

The effect of ring size on vibrational spectroscopy and hydrogen bonding properties for the complexes between small ring carbonyl compounds with HF and HCl: Theoretical analysis

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Abstract The effect of the molecular structure on the properties of C=O...HX (X=F, Cl) bonds was investigated in a set of small cyclic carbonyl compounds, using vibrational spectroscopy and B3LYP/6–311G** calculations. Two main effects were studied: the size of the ring and the inclusion of oxygen atoms in the ring. In these complexes the C=O and H–X participating bonds in the hydrogen–bond are elongated, while others bonds are compressed. The calculated vibrational spectra were interpreted and band assignments were reported. Surface potential energy calculations are carried out with scanning HCl and HF near oxygen atom.

Keywords Carbonyl stretching mode ·
C=O...H hydrogen bonds ·
Small ring carbonyl compounds HX (X=F · Cl) complexes

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Introduction

The prediction of the properties of hydrogen bonds has frequently been the subject of investigations since such interactions play important roles in many chemical, physical and biological processes [1–3]. For example, hydrogen bonds belong to the relatively strong and directional intermolecular interactions and are hence responsible for crystal packing [4, 5]. Computational chemistry methods are very useful for the analysis of H-bond complexes, yielding information about their geometries and energies as well as about their vibrational and NMR spectra [3].

The purpose of this paper is to analyze the above mentioned properties of C=O...HX (X=F, Cl) dimmers and of related complexes. The complexes were chosen because of their simplicity and because of their molecular structures, allowing to study not only the properties of HF and HCl proton donating bonds, but also those of the C=O acceptor.

The proton-accepting properties of the carbonyl group have been theoretically investigated for a complex between formaldehyde and water, but a variety of fairly small basis sets have been used [4]. A small stretch of both the O–H donating covalent bond and the C=O bond has been detected which is in line with results from neutron diffraction studies on H...O=C systems. The correlation between C=O bond length and H...O distance suggested that the C=O bond length might be used as a measure of the H-bond strength [5].

The structural parameters, vibrational frequencies and interaction energies were parameterized in the same manner as for the cyclic ketones discussed in a previous article [6]. In this work we discuss the effect of ring size on hydrogen bonding of a number of small ring carbonyl compounds,

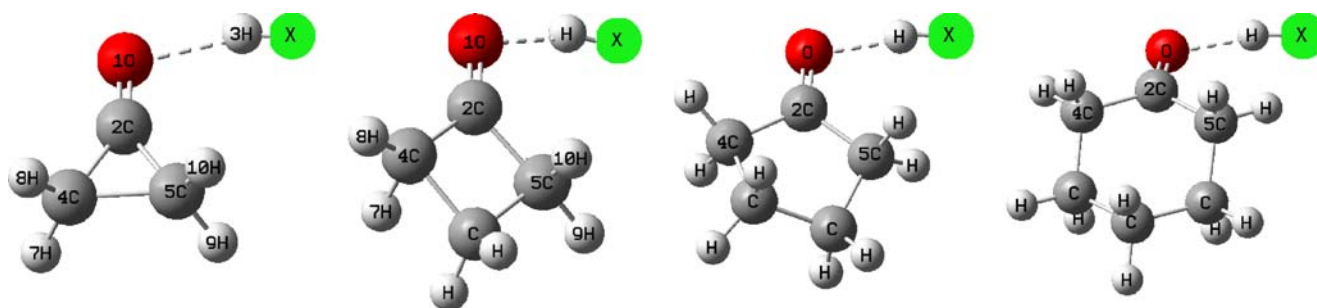


Fig. 1 The B3LYP/6–311G** optimized structures of the small ring carbonyl compounds HX (X=F, Cl) complexes

HX [X=F, Cl, n (number of carbon)=3–6] complexes and comparison properties with single ring monomer. Of this category X–H \cdots π type complexes have been investigated experimentally by Fourier transform microwave spectroscopy [7–12] and IR detection [13] and theoretically by ab initio and DFT calculations [14–18], where a hydrogen halide HX (X=F, Cl) acts as a proton donor and a phenyl ring or multiple bonds as an acceptor. Two main structural

changes are considered: (1) the ring size and (2) the presence of oxygen atoms in the ring [19].

Methods

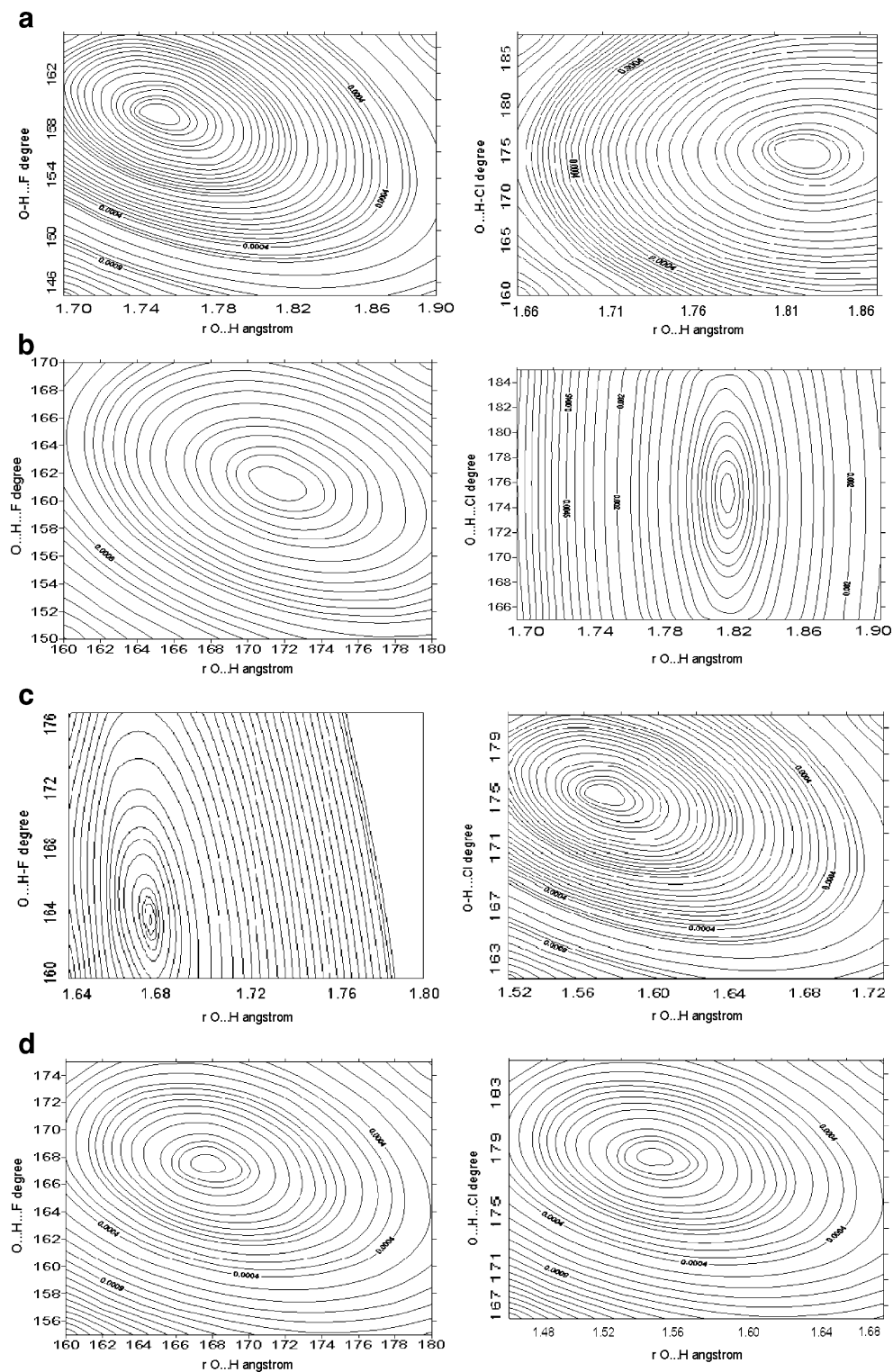
All the calculations have been carried out with Gaussian view 3.01, Gaussian 03 [20] using the 6–311G** basis set

Table 1 Geometry parameters of the small ring carbonyl compounds HX (X=F, Cl) complexes computed at the B3LYP/6–311G** method and basis set

Parameter	C _n –HF				C _n –HCl			
	C3	C4	C5	C6	C3	C4	C5	C6
Bond lengths								
rO...H	1.755	1.717	1.684	1.677	1.845	1.811	1.770	1.770
rO–X	2.650	2.626	2.606	2.608	3.154	3.123	3.090	3.090
rO=C	1.204	1.207	1.216	1.221	1.202	1.205	1.214	1.219
	+(0.009)	+(0.011)	+(0.012)	+(0.011)	+(0.007)	+(0.009)	+(0.009)	+(0.009)
rH–X	0.937	0.941	0.944	0.945	1.311	1.315	1.320	1.321
	(+0.007)	(+0.011)	(+0.014)	(+0.015)	(+0.024)	(+0.028)	(+0.033)	(+0.034)
rC2–C5	1.458	1.525	1.521	1.514	1.463	1.528	1.523	1.515
	(–0.013)	(–0.013)	(–0.012)	(–0.008)	(–0.008)	(–0.009)	(–0.009)	(–0.007)
rC2–C4	1.463	1.526	1.521	1.513	1.464	1.527	1.522	1.515
	(–0.008)	(–0.012)	(–0.012)	(–0.009)	(–0.007)	(–0.010)	(–0.010)	(–0.008)
rC–H	1.085	1.093	1.098	1.098	1.085	1.093	1.098	1.098
	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
rC–H	1.085	1.093	1.091	1.091	1.085	1.093	1.091	1.091
	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
Bond angles								
θ O–H–X	158.66	161.46	164.57	167.43	174.45	174.85	176.65	178.46
θ C4–C2–C5	65.21	93.18	109.18	116.16	64.99	93.00	108.99	115.84
θ C–O–H	102.69	106.07	110.64	115.54	116.83	118.99	121.89	125.65
θ O=C2–C4	147.71	133.20	124.86	121.14	147.03	132.87	124.69	121.04
	(–0.02)	(–0.604)	(–0.986)	(–1.29)	(–0.65)	(–0.93)	(–1.156)	(–1.39)
θ O=C2–C5	147.08	133.61	125.95	122.69	147.97	134.13	126.31	123.11
	(–0.58)	(–0.19)	(+0.093)	(+0.261)	(+0.28)	(+0.33)	(+0.45)	(+0.68)
Torsion angles								
φ C–O–H–X	0.00	0.00	4.45	5.73	1.487	0.00	4.00	14.92
φ C5–C2–O–H	0.00	0.00	3.95	2.15	0.946	0.00	1.67	0.318
φ C4–C2–O–H	180.0	180.0	–176.01	–177.46	–178.6	–180.00	–178.51	–179.62

Changes in values from the corresponding sing ring monomer are given in parentheses. (Complex-sing ring monomer)

Fig. 2 **a** Potential energy for the complexes of the cyclopropanone HX, **b** cyclobutanone HX, **c** cyclopentanone HX, and **d** cyclohexanone, as a function of the hydrogen-bond (O...X) and (O-H-X) calculated by B3LYP/6–311G** method and basis set



at the Becke's three-parameters exchange functional combined with the LYP correlation functional (B3LYP) [21, 22]. The structure of the molecule was completely optimized without any symmetry in all the levels. The

harmonic vibrational frequencies and the infrared intensities were calculated analytically on the resulting ground-state optimized molecular geometries. Atomic charges were obtained from natural bond orbital (NBO) analysis [23],

Table 2 Hydrogen bonding geometry (\AA^0) of the small ring carbonyl compounds $\text{HX}(\text{X}=\text{F}, \text{Cl})$ complexes computed at the B3LYP/6–311G** method and basis set

Cn...HC	F-H...O				Cl-H...O			
	F-H	H...O	F-O	F-H...O	Cl-H	H...O	Cl...O	Cl-H...O
C3_HX	0.9370	1.7550	2.6504	158.61	1.3110	1.8450	3.1538	174.60
C4...HX	0.9410	1.7171	2.6262	161.31	1.3841	1.6241	3.1236	175.01
C5_HX	0.9441	1.6841	2.6064	164.60	1.3991	1.5672	2.9643	176.11
C6...HX	0.9451	1.6770	2.6082	167.43	1.4001	1.5621	2.9622	179.00

as implemented in Gaussian 03. The calculations are carried out on a Pentium 4 double processor computer.

Results and discussion

Geometrical structure

Figure 1 shows the optimized structures of the number of small ring carbonyl compounds $\text{HX}(\text{X}=\text{F}, \text{Cl})$ complexes with the B3LYP/6–311G** level, and in Table 1 the major structural parameters of complexes are summarized. In complexes the n orbital of the oxygen atom of carbonyl groups interacts with the hydrogen atom of HX . In the complexes the C–O, H–X and C4–C2–C5 bonds which are participating in the hydrogen–bond are elongated, while other bonds shrink. Changes in values from the corresponding single ring monomer are given in parentheses. Calculations at B3LYP/6–311G** method and basis set indicate that the C–O, H–X, bond lengths and O–H–X, C–O–H bond angles increase by increasing the ring size. In cyclopropanone and cyclobutanone $\text{HX}(\text{X}=\text{F}, \text{Cl})$ complexes the lengths of the four C–H bonds were calculated to be the same within the error limits the four C–H bonds are equivalent.

Therefore, the lengths of the four C–H bonds are represented by $r_{\text{C}_n\text{H}}$. However, for cyclopentanone and cyclohexanone HX complexes only two bonds are equivalent. The structural parameters which are responsible and have the most effect on the ring strain are C=O bond length and C–C=O bond angle. The decrease in the C=O bond length and the increase in the C–C=O bond angle increase the ring strain.

Surface potential energy calculations are carried out with scanning O–H bond participating in the hydrogen–bond. The nonlinear hydrogen bonds (O...H) of 1.75 \AA , 1.84 \AA , O–H–X angles 158.5, 174.5 degree for cyclopropanone complexes with HF and HCl, 1.72 \AA , 1.62 \AA , 161, 175 degree for cyclobutanone complexes with HF and HCl, 1.68 \AA , 1.56 \AA , 165, 176 degree for cyclopentanone complexes with HF and HCl, 1.67 \AA , 1.56 \AA , 167, 179 degree for cyclohexanone complexes with HF and HCl, respectively (Fig. 2a–d).

Hydrogen bonding geometry of the small ring carbonyl compounds $\text{HX}(\text{X}=\text{F}, \text{Cl})$ complexes, computed at the B3LYP/6–311G** method and basis set, and the major structural parameters of complexes are summarized in Table 2. Calculation at the B3LYP/6–311G** indicate that the X–H and X–H–O bond length and angle increase

Table 3 Calculated dipole moments (D), zero-point vibrational energy (kcal/mol), thermal energy (kcal/mol), thermal correction to enthalpy and Gibbs free energy (kcal/mol) of the small ring carbonyl compounds $\text{HX}(\text{X}=\text{F}, \text{Cl})$ complexes

Parameter	Cn...HF ^a				Cn...HCl			
	C3	C4	C5	C6	C3	C4	C5	C6
Eth	50.05 (+9.47)	69.32 (+9.50)	88.86 (+9.57)	108.1 (+9.69)	48.02 (+7.44)	67.25 (+8.05)	86.80 (+7.51)	106.1 (+7.67)
D.Mon	4.33 (+1.38)	4.39 (+1.61)	4.99 (+2.06)	5.22 (+2.00)	5.13 (+2.36)	5.36 (+2.57)	7.31 (+4.37)	7.80 (+4.39)
Z.P.V	43.08 (+5.01)	64.79 (+8.08)	84.00 (+8.20)	102.6 (+8.32)	43.8 (+5.73)	62.44 (−5.77)	81.82 (−6.02)	100.5 (−6.16)
H _{con}	50.64 (+9.47)	69.28 (+9.50)	89.45 (+9.54)	108.7 (+9.68)	48.61 (+7.44)	67.84 (−7.41)	87.39 (−7.50)	106.7 (−7.68)
G _{con}	27.05 (+5.21)	45.30 (+5.40)	63.34 (+5.80)	81.13 (+5.90)	23.54 (+1.29)	40.35 (+1.54)	60.18 (−2.64)	78.13 (−2.87)

Changes in values from the corresponding single ring monomer are given in parentheses. (Complex–sing ring monomer)

^an=number of carbon

Table 4 Scaled harmonic vibrational frequencies (cm^{-1}) calculated at the B3LYP/6–311G** level of Theory

Description	$\text{C}_n\text{---HF}$				$\text{C}_n\text{---HCl}$			
	C3	C4	C5	C6	C3	C4	C5	C6
nO_H-X	214	211	209	219	146	141	173	194
g C=O	284	391	441	639	293	392	441	642
d C=O	502	471	483	506	484	454	472	496
g HX	677	793	844	847	561	718	831	818
d HX	678	715	793	818	522	663	785	793
d CCOC	687	655	552	399	699	663	569	402
na CCC		891	1000	1036		892	1014	1058
na CCOC	1052	1084	1134	1221	1047	1073	1158	1246
CH_2Tw_-	1080	1157	1143	1106	870	1160	1159	1124
CH_2Tw_-	1121	1184	1226	1266	894	1186	1252	1285
CH_2Wag	967	1181	1263	1301	954	1184	1288	1315
CH_2Wag	987	1236	1305	1343	989	1237	1331	1363
$\text{CH}_2\text{Scis.}$	1368	1380	1404	1422	1372	1382	1437	1455
$\text{CH}_2\text{Scis.}$	1387	1453	1467	1461	1389	1454	1496	1496
n C=O	1858	1776	1728	1704	1857	1778	1605	1584
	(-25)	(-43)	(-44)	(-39)	(-26)	(-41)	(-167)	(-159)
ns CH_2	3016	2960	2931	2914	3018	2480	2922	2907
ns CH_2	3021	2989	2950	2936	3019	2965	2944	2928
ns CH_2	3094	3005	3001	2972	3093	2990	2998	2969
ns CH_2	3107	3040	3021	3024	3106	3009	3011	3012
n HF	3627	3552	3485	3471	2529	3041	1872	1853

Changes in values from the corresponding single ring monomer are given in parentheses. (Complex-single ring monomer)

^an, stretching; d, in-plane bending; g, out-of-plane bending; w, wagging; a, asymmetric; s, symmetric; r, rocking; Tw₋, twisting; Scis., scissoring

by increasing the ring size, therefore H-O bond length decreases.

Calculated interaction energies including zero-point vibrational energy (kcal/mol), thermal energy(kcal/mol), thermal correction to enthalpy and Gibbs free energy(kcal/mol) of the small ring carbonyl compounds HX (X=F, Cl) complexes for two complexes at B3LYP/6–311G** and selected properties are listed in Table 3. The sum of the internal energy and dipole moments of the small ring carbonyl compound monomers are less than the corresponding complex, therefore the heat capacity of the complexes are increased due to the newly generated hydrogen bond. Changes in values from the corresponding single ring monomer are given in parentheses. Calculations at B3LYP/6–311G** method and basis set indicate that all of the parameters increase by increasing the ring size and complexation. For example Dipole moments of Cyc3, 4, 5, 6...HF complexes are calculated to be 4.33, 4.39, 4.99 and 5.22 (D), respectively.

Vibrational spectra

The harmonic vibrational frequencies and the infrared intensities were calculated analytically on the resulting ground-state optimized molecular geometries. Cyclopropa-

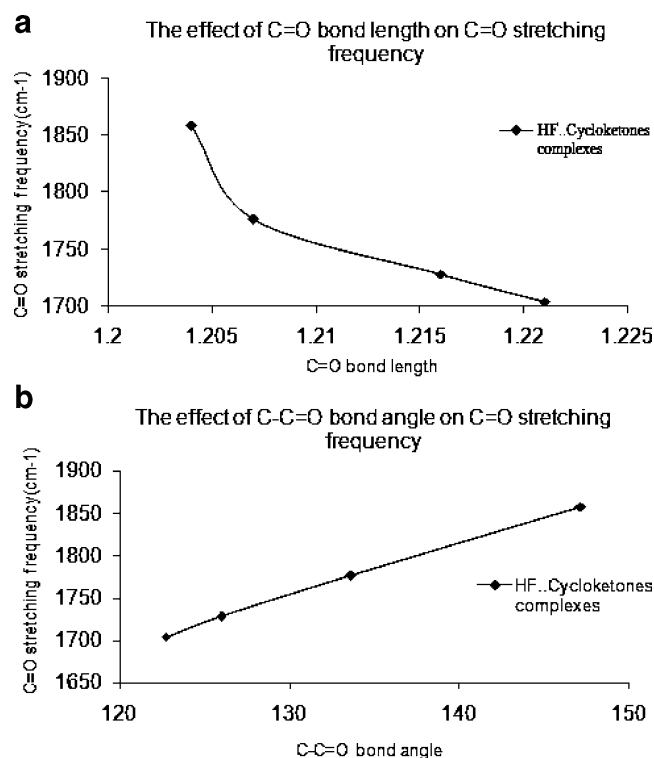
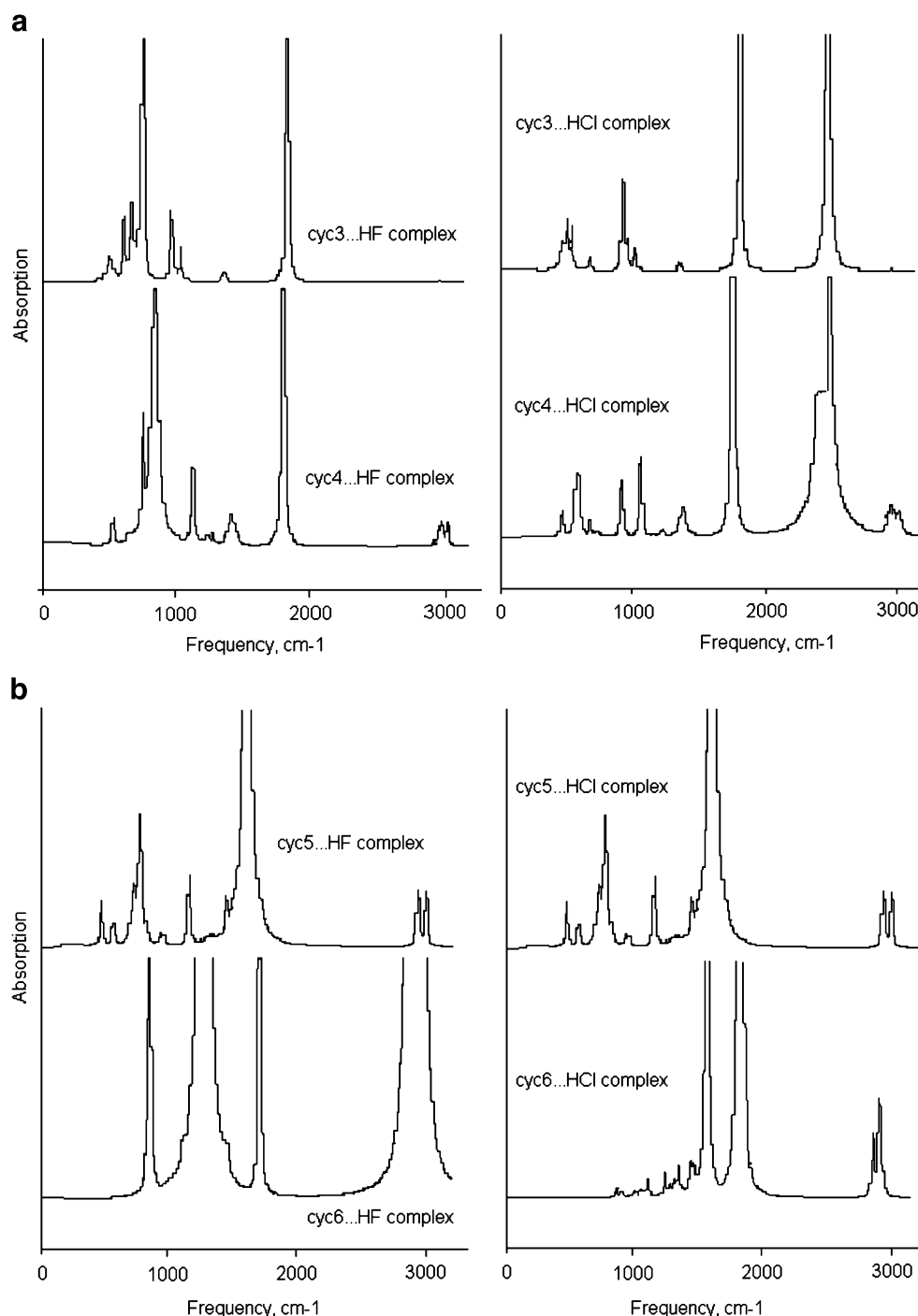


Fig. 3 Variation of the C=O stretching mode with C=O, C–C=O bond length and angle of the cycloketones-HF complexes

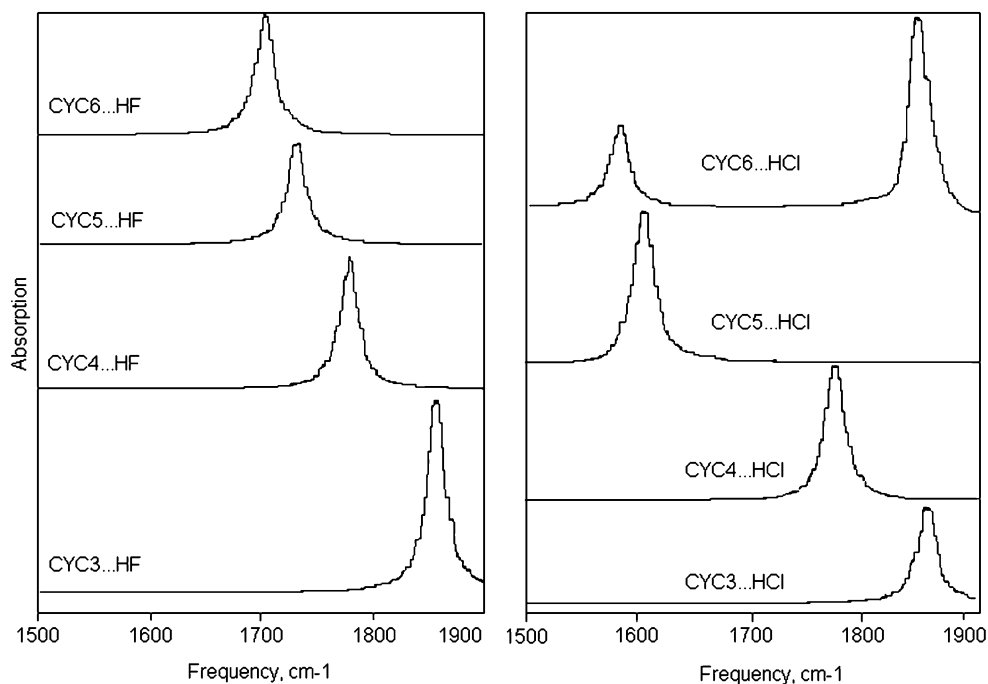
Fig. 4 Simulated IR absorption spectra of the small cyclic carbonyl compounds HX (X=F, Cl) complexes



none, cyclobutanone, cyclopentanone and cyclohexanone HX (X=F, Cl) complexes contains 10, 13, 16 and 19 atoms so that, it has 24, 33, 42 and 51 normal modes, respectively. Table 4 show the selected vibrational frequencies and assignments of the vibrational frequencies (cm^{-1}) of the small ring carbonyl compounds HX (X=F, Cl) complexes. Changes in values from the corresponding monomer are given in parentheses. The theoretical frequencies were uniformly scaled down by a factor of 0.97 [24]. All quoted

vibrational frequencies reported in the paper are thus scaled values. Frequency changes well reflect the geometry changes. Significant changes in frequency and intensity take place in the H–X stretching vibration. As the magnitude of the shift in HX stretching vibrational frequency is known to represent a measure of the intermolecular interaction, the difference in frequency is in good agreement with that in interaction energy. As for the cycloketones moiety, the C=O and HX stretching

Fig. 5 IR spectra in the ν C=O mode region at the B3LYP/6-311G**



vibrational frequencies show the red shifts for the complexes barring cyclobutanone, cyclopentanone and cyclohexanone and contrarily the blue shifts for the remainder frequencies. Changes in values from the corresponding single ring monomer are given in parentheses.

The calculated band frequency of C=O stretching indicates that, the structural parameters expected to be responsible and have the most effect on the ring strain are C=O bond length and C-C=O bond angle. The decrease of the C=O bond length and increase of the C-C=O bond angle increase ring strain. This causes a reduction in the p orbital character and increases the s orbital character of the σ bond in C=O. The net effect would be an increase in the stability and strength of the C=O bond and hence in its stretching frequency. The effect of ring strain can be studied using vibrational frequencies. Strength of bond is in reverse relation with bond length, as it increases the bond strength decreases. Vibrational frequency is directly proportional to the square root of the bond length. C=O bond length decreases as ring size decreases then the strength of the bond increases and therefore vibrational frequency increases, this can be seen in Fig. 3.

The simulated IR spectrum obtained from B3LYP/6-311G** as the best method is presented in Figs. 4 and 5. From the calculated frequencies the higher intensities correspond to the HX out-of-plane bending, C=O stretching and HF stretching. The strongest bands at 1584–1858 cm^{-1} have been assigned to the C=O stretching groups modes. As for the small ring carbonyl compounds moiety, the C=O stretching vibrational frequencies show the red shifts for HF and HCl of the

complexes and steadily increases as the ring gets smaller. Also by the increase to ring size and decrease to ring strain therefore C=O and HX stretching vibrational frequencies decreases, this can be seen from Fig. 6.

^1H and ^{13}C NMR

The ^1H and ^{13}C NMR chemical shifts were referenced to TMS: δ ^1H and ^{13}C (CH_3) $_4\text{Si}$ =0.00 ppm. ^{13}C NMR predicts two magnetically different nuclei, B3LYP/C, C1 signal appear in low shielding, 226.8, 226.6, 234.9 and 225.8 ppm, for cyclopropanone, cyclobutanone, cyclopentanone and cyclohexanone complexes with HF respectively and 223.38, 223.38, 245.35 and 236.3 ppm for cyclopropanone, cyclobutanone, cyclopentanone and cyclohexanone complexes with HCl respectively due to charge withdrawal of the oxygen atom while C3 appear with respect to TMS, Tables 5 and 6.

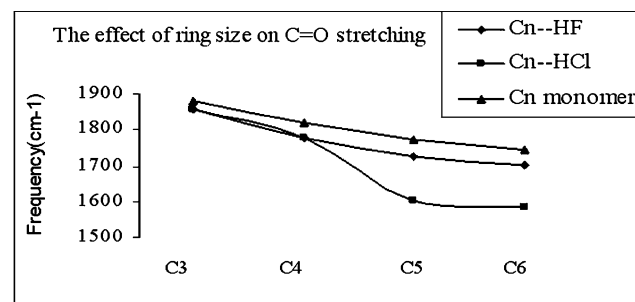


Fig. 6 The effect of ring size on C=O stretching vibrational frequency

Table 5 ^{13}C NMR chemical shifts (ppm from TMS, $\Delta\text{TMS}=0.00$) for cycloketones-HC (X=F, Cl) complexes computed at the B3LYP/6-311G** method and basis set

Parameter	Cn—HF			Cn—HCl				
	C3	C4	C5	C6	C3	C4	C5	C6
C1	226.8 (+15.1)	226.6 (+16.7)	234.9 (+14.3)	225.7 (+14.4)	223.5 (+11.8)	223.38 (+13.48)	245.2 (+24.6)	236.2 (+24.9)
C3	6.0 (-1.9)	49.4 (-2.6)	42.8 (-4.9)	46.1 (-0.2)	5.5 (-1.4)	50.28 (-1.72)	43.3 (-4.4)	45.6 (-0.7)
C2	7.4 (-3.3)	52.0 (-0.0)	42.8 (-4.9)	43.2 (-3.1)	6.2 (-2.1)	50.62 (-1.38)	41.6 (-6.1)	42.6 (-3.7)
C4		13.7 (+0.5)	27.8 (+0.1)	29.7 (+0.3)		13.54 (+0.34)	28.3 (+0.4)	32.8 (+2.4)
C5			27.8 (+0.1)	32.7 (+2.3)			27.5 (+0.4)	32.9 (+2.5)
C6				32.3 (+1.9)				29.3 (+0.7)

Changes in values from the corresponding single ring monomer are given in parentheses. (Complex-single ring monomer)

Table 6 ^1H NMR chemical shifts (ppm from TMS, $\Delta\text{TMS}=0.00$) for cycloketones-HX (X=F, Cl) complexes computed at the B3LYP/6-311G** method and basis set

Parameter	Cn—HF			Cn—HCl				
	C3	C4	C5	C6	C3	C4	C5	C6
H11	16.3	6.43	7.21	7.15	6.51	6.84	12.52	12.82
H4	1.46	3.11	12.2	1.72	1.46	3.22	1.34	2.20
H3	1.46	3.10	02.4	2.32	1.46	3.26	2.78	2.99
H2	1.52	3.27	2.84	3.13	1.53	3.12	2.49	2.38
H1	1.52	3.29	2.05	2.05	1.53	3.19	2.37	2.52
H5		1.97	1.74	1.72		1.99	1.84	1.71
H6		1.97	1.77	1.74		2.00	2.10	2.05
H7			2.05	2.05			1.82	1.74
H8			2.05	2.07			2.06	2.07
H9				1.80				1.79
H10				1.61				1.61

Table 7 Selected atomic charges of cycloketones-HX(X=F, Cl) complexes calculated with the B3LYP/6–311G** method and basis set and base pairs from NBO charge

atom	C _n —HF				C _n —HCl			
	C3	C4	C5	C6	C3	C4	C5	C6
O1	−0.535 (0.0442)	−0.568 (0.0438)	−0.589 (0.0431)	−0.592 (0.043)	−0.52 (0.029)	−0.554 (0.03)	−0.576 (0.03)	−0.580 (0.03)
C2	0.611 (−0.0163)	0.636 (−0.021)	0.646 (−0.03)	0.645 (−0.03)	0.613 (−0.05)	0.636 (−0.022)	0.654 (−0.038)	0.653 (−0.044)
H3	0.536 (−0.008)	0.536 (−0.008)	0.536 (−0.008)	0.653 (−0.125)	0.281 (−0.023)	0.283 (−0.025)	0.306 (−0.048)	0.307 (−0.049)
C4	−0.485 (−0.01)	−0.488 (−0.008)	−0.490 (−0.004)	−0.476 (−0.002)	−0.482 (−0.013)	−0.488 (−0.008)	−0.487 (−0.008)	−0.474 (−0.004)
C5	−0.480 (0.015)	−0.497 (0.01)	−0.505 (0.01)	−0.492 (0.013)	−0.484 (0.011)	−0.494 (0.002)	−0.499 (0.004)	−0.485 (0.006)
X	−0.572 (0.044)	−0.576 (0.048)	−0.582 (0.054)	−0.583 (0.055)	−0.327 (0.069)	−0.335 (0.077)	−0.408 (0.150)	−0.411 (0.153)
H7	0.229 (−0.0074)	0.227 (−0.006)	0.229 (−0.007)	0.191 (−0.027)	0.229 (−0.007)	0.228 (−0.007)	0.236 (−0.014)	0.192 (−0.016)
H8	0.229 (−0.0074)	0.228 (−0.007)	0.231 (−0.006)	0.216 (−0.008)	0.229 (−0.007)	0.228 (−0.007)	0.236 (−0.011)	0.221 (−0.003)
H9	0.233 (−0.0114)	0.238 (−0.017)	0.248 (−0.045)	0.240 (−0.022)	0.231 (−0.009)	0.232 (−0.011)	0.245 (−0.02)	0.236 (−0.018)
H10	0.233 (−0.0114)	0.236 (−0.015)	0.234 (−0.012)	0.216 (−0.008)	0.231 (−0.009)	0.232 (−0.011)	0.241 (−0.019)	0.223 (−0.015)

Changes in values from the corresponding single ring monomer are given in parentheses. (Complex-single ring monomer)

To clarify the nature of the complexation, the NBO, [25–27] analysis was carried out. Table 7 gives the natural atomic charges for complexes and the changes in natural atomic charges for the monomer calculated with the B3LYP/6–311G** method and basis set. The results of NBO analysis allow many of the quantitative trends in molecular structure, stability and spectroscopic properties to be rationalized in terms of non-pairwise-additive charge transfer delocalization between monomers. In complexes the in-contact O and X atoms gain charges. Calculation atomic charges at B3LYP/6–311G** at first line indicate that the O, X atomic charges increase by increasing the ring size and complexation, but for the other atoms atomic charge decrease by increasing the ring size and complexation.

Conclusions

The effect of ring size on hydrogen bonding of a number of small ring carbonyl compounds HX [X=F, Cl, n (number of carbon)=3–6] complexes and comparison properties with single ring monomer have been studied using B3LYP/6–311G** level of DFT method. The geometrical parameters, total energy, interaction energy, dipole moment, atomic charges and vibrational spectra have been determined. In complexes the n orbital of the oxygen atom of carbonyl

group interacts with the hydrogen atom of HX. Calculations at B3LYP/6–311G** method and basis set indicate that a) the C=O, H-X, bond lengths and O-H-X, C-O-H bond angles increase by increasing the ring size. b) In the complexes the C–O and H-X bonds which are participating in the hydrogen-bond are elongated, while other bonds shrink. c) Due to the increase to ring size and decrease to ring strain, C=O and HX stretching vibrational frequencies decreases. d) As for the cycloketones moiety, the C=O and HX stretching vibrational frequencies show the red shifts for the complexes. e) The former complex is more stabilized than the latter. f) HX molecules are a good probe for the magnitude of the interaction. g) The stronger the interaction energy, the longer the bond length and the lower the stretching vibrational frequency. h) Strength of the bond is in reverse relation with the bond length, as it increases, the bond strength decreases.

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