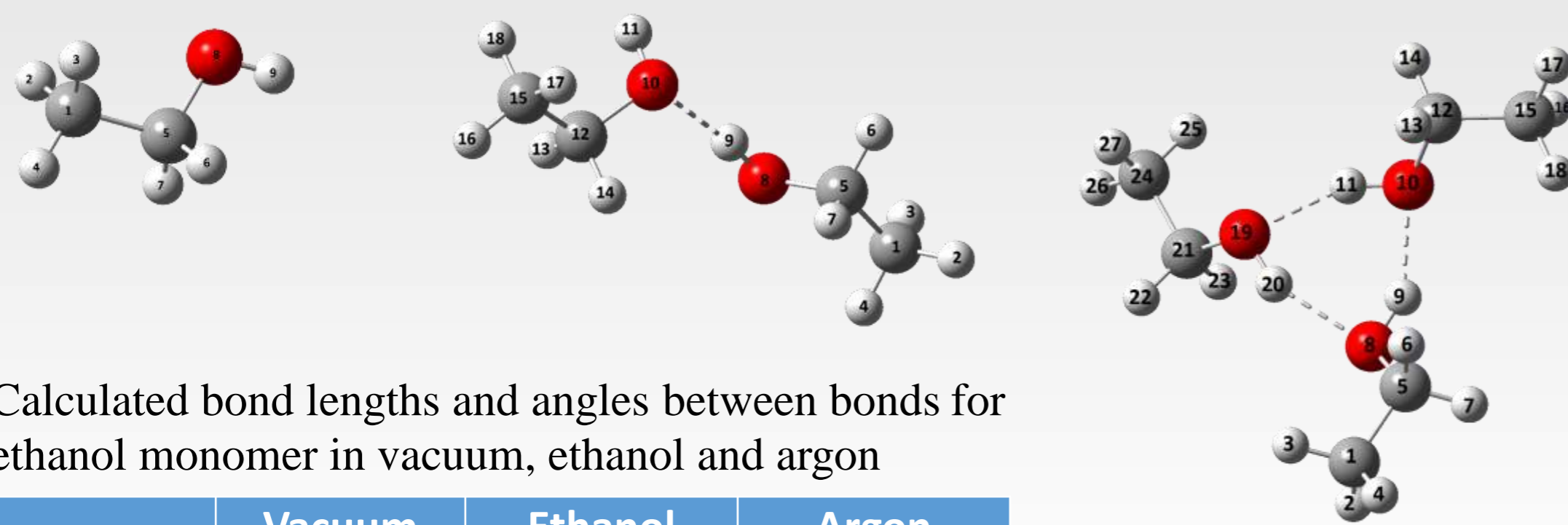
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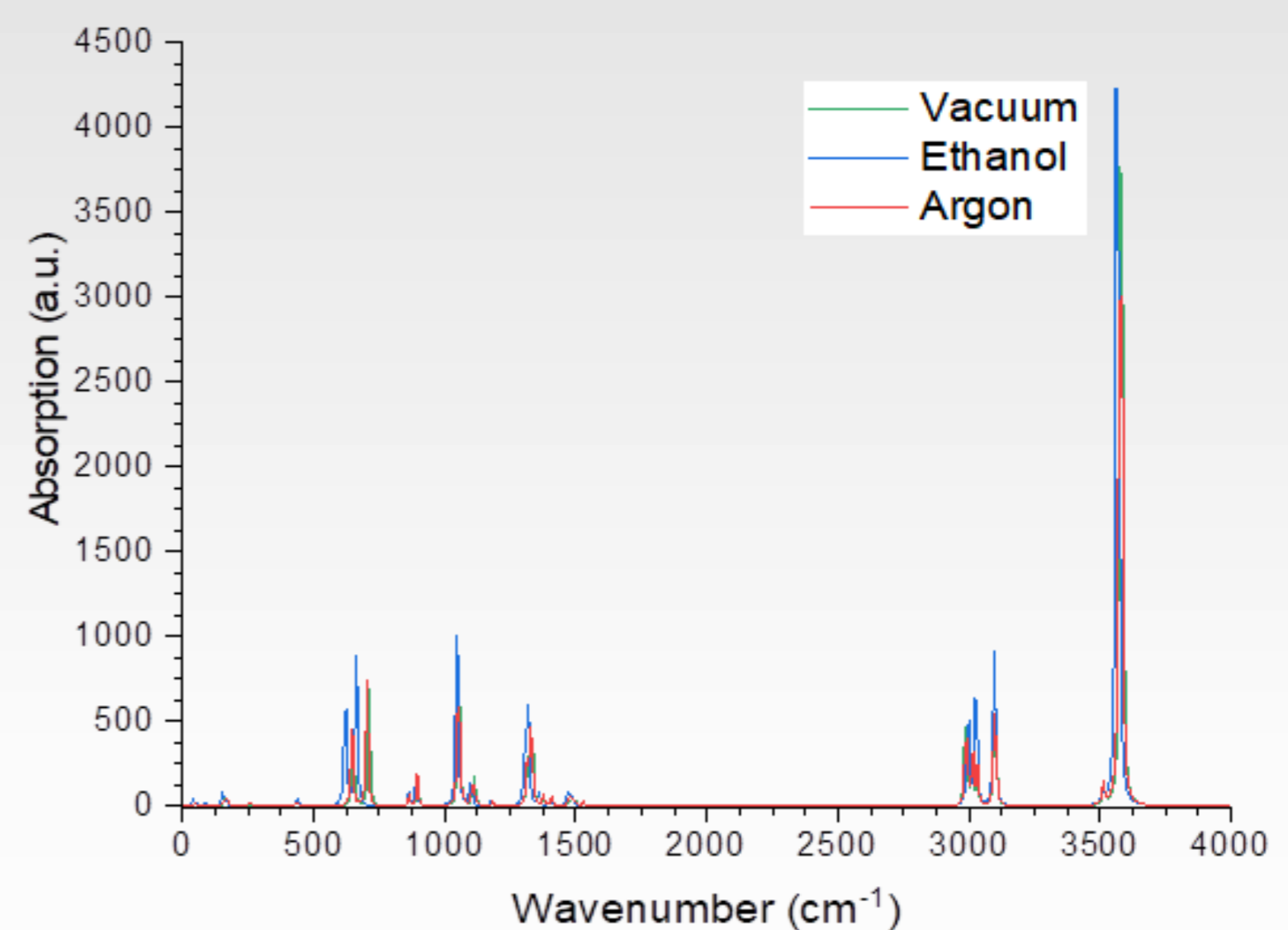
Ethanol as one of monohydric alcohols in the liquid state can be considered as a partially ordered system. Partial order in liquid alcohols is due to the formation of hydrogen-bonded molecular associates (clusters). Spectroscopic methods for studying the structure and properties of liquids allow one to obtain only generalized information averaged over the volume, but do not make it possible to study individual molecules or their small associates. The way out of this situation is to use the matrix isolation method, the essence of which is that the molecules under study are frozen in a matrix formed by an inert gas (most often argon) at low temperatures (about 10 K). One of the main advantages of the matrix isolation method is the absence of interaction of the matrix with objects isolated in it, however, in numerous experimental studies, a weak influence of the matrix is observed, which manifests itself in a slight (up to several percent) shift of the spectral bands compared to the spectra of the gas phase. Geometry optimization of ethanol monomer and trimer in vacuum, as well as in ethanol and argon environments, was performed using methods of quantum-chemical simulation (DFT, B3LYP/cc-pVTZ level of theory).

Optimized geometry of ethanol monomer, dimer and trimer



Calculated bond lengths and angles between bonds for ethanol monomer in vacuum, ethanol and argon

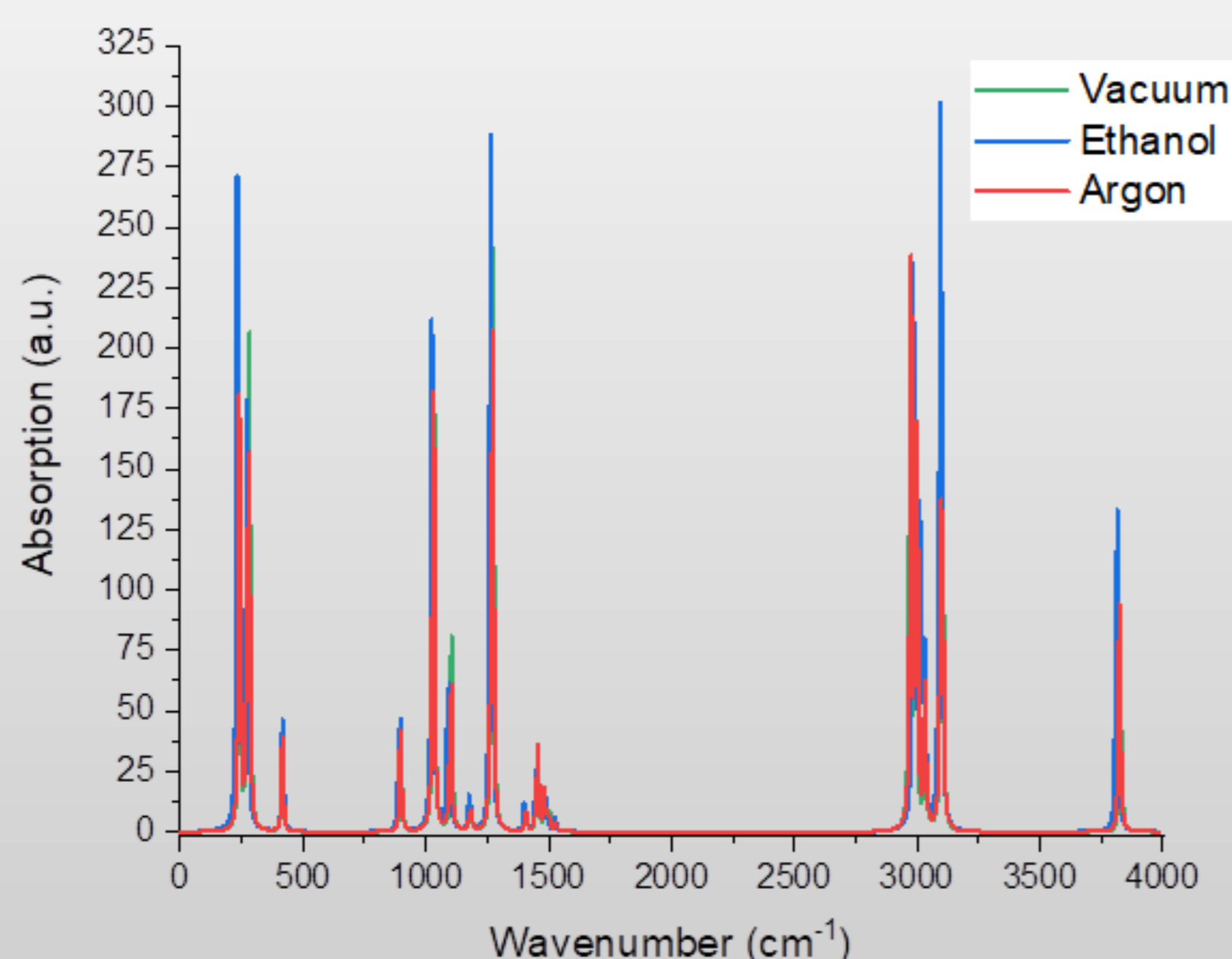
	Vacuum	Ethanol	Argon
C ₅ -O ₈	1.4267 Å	1.4316 Å	1.4277 Å
O ₈ -H ₉	0.961 Å	0.9622 Å	0.9612 Å
C ₁ -H ₂	1.0903 Å	1.0909 Å	1.0904 Å
C ₁ -H ₃	1.0903 Å	1.0909 Å	1.0904 Å
C ₁ -H ₄	1.0911 Å	1.0907 Å	1.0911 Å
C ₅ -H ₆	1.0968 Å	1.0952 Å	1.0965 Å
C ₅ -H ₇	1.0968 Å	1.0952 Å	1.0965 Å
C ₁ -C ₅	1.5144 Å	1.514 Å	1.5143 Å
C ₅ -O ₈ -H ₉	108.723 °	108.2404 °	108.6274 °
H ₂ -C ₁ -C ₅	110.4809 °	110.7009 °	110.5247 °
H ₄ -C ₁ -C ₅	110.5315 °	110.2971 °	110.4796 °
H ₃ -C ₁ -C ₅	110.4802 °	110.6998 °	110.5239 °
C ₁ -C ₅ -H ₆	110.0337 °	110.1585 °	110.0537 °
C ₁ -C ₅ -H ₇	110.0315 °	110.1564 °	110.0515 °
C ₁ -C ₅ -O ₈	107.963 °	108.2652 °	108.0358 °
O ₈ -C ₅ -H ₆	110.6253 °	110.3188 °	110.5598 °
O ₈ -C ₅ -H ₇	110.6245 °	110.3178 °	110.5589 °
H ₂ -C ₁ -H ₃	108.259 °	108.4133 °	108.2852 °
H ₂ -C ₁ -H ₄	108.5088 °	108.3249 °	108.4774 °
H ₃ -C ₁ -H ₄	108.509 °	108.3251 °	108.4776 °
H ₆ -C ₅ -H ₇	107.572 °	107.6298 °	107.5896 °



IR spectra of ethanol trimer in different environments

Calculated vibrational frequencies and intensities of IR absorption bands of ethanol trimers in vacuum, ethanol and argon environments, as well as the corresponding band shifts

mode	vacuum		ethanol		argon		v _e -v _{v'} cm ⁻¹	v _a -v _{v'} cm ⁻¹
	v, cm ⁻¹	I, a.u.	v, cm ⁻¹	I, a.u.	v, cm ⁻¹	I, a.u.		
1	38.0	48.2	41.1	546.9	35.2	104.5	3.1	-2.8
2	56.8	84.0	58.2	117.1	58.0	100.4	1.3	1.2
3	119.7	2.8	116.5	48.8	118.8	3.5	-3.2	-0.9
4	176.3	60.3	171.4	46.9	175.4	56.8	-4.9	-0.9
5	263.5	24.7	261.1	6.2	263.9	29.6	-2.4	0.4
6	443.9	64.1	438.8	107.2	442.9	70.6	-5.1	-1.0
7	818.2	3.0	817.6	3.0	818.1	2.9	-0.7	-0.2
8	820.2	3.6	819.0	3.0	820.0	3.4	-1.2	-0.2
9	897.7	112.8	892.3	210.6	896.5	113.4	-5.5	-1.3
10	1050.7	390.4	1043.0	466.0	1049.1	408.8	-7.7	-1.5
11	1109.9	68.8	1097.2	43.4	1107.0	65.5	-12.7	-2.9
12	1182.5	4.8	1179.5	14.7	1181.8	8.6	-3.0	-0.7
13	1301.8	1.6	1300.0	78.5	1301.7	2.6	-1.9	-0.1
14	1317.1	328.0	1307.0	261.5	1315.3	329.5	-10.1	-1.8
15	1409.6	18.8	1404.3	18.9	1408.6	19.6	-5.3	-1.0
16	1484.8	15.5	1473.9	19.3	1482.6	17.6	-10.8	-2.1
17	1490.8	4.6	1477.0	9.8	1488.1	4.8	-13.8	-2.7
18	1501.7	6.0	1489.5	23.4	1499.3	10.8	-12.2	-2.4
19	1532.0	3.0	1525.7	1.4	1531.0	3.8	-6.3	-1.0
20	2989.9	69.2	2997.9	23.0	2991.8	71.1	8.0	1.8
21	3015.0	48.5	3024.4	68.7	3017.3	51.6	9.4	2.3
22	3033.3	23.4	3031.4	27.3	3032.8	23.6	-1.9	-0.5
23	3097.6	49.6	3095.3	83.7	3097.5	54.7	-2.3	-0.1
24	3102.1	81.3	3099.1	64.1	3101.1	87.9	-3.0	-0.9
25	3585.1	1029.8	3570.9	1204.0	3582.0	1065.0	-14.2	-3.1



IR spectra of ethanol monomer in different environments

Conclusions

Influence of the environment on the structure of the ethanol molecule consists in an increase in the length of C – H and O – H bonds, which is manifested in the IR absorption spectra in the form of a red shift of the corresponding spectral bands. With an increase in the size of the cluster, the magnitude of the shift of the spectral bands under the influence of the environment decreases, which is associated with the higher symmetry of the dimer and trimer compared to the monomer. It is shown that the argon environment has a weaker effect on the structure and vibrational spectra of ethanol clusters than the ethanol environment.