

# Density functional and Møller–Plesset studies of cyclobutanone···HF and ···HCl complexes

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Received: 24 November 2007 / Accepted: 22 September 2008 / Published online: 17 December 2008  
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**Abstract** The molecular structure (hydrogen bonding, bond distances and angles), dipole moment and vibrational spectroscopic data [vibrational frequencies, IR and vibrational circular dichroism (VCD)] of cyclobutanone···HX (X=F, Cl) complexes were calculated using density functional theory (DFT) and second order Møller–Plesset perturbation theory (MP2) with basis sets ranging from 6–311G, 6–311G\*\*, 6–311++G\*\*. The theoretical results are discussed mainly in terms of comparisons with available experimental data. For geometric data, good agreement between theory and experiment is obtained for the MP2 and B3LYP levels with basis sets including diffuse functions. Surface potential energy calculations were carried out with scanning HCl and HF near the oxygen atom. The nonlinear hydrogen bonds of 1.81 Å and 175° for HCl and 1.71 Å and 161° for HF were calculated. In these complexes the C=O and H–X bonds participating in the hydrogen bond are elongated, while others bonds are compressed. The calculated vibrational spectra were interpreted and the band assignments reported are in excellent agreement with experimental IR spectra. The C=O stretching vibrational frequencies of the complexes show red shifts with respect to cyclobutanone.

**Keywords** Cyclobutanone···HCl complex ·  
Cyclobutanone···HF complex ·  
Møller–Plesset perturbation · Density functional theory ·  
Hydrogen bond · Vibrational assignments · Dipole moment

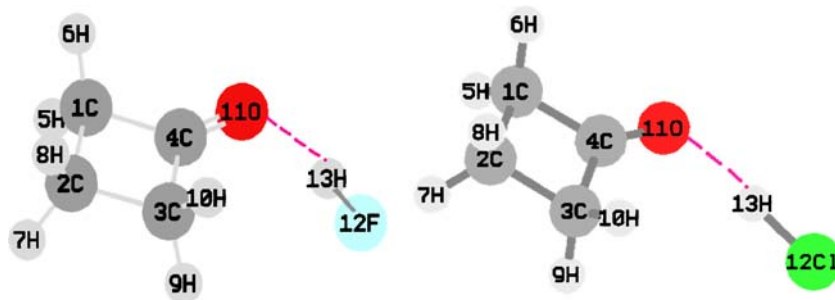
## Introduction

The geometries, dipole moments and vibrational frequencies of cyclic ketones have been parameterized and discussed in the literature [1, 2]. The molecular structure of cyclobutanone was investigated by a combined electron diffraction/microwave (ED/MW) spectroscopy study by Tamagawa and Hilderbrandt [3] and by a separate MW study by Scharpen and Laurie [4]. These authors found that this molecule has a large amplitude ring-puckering motion at around 65 cm<sup>-1</sup>. Hydrogen bonds play an important role in reactivity, solvation and chemical properties. In aqueous solution, hydrogen bonds have the greatest effect on large shifts in spectroscopic quantities. Shifts in spectroscopic phenomena can be studied by employing cyclobutanone···HX complexes in gas phase. Of this category, X–H···π-type complexes have been investigated experimentally by Fourier transform MW spectroscopy [5–10] and infrared (IR) detection [11], and theoretically by ab initio and density functional theory (DFT) calculations [12–16], where a hydrogen halide HX (X=F, Cl) acts as a proton donor and a phenyl ring or multiple bonds as an acceptor. Acetylene [5, 6], ethylene [7, 8], cyclopropane [9, 10] and cyclobutanone form complexes with HX in such a manner that a hydrogen atom of the HX points perpendicularly to a π bond or pseudo π bond. In the present study, the significance of the hydrogen bonding of cyclobutanone···HX (X=F, Cl) complexes is discussed, and their related parameters are compared to those of cyclobutanone.

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**Fig. 1** B3LYP/C molecular structures with atom numbering of cyclobutanone...HF (*left*) and ...HCl (*right*) complexes



## Methods

Geometry optimizations were performed using second-order Møller–Plesset theory (MP2) and Becke’s three-parameter hybrid DFT [17] in combination with the

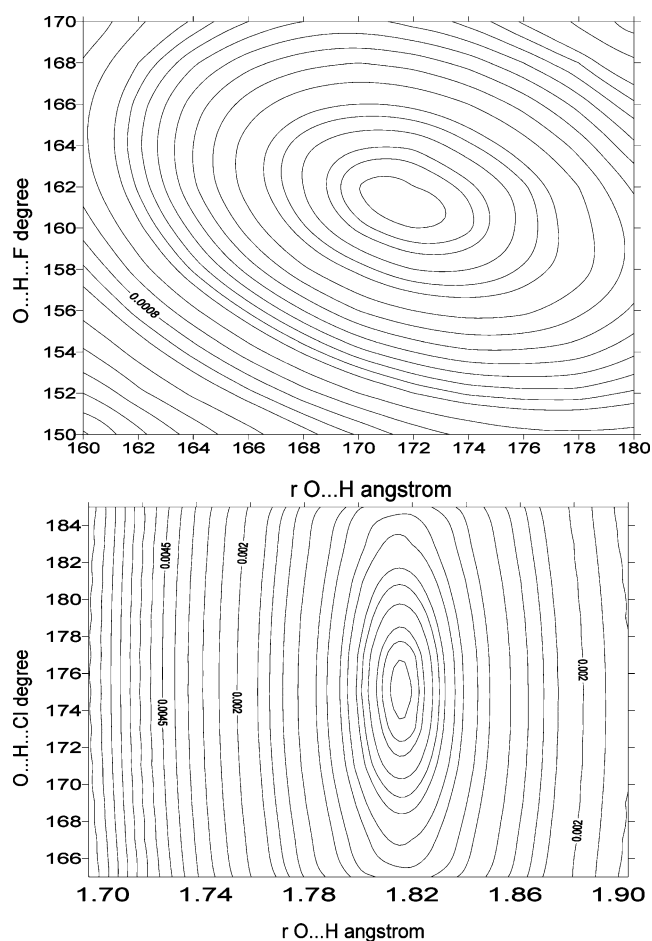
Lee–Yang–Parr correlation functional (B3LYP) [18]. For weak bonding, both diffuse and polarization functions are included in the basis set. All calculations were performed using Gaussian view 3.01, Gaussian 03 [19].

**Table 1** Structural parameters of cyclobutanone...HX complexes computed with second-order Møller–Plesset theory (MP2)/A=6–311G, B=6–311G\*\*, C=6–311++G\*\* and B3LYP/ A=6–311G, B=6–311G\*\*, C=6–311++G\*\* levels

Parameter <sup>a</sup>	B3LYP			MP2			Experimental <sup>b</sup>
	A	B	C	A	B	C	
<b>Cyc4</b>							
r <sub>C4O11</sub>	1.224	1.196	1.198	1.242	1.203	1.206	1.202
r <sub>C1C4</sub>	1.535	1.538	1.536	1.542	1.538	1.536	1.527
r <sub>CH</sub>	1.091	1.094	1.093	1.095	1.095	1.096	1.100
θ <sub>C1C4C3</sub>	93.00	92.40	92.50	92.50	92.50	92.70	93.1
θ <sub>C1C2C3</sub>	90.57	90.75	90.68	91.09	91.18	91.12	90.9
r <sub>HF</sub>	0.939	0.920	0.922	0.913	0.937	0.922	0.917
<b>Cyc4...HF</b>							
r <sub>C4O11</sub>	1.236	1.207	1.208	1.250	1.212	1.214	
r <sub>C1C4</sub>	1.522	1.526	1.524	1.531	1.527	1.524	
r <sub>C3C4</sub>	1.522	1.525	1.525	1.533	1.528	1.527	
r <sub>C1C2</sub>	1.568	1.562	1.562	1.576	1.558	1.559	
r <sub>CH</sub>	1.09	1.090	1.093	1.094	1.092	1.092	
r <sub>H13F12</sub>	0.965	0.941	0.946	0.954	0.929	0.935	
θ <sub>C4O11H13</sub>	107.39	106.11	117.12	106.47	104.80	112.28	
θ <sub>O11H13F12</sub>	158.25	161.34	170.96	158.73	162.67	169.79	
θ <sub>C1C4C3</sub>	93.77	93.18	93.23	94.27	92.41	92.50	
θ <sub>C1C2C3</sub>	90.29	90.42	90.39	90.93	90.15	90.03	
∠ <sub>C4O11H13F12</sub>	0.169	-0.24	0.362	-0.112	0.984	-7.38	
r <sub>HCl</sub>	1.329	1.287	1.287	1.328	1.273	1.273	1.275
<b>Cyc4...HCl</b>							
r <sub>C4O11</sub>	1.235	1.205	1.206	1.248	1.210	1.212	
r <sub>C1C4</sub>	1.521	1.527	1.526	1.532	1.529	1.527	
r <sub>C3C4</sub>	1.523	1.529	1.529	1.536	1.532	1.531	
r <sub>C1C2</sub>	1.568	1.561	1.562	1.576	1.557	1.558	
r <sub>CH</sub>	1.091	1.093	1.093	1.095	1.09	1.09	
r <sub>H13 Cl12</sub>	1.384	1.315	1.313	1.355	1.291	1.291	
θ <sub>C4O11H13</sub>	120.69	119.27	120.87	122.19	112.86	112.75	
θ <sub>O11H13Cl12</sub>	175.02	175.02	174.88	174.52	170.26	169.02	
θ <sub>C1C4C3</sub>	93.75	92.97	93.06	94.13	92.13	92.28	
θ <sub>C1C2C3</sub>	90.29	90.48	90.46	90.94	90.12	90.10	
∠ <sub>C4O11H13 Cl12</sub>	-0.44	-2.46	1.508	0.115	-1.56	-6.61	

<sup>a</sup> Bond lengths and angles are in Å and degrees, respectively

<sup>b</sup> From reference [1]



**Fig. 2** **a** Potential energy of the cyclobutanone...HF complex as a function of the hydrogen bond (H13...O11) and (O11- H13-F12) calculated using the B3LYP/C /6-311G\*\* method and basis set. **b** Potential energy of the cyclobutanone...HCl complex as a function of the hydrogen bond (H13...O11) and (O11- H13-Cl12) calculated using the B3LYP/C /6-311G\*\* method and basis set

## Results and discussion

### Geometrical structure

Figure 1 shows the optimized structure of the cyclobutanone...HX complexes. Non-bonding electrons of the oxygen atom on the carbonyl group interact with the hydrogen atom of HX. Experimental (determined by ED and MW measurement) and calculated bond distances and angles using

B3LYP/A=6-311G, B=6-311G\*\*, C=6-311++G\*\* and MP2/A=6-311G, B=6-311G\*\*, C=6-311++G\*\* levels of the cyclobutanone monomer and cyclobutanone...HX complexes are listed in Table 1. For cyclobutanone monomer geometric data, good agreement between theory and experiment is obtained for the MP2 and B3LYP levels with basis sets including diffuse functions. In the complexes, the C4-O11 and H13-X12 bonds, which participate in the hydrogen bond, are elongated, while other bonds shrink. The changes in geometry between the complexes and cyclobutanone have a similar trend for both the MP2 and B3LYP methods.

The HX (X=F, Cl) scan area shows that the minimum potential is located at hydrogen bonds of 1.71, 1.81 Å and OH-F, OH-Cl angles of 161, 175 degrees for HF and HCl, respectively (Fig. 2).

Table 2 summarizes the comparison of the hydrogen bonding geometry calculated using the B3LYP/6-311G\*\* method and the basis set of isolated molecules and complexes. In the complexes, the C=O and D-H bonds, which are participating in the hydrogen bond, are elongated. The calculated rotational constants of cyclobutanone, HF, HCl and their complexes are listed in Table 3. The values of the rotational constants,  $A_0$  (all in GHz), at the B3LYP/6-311G\*\* level for cyclobutanone and its complexes are 10.83 (Cyc4), 6.71(Cyc4...HF) and 7.25 (Cyc4...HCl), respectively. The rotational constants of HF and HCl are in good agreement with reported experimental values [1]. Inspection of Table 3 shows that cyclobutanone is an asymmetric top molecule, whereas the complexes are close to a symmetric top (oblate) molecule, with the expected major shifts in spacing in rotational spectra and changes in the type of the rovibrational branches.

The dipole moment of the Cyc4, Cyc4...HF and Cyc4...HCl molecules were computed at the different levels of theory employed in this work. The calculated dipole moments (B3LYP/6-311G\*\* level) are 2.788, 4.394 and 5.359D for Cyc4, Cyc4...HF and Cyc4...HCl respectively. The MP2 method gives the largest value of the dipole moment. The dipoles computed at the B3LYP/6-311G\*\* level are in the range from 1.42 to 5.36 D, which corresponds better with experimental values (measured at room temperature in CCl<sub>4</sub> solution), but are probably still higher than in the gas phase. Values in solution are usually

**Table 2** Hydrogen bonding geometry calculated using the B3LYP/6-311G\*\* method and basis set (changes compared to the corresponding experimental values are in parentheses)

D-H...A	Complex				Monomer		
	D-H	H...A	D...A	D-H...A	C=O	D-H	C=O
F12-H13...O11	0.9411	1.7172	2.6266	161.46	1.2073	0.920 (-0.003)	1.1958 (0.006)
Cl12-H13...O11	1.3153	1.8113	3.1236	174.85	1.2051	1.287 (-0.012)	1.1958 (0.006)

**Table 3** Calculated rotational constants (GHz) of the HX, Cyc4 and Cyc4–HX complexes

Parameter	B3LYP			MP2			Experimental <sup>a</sup>
	A	B	C	A	B	C	
Cyc4							
A <sub>0</sub>	10.79	10.83	10.83	10.61	10.80	10.80	10.78
B <sub>0</sub>	4.73	4.79	4.79	4.68	4.78	4.78	4.806
C <sub>0</sub>	3.50	3.54	3.54	3.46	3.53	3.54	3.558
HF							
A <sub>0</sub>	598.2	623.76	620.85	601.81	633.74	628.48	628.23
Cyc4⋯HF							
A <sub>0</sub>	6.69	6.71	7.54	6.52	6.63	7.10	
B <sub>0</sub>	1.97	1.98	1.69	1.92	1.98	1.78	
C <sub>0</sub>	1.57	1.57	1.42	1.53	1.58	1.48	
HCl							
A <sub>0</sub>	292.06	311.55	311.57	292.54	318.18	318.25	317.58
Cyc4⋯HCl							
A <sub>0</sub>	7.36	7.25	7.34	7.28	6.63	6.61	
B <sub>0</sub>	1.01	0.99	0.97	0.95	1.07	1.08	
C <sub>0</sub>	0.91	0.89	0.87	0.85	0.94	0.95	

<sup>a</sup> From reference [1]

higher than those measured in the gas phase. The transition moments, and hence the line intensities, are expected to increase with the same trends. The sum of the internal energy Cyc4+HX is less than that of the corresponding complex, therefore the heat capacity of the complexes is increased due

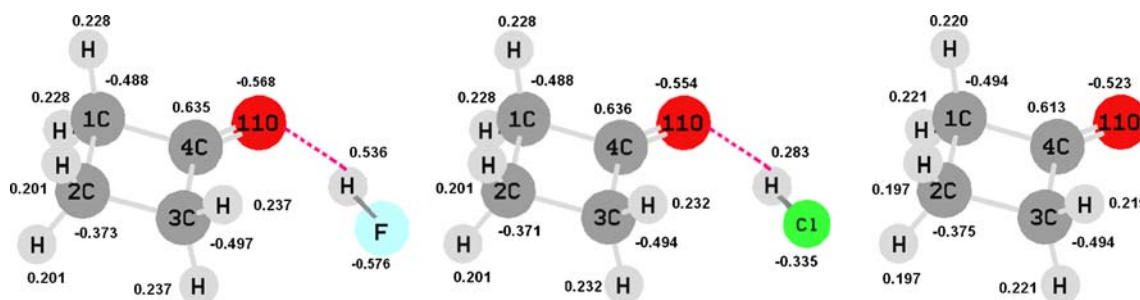
to the newly generated hydrogen bond. Zero-point vibrational energy, thermal energy and potential energy, and other selected properties of the cyclobutanone⋯HX complex, cyclobutanone, and HX molecules are listed in Table 4. The dipole moments of cyclobutanone, HF, and HCl are

**Table 4** Calculated dipole moments (D. Mom), zero-point vibrational (ZPV) energy (kJ/mol), and thermal energy (E thermal; kcal/mol). For definitions of theory levels, see Table 1

Parameter	B3LYP			MP2			Experimental
	A	B	C	A	B	C	
Cyc4							
D. Mom	3.113	2.788	3.107	3.807	3.370	3.644	2.89 <sup>a</sup>
ZPV	238.9	236.88	236.80	238.78	239.9	239.2	236.3 <sup>a</sup>
E (Thermal)	60.16	59.20	59.77	59.62	59.93	59.75	
HF							
D. Mom	2.193	1.880	1.957	2.360	2.011	2.066	1.82 <sup>b</sup>
ZPV	22.764	24.617	24.498	22.972	25.431	25.113	
E (Thermal)	6.922	7.365	7.336	6.972	7.559	7.483	
Cyc4⋯HF							
D. Mom	4.898	4.394	5.533	5.328	4.820	5.670	
ZPV	271.1	270.1	269.6	271.8	276.5	274.5	
E (Thermal)	69.265	68.714	69.147	69.472	70.517	70.138	
HCl							
D. Mom	1.812	1.422	1.404	1.902	1.457	1.439	1.08 <sup>b</sup>
ZPV	15.996	17.521	17.511	16.157	18.471	18.466	
E (Thermal)	5.304	5.669	5.667	5.343	5.896	5.895	
Cyc4⋯HCl							
D. Mom	6.819	5.359	5.329	6.769	5.219	5.188	
ZPV	262.3	262.1	260.7	262.4	266.7	265.0	
E (Thermal)	67.295	67.257	67.186	67.477	68.47	68.15	

<sup>a</sup> From reference [4]

<sup>b</sup> From reference [1]



**Fig. 3** B3LYP/6–311G\*\* natural bond orbital (NBO) charge on each atom of cyclobutanone and the cyc4···HX complex

calculated to be 2.788, 1.880, and 1.422 D, respectively, at the B3LYP/6–311G\*\* level. The computed dipole moments of the HF and HCl complexes are 4.394, and 5.359 D, respectively. The zero-point vibrational energies of cyclobutanone, HF, and HCl are calculated to be 236.88, 24.617 and 17.521 (kJ/mol), respectively, at the B3LYP/6–311G\*\* level but the zero point vibrational energy of the complexes are 270.1, 262.1 (kJ/mol) for HF and HCl, respectively.

For the cyclobutanone, HF, HCl and cyclobutanone···HX complexes, the wavefunctions were analyzed by the natural bond orbital (NBO) method [20–22]—a standard program option of Gaussian 03. NBO analysis transforms the delocalized many-electron wave functions into optimized electron pair bonding units, corresponding to the Lewis structure picture. Starting from a given input atomic orbital basis set, the program performs a transformation to form a set of high occupancy Lewis-type (bond, lone pair) NBOs, each of which is taken to be doubly occupied. This is said to represent the ‘natural Lewis structure’ of the molecule. Delocalized effects, which appear as weak departures from the idealized localized picture, appear as

non-zero occupancies of non-Lewis (anti-bond, Rydberg) NBOs. The total non-Lewis occupancy ( $\_NL$ ) constitutes a quantitative measure of electronic delocalization. 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.

To clarify the nature of the complexation, NBO and Mulliken analyses were carried out. The small interaction energy between Cyc4 and HX is also reflected in the electron distribution at the atoms involved in hydrogen bonding and their corresponding charges (Fig. 3). Table 5 gives the natural atomic charges of cyclobutanone, HF, HCl molecules and Cyc4···HX complexes calculated with the B3LYP/6–311G\*\* method and basis set. In the complexes, the electronegative atoms involved (O<sub>11</sub> and X<sub>12</sub>) gain charge, while other atoms lose charge. In the Cyc4···HF complex the charge on C<sub>1</sub>, C<sub>3</sub>, C<sub>4</sub>, H<sub>5</sub>, H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub>, H<sub>9</sub> and H<sub>10</sub> increases by 0.006, 0.002, 0.003, 0.008, 0.004 and 0.016, respectively, whereas the charge decreases at C<sub>3</sub>, O<sub>11</sub>, and F<sub>12</sub> are 0.003, 0.045, and 0.048, respectively. In

**Table 5** Selected atomic charges of Cyc4 and Cyc4···HX complexes and base pairs from natural bond orbital (NBO) charge and Mulliken population analyses (B3LYP/6–311G\*\*)

Atom	NBO charge			Mulliken charge		
	C4···HF	C4···HCl	Cyc4	C4···HF	C4···HCl	Cyc4
C1	–0.488	–0.488	–0.494	–0.228	–0.229	–0.242
C2	–0.373	–0.371	–0.375	–0.246	–0.246	–0.247
C3	–0.497	–0.494	–0.494	–0.225	–0.250	–0.242
C4	0.635	0.636	0.613	0.211	0.219	0.184
H5	0.228	0.229	0.221	0.152	0.154	0.143
H6	0.228	0.228	0.220	0.152	0.152	0.141
H7	0.201	0.201	0.197	0.131	0.131	0.123
H8	0.201	0.201	0.197	0.130	0.133	0.126
H9	0.237	0.232	0.221	0.159	0.160	0.141
H10	0.237	0.232	0.219	0.159	0.160	0.143
O11	–0.568	–0.554	–0.523	–0.328	–0.308	–0.269
			HCl/HF			HCl/HF
F12	–0.576		–0.528	–0.358		–0.297
Cl12		–0.335	–0.258		–0.285	–0.176
H13	0.536	0.283		0.322	0.209	

**Table 6** Band assignments for vibrational spectra ( $\text{cm}^{-1}$ ; scaled by 0.97) of cyclobutanone.  $\nu$  Stretching (*a* asymmetric, *s* symmetric),  $\delta$  in-plane bending,  $\gamma$  out-of-plane bending, *Wag* wagging,  $\rho$  rocking, *Tw* twisting, *Scis* scissoring. For definitions of theory levels, see Table 1

Assignments	B3LYP			MP2			Experimental <sup>a</sup>
	A	B	C	A	B	C	
Ring puckering	53.0	47.41	7.67	31.32	121.23	113.96	135
$\gamma\text{C}=\text{O}$	392.1	391.0	390.18	371.31	391.46	388.16	395
$\delta\text{C}=\text{O}$	440.8	444.0	445.97	441.35	448.2	448.9	454
$\rho\text{CH}_2$	651.1	610.7	604.86	647.92	608.2	645.15	
$\delta\text{C}2\text{C}6\text{C}3$	661.6	653.0	653.5	698.4	648.5	652.0	670
$\rho\text{CH}_2$	734.9	717.1	718.4	737.5	719.7	717.8	735
$\nu\text{sC}2\text{C}6\text{C}3$	820.2	813.6	809.44	824.21	861.9	859.5	856
$\nu\text{aC}2\text{C}1\text{C}3$	894.0	891.4	891.21	897.5	913.3	909.2	902
$\text{CH}_2$ Tw	934.8	920.1	920.1	934.35	926.2	919.0	953
$\nu\text{sC}2\text{C}1\text{C}3$	954.0	937.5	936.06	950.11	966.2	963.2	956
$\nu\text{aC}3\text{C}6\text{C}2$	1,062.9	1,042.0	1,046.9	1,074.6	1,056.5	1,055.5	1,073
$\rho\text{CH}_2$	1,089.2	1,062.0	1,061.4	1,097.1	1,069.7	1,067.2	1,124
$\text{CH}_2$ Wag	1,190.4	1,150.0	1,152.5	1,190.2	1,140.6	1,134.6	1,162
$\text{CH}_2$ Tw	1,201.4	1,182.0	1,182.5	1,193.1	1,195.7	1,187.9	1,191
$\text{CH}_2$ Tw	1,201.7	1,186.0	1,184.2	1,206.3	1,208.9	1,199.5	1,209
$\text{CH}_2$ Wag	1,226.7	1,199.0	1,199.7	1,252.7	1,210.0	1,206.0	1,211
$\text{CH}_2$ Wag	1,258.9	1,231.0	1,230.4	1,252.8	1,238.4	1,227.4	1,332
$\text{CH}_2$ Scis	1,424.0	1,387.0	1,384.1	1,452.7	1,411.7	1,406.2	1,402
$\text{CH}_2$ Scis	1,436.5	1,402.0	1,398.4	1,463.7	1,427.5	1,422.7	1,402
$\text{CH}_2$ Scis	1,482.4	1,455.0	1,452.6	1,501.0	1,472.1	1,467.0	1,464
$\nu\text{C}=\text{O}$	1,714.7	1,819.0	1,802.9	1,638.5	1,799.5	1,780.3	1,816
$\nu\text{sCH}_2$	2,949.7	2,956.0	2,955.6	2,944.0	3,005.0	3,002.4	2,930
$\nu\text{sCH}_2$	2,954.0	2,960.0	2,959.8	2,946.1	3,008.6	3,005.8	2,930
$\nu\text{sCH}_2$	2,980.4	2,984.0	2,983.7	2,967.7	3,028.3	3,025.9	2,956
$\nu\text{aCH}_2$	2,996.1	3,001.0	2,999.0	3,002.2	3,076.5	3,074.4	2,975
$\nu\text{aCH}_2$	3,002.1	3,007.0	3,005.3	3,009.5	3,081.1	3,079.2	2,975
$\nu\text{aCH}_2$	3,033.7	3,034.0	3,032.7	3,033.9	3,099.2	3,097.2	3,004

<sup>a</sup> From reference [1]

the  $\text{Cyc}4\cdots\text{HCl}$  complex the charge on  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$ ,  $\text{H}_7$ ,  $\text{H}_8$ ,  $\text{H}_9$  and  $\text{H}_{10}$  increases by 0.006, 0.004, 0.023, 0.008, 0.004 and 0.011, respectively, whereas the electron distribution on  $\text{C}2$  is unchanged with respect to the single cyclobutanone at the  $\text{HCl}$  molecule; the decreases at  $\text{O}_{11}$  and  $\text{Cl}_{12}$  are 0.039 and 0.079, respectively.

### Vibrational spectra

Vibrational analysis is performed by DFT and ab initio correlated methods. Tables 6, 7, and 8 show selected scaled 0.97 vibrational frequencies and assignments of cyclobutanone, HF and HCl and their complexes using different levels of calculations. The model spectra of IR and vibrational circular dichroism (VCD) of the molecules computed at the B3LYP/6–311G\*\* level of theory are presented graphically in Figs. 4, 5, 6, 7, 8, and 9. These model spectra are compared in Fig. 10.  $\text{C}=\text{O}$  stretching with B3LYP/C at  $1,818.7\text{ cm}^{-1}$  and experimental at  $1,816\text{ cm}^{-1}$  are in good agreement with each other, but the MP2/C

value of  $1,795.5\text{ cm}^{-1}$  shows a larger deviation. At the B3LYP/C level,  $\text{C}=\text{O}$  out-of-plane bending and  $\text{C}=\text{O}$  in-plane bending deviations are  $4.0$  and  $10.0\text{ cm}^{-1}$ , respectively. It could be that the scaling factor of 0.97 may need to be altered for lower frequencies. The frequency changes well reflect the geometry changes. Significant changes in frequency and intensity take place in the  $\text{H}-\text{X}$  stretching vibration. As the magnitude of the shift in  $\text{HX}$  stretching vibrational frequency is known to represent a measure of the intermolecular interaction, the difference in frequency is in good agreement with the interaction energy. At the B3LYP/6–311G\*\* level, the stretching vibrational frequencies of HF and HCl of the complex are found to absorb at  $3,552.6\text{ cm}^{-1}$  and  $2,480.3\text{ cm}^{-1}$ , respectively. For cyclobutanone and its  $\cdots\text{HF}$  and  $\cdots\text{HCl}$  complexes, the calculated  $\text{C}=\text{O}$  stretching vibrational frequencies are  $1,818.7$ ,  $1,776.2$  and  $1,778.7\text{ cm}^{-1}$  respectively. As for the cyclobutanone moiety, the  $\text{C}=\text{O}$  stretching vibrational frequencies show red shifts ( $-42.5$ ,  $-40.0\text{ cm}^{-1}$ ) for HF and HCl moieties in the complex.

**Table 7** Band assignments for vibrational spectra ( $\text{cm}^{-1}$ ; scaled by 0.97) of the cyclobutanone $\cdots$ HF complex. For definitions of theory levels, see Table 1

Assignments	B3LYP			MP2		
	A	B	C	A	B	C
Cyc4 $\cdots$ HF						
CCC bending	48.97	23.3	20.9	43.7	52.4	43.6
CCC bending	72.72	56.2	43.1	61.2	98.0	47.4
HF $\cdots$ C=O bending	100.30	96.0	56.8	93.2	113.5	112.5
$\nu$ H $\cdots$ O	230.65	211.5	205.2	208.5	197.0	192.0
$\gamma$ C=O	393.45	390.7	393.8	372.5	390.0	388.6
$\delta$ ;C=O	472.49	471.5	467.5	467.7	473.4	470.5
HF Be	648.34	595.6	596.0	645.1	636.3	632.1
+ $\nu$ CH <sub>2</sub>						
C <sub>1</sub> C <sub>4</sub> C <sub>3</sub> bending	652.11	654.8	658.6	648.7	660.66	663.5
$\rho$ CH <sub>2</sub>	713.33	699.4	709.9	700.5	687.0	668.3
	730.98	714.8	717.8	738.2	722.7	721.7
	830.61	792.5	769.2	756.7	757.0	743.0
	841.03	820.7	821.6	832.2	866.2	866.8
vaC-C	893.53	892.3	891.5	898.2	912.8	906.0
vsC-C	935.66	924.5	928.3	934.1	931.8	925.2
CH <sub>2</sub> Tw	961.13	938.0	938.0	959.8	967.1	963.8
$\nu$ CH <sub>2</sub>	1,094.1	1,065.1	1,065.9	1,107.7	1,073.8	1,071.7
va C <sub>1</sub> C <sub>4</sub> C <sub>3</sub>	1,107.4	1,084.8	1,083.5	1,110.6	1,092.6	1,086.4
	1,197.6	1,158.7	1,161.1	1,195.0	1,149.0	1,140.7
CH <sub>2</sub> Wag	1,198.6	1,180.5	1,182.0	1,199.0	1,114.0	1,190.2
CH <sub>2</sub> Tw	1,203.7	1,184.2	1,187.0	1,203.8	1,209.6	1,201.8
CH <sub>2</sub> Wag	1,234.1	1,205.7	1,208.6	1,257.1	1,215.5	1,213.5
CH <sub>2</sub> Wag	1,263.7	1,236.5	1,236.7	1,260.1	1,244.3	1,234.1
CH <sub>2</sub> Scis	1,419.0	1,379.3	1,378.7	1,448.2	1,406.5	1,403.5
CH <sub>2</sub> Scis	1,431.1	1,394.6	1,393.3	1,460.0	1,423.0	1,420.1
CH <sub>2</sub> Scis	1,482.0	1,453.1	1,429.4	1,501.5	1,471.7	1,467.3
$\nu$ C=O	1,679.0	1,776.1	1,769.4	1,634.5	1,777.8	1,764.1
vsCH <sub>2</sub>	2,956.0	2,961.3	2,960.3	2,949.0	3,009.0	3,006.0
vsCH <sub>2</sub>	2,968.6	2,973.5	2,965.3	2,959.0	3,017.0	3,009.9
vsCH <sub>2</sub>	2,987.3	2,990.0	2,990.5	2,973.1	3,033.2	3,031.2
vaCH <sub>2</sub>	3,002.7	3,004.4	3,003.7	3,008.0	3,081.7	3,080.7
vaCH <sub>2</sub>	3,012.0	3,013.8	3,008.9	3,017.7	3,094.3	3,085.6
vaCH <sub>2</sub>	3,042.1	3,040.0	3,040.9	3,040.0	3,106.0	3,103.1
$\nu$ HF	3,193.5	3,552.0	3,468.7	3,389.2	3,773.9	3,661.8

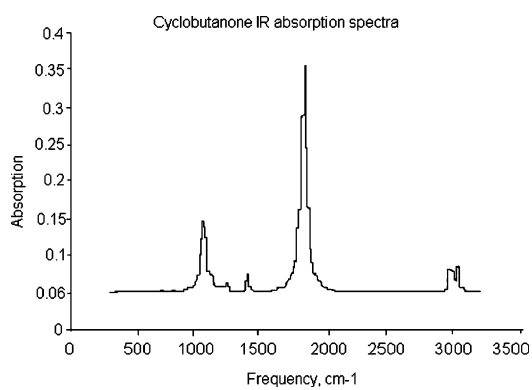
Table 9 shows the scaled vibrational frequencies of the HF and HCl molecules calculated at the B3LYP and MP2 levels. At the B3LYP/6–311G\*\* level, the stretching vibrational frequencies of the HF, HCl molecules and complex are calculated to be 3,992.1, 2,841.4, 3,552.0 and 2,480.3  $\text{cm}^{-1}$  respectively. Comparison of these results shows the red shifts ( $-440.1$ ,  $-361.1$   $\text{cm}^{-1}$ ) for HF and HCl in the complexes. At the MP2/6–311G\*\* level, calculated vibrational frequencies are in good agreement with those reported experimentally [1]. Figures 11 and 12 show the experimental and calculated variation in C=O and HX

stretching of cyclobutanone $\cdots$ HF and  $\cdots$  HCl molecules and complexes.

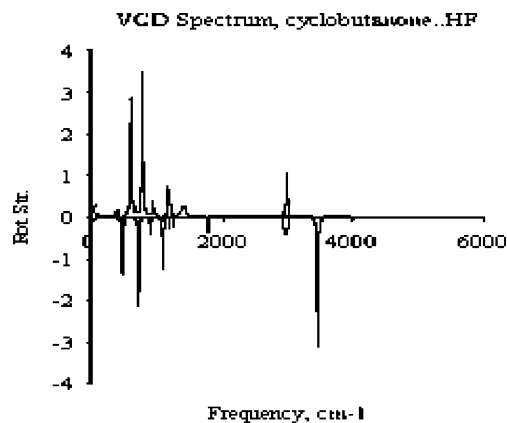
VCD spectroscopy in the near infrared (NIR) range was successfully tried decades ago [23], in one case even earlier than the more well known and used VCD spectroscopy in the IR range. More recently, there have been some advancements in developing new instrumentation, based either on dispersive or Fourier transform interferometric technologies [24, 25]. The usability of NIR-VCD data

**Table 8** Band assignments for vibrational spectra ( $\text{cm}^{-1}$ ; scaled by 0.97) for the equilibrium stable cyclobutanone $\cdots$ HCl complex. For definitions of theory levels, see Table 1

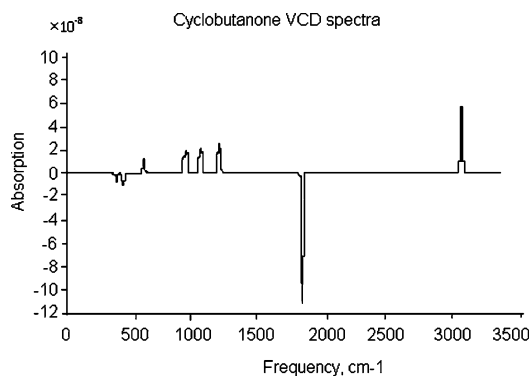
Parameter	B3LYP			MP2		
	A	B	C	A	B	C
Cyc4 $\cdots$ HCl						
CCC bending	39.8	22.8	9.6	29.7	34.75	30.04
HCl $\cdots$ C=O bending	40.7	34.9	30.9	29.8	44.06	40.67
CCC bending	72.8	47.1	40.7	52.7	118.3	110.8
$\nu$ H $\cdots$ O	174.6	141.6	135.8	142.4	132.3	131.5
$\gamma$ C=O	396.2	391.8	391.9	374.1	391.7	385.5
$\delta$ C=O	458.8	453.9	452.0	450.7	455.4	421.9
HF Be	645.2	547.0	519.0	565.4	506.5	451.7
+ $\rho$ CH <sub>2</sub>	653.8	579.1	552.9	575.2	533.0	508.3
C <sub>1</sub> C <sub>4</sub> C <sub>3</sub> bending	690.6	607.2	602.0	660.0	649.5	644.1
$\rho$ CH <sub>2</sub>	727.5	663.0	661.5	696.5	668.3	666.4
$\rho$ CH <sub>2</sub>	734.3	718.4	717.7	741.1	725.7	721.7
C <sub>1</sub> C <sub>2</sub> C <sub>3</sub> bending	833.2	819.1	817.7	828.9	866.6	864.1
va C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	894.3	892.5	891.5	898.5	912.2	907.0
vs C-C	935.7	927.1	927.3	934.1	931.8	922.5
CH <sub>2</sub> Tw	964.2	938.6	937.4	957.9	967.0	963.2
$\rho$ CH <sub>2</sub>	1,096.1	1,065.6	1,063.9	1,100.9	1,073.5	1,068.9
va C <sub>1</sub> C <sub>4</sub> C <sub>3</sub>	1,101.9	1,073.3	1,072.8	1,107.7	1,081.9	1,074.7
CH <sub>2</sub> Tw	1,199.9	1,160.1	1,159.1	1,195.6	1,148.8	1,136.0
CH <sub>2</sub> Wag	1,201.8	1,184.4	1,182.5	1,198.5	1,197.9	1,188.2
CH <sub>2</sub> Tw	1,206.7	1,186.3	1,185.8	1,204.6	1,210.2	1,200.0
CH <sub>2</sub> Wag	1,237.1	1,208.1	1,206.7	1,257.9	1,216.3	1,210.5
CH <sub>2</sub> Wag	1,266.8	1,236.8	1,235.5	1,259.3	1,243.0	1,229.0
CH <sub>2</sub> Scis	1,419.0	1,382.1	1,380.0	1,450.2	1,407.5	1,403.6
CH <sub>2</sub> Scis	1,430.8	1,396.8	1,393.9	1,460.7	1,424.0	1,420.1
CH <sub>2</sub> Scis	1,482.2	1,454.0	1,452.8	1,502.0	1,472.0	1,467.6
$\nu$ C=O	1,665.9	1,778.7	1,771.6	1,634.5	1,778.3	1,764.0
$\nu$ HCl	2,008.7	2,480.3	2,511.3	2,305.2	2,741.2	2,741.2
vsCH <sub>2</sub>	2,956.1	2,960.5	2,959.5	2,948.4	3,008.6	3,004.1
vsCH <sub>2</sub>	2,961.1	2,964.9	2,963.8	2,950.7	3,012.2	3,008.0
vsCH <sub>2</sub>	2,989.5	2,990.5	2,989.5	2,974.0	3,033.0	3,029.3
vaCH <sub>2</sub>	3,002.2	3,004.3	3,002.9	3,006.0	3,081.7	3,078.8
vaCH <sub>2</sub>	3,007.0	3,008.9	3,008.0	3,012.3	3,086.5	3,083.5
vaCH <sub>2</sub>	3,044.6	3,040.9	3,039.8	3,040.9	3,104.8	3,101.1



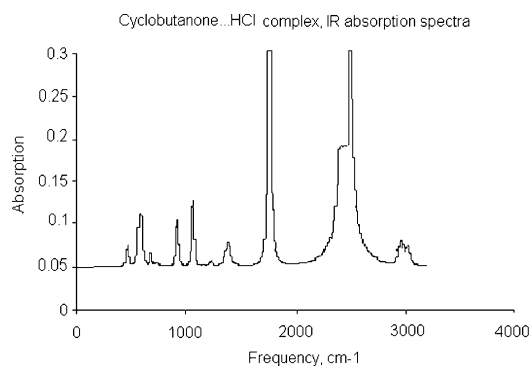
**Fig. 4** B3LYP/C infrared (IR) absorption spectrum of the cyclobutanone monomer



**Fig. 7** B3LYP/C VCD spectrum of the Cyc4...HF complex

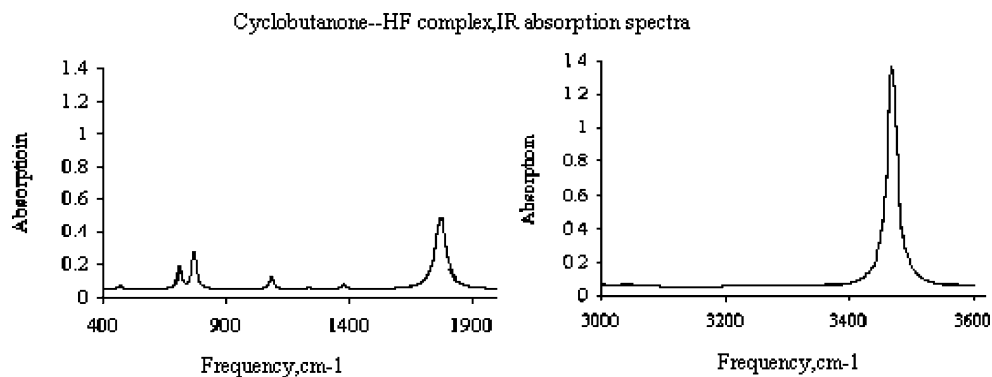


**Fig. 5** B3LYP/C vibrational circular dichroism (VCD) spectrum of the cyclobutanone monomer

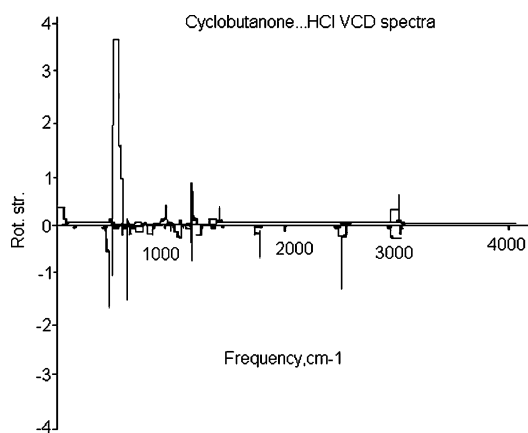


**Fig. 8** B3LYP/C IR absorption spectrum of the Cyc4...HCl complex

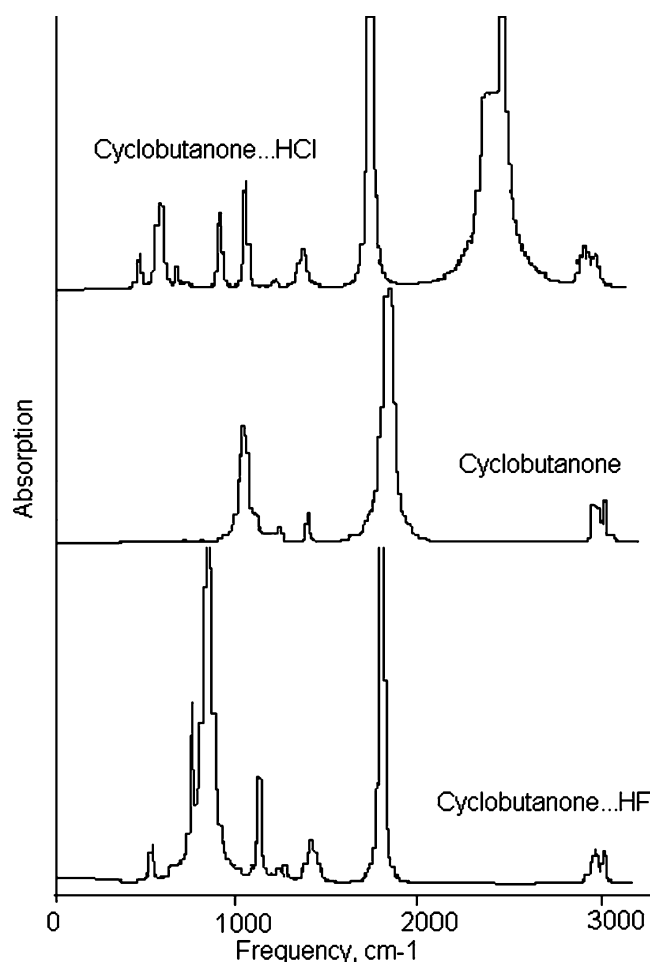
**Fig. 6**  $\tau$  B3LYP/C IR absorption spectrum of the Cyc4...HF complex







**Fig. 9** B3LYP/C VCD spectrum of the Cyclobutanone...HCl complex



**Fig. 10** Comparison of IR absorption spectra of cyclobutanone and cyclobutanone...HX complexes

requires a parallel advancement in the interpretation of the spectra. Such interpretation is hampered by many factors, two of which are of the utmost importance: (1) the enormous number of modes that may in principle contribute to the overtone regions, and (2) the essential role played by anharmonic terms in determining both the wave functions and the functional form of the electric and magnetic dipole moment operators. It is necessary to resort to some kind of approximation. The optical activity of asymmetric molecules is explained when a plane-polarized radiation passes through an active medium. The plane of the emergent plane-polarized radiation rotates by an angle. The plane-polarized beam can be considered as a superimposition of two oppositely rotating circularly polarized components. The absorbance coefficient is defined as  $\Delta\varepsilon = \varepsilon_R - \varepsilon_L$ .

Gauss View can display a variety of computed spectra, including IR, VCD,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR. Computed NMR spectra of cyclobutanone...HX complexes are shown in Figs. 13 and 14) [26].

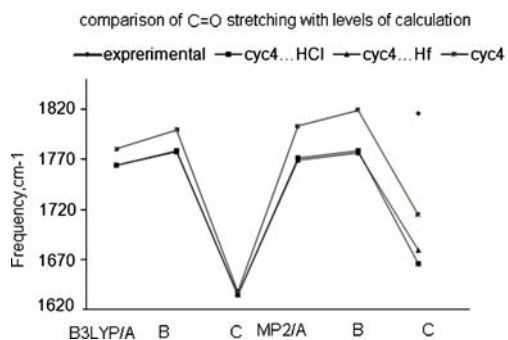
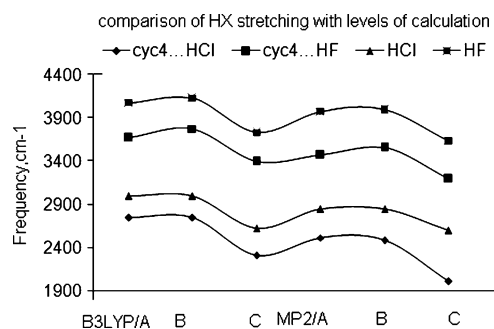
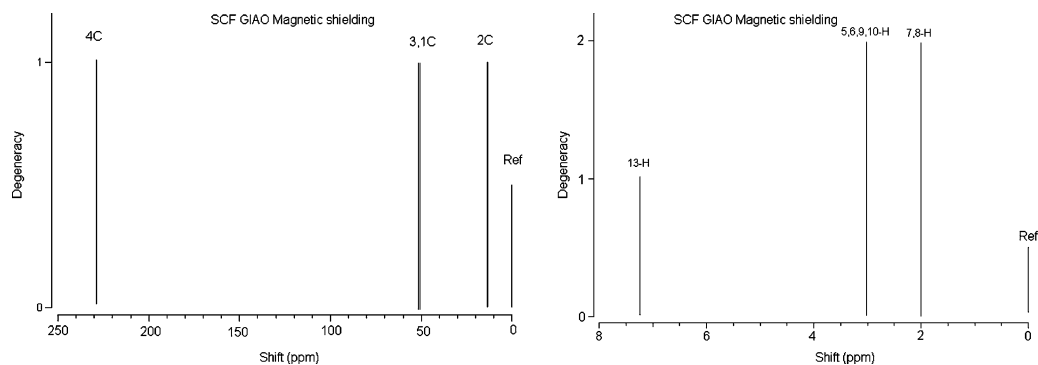
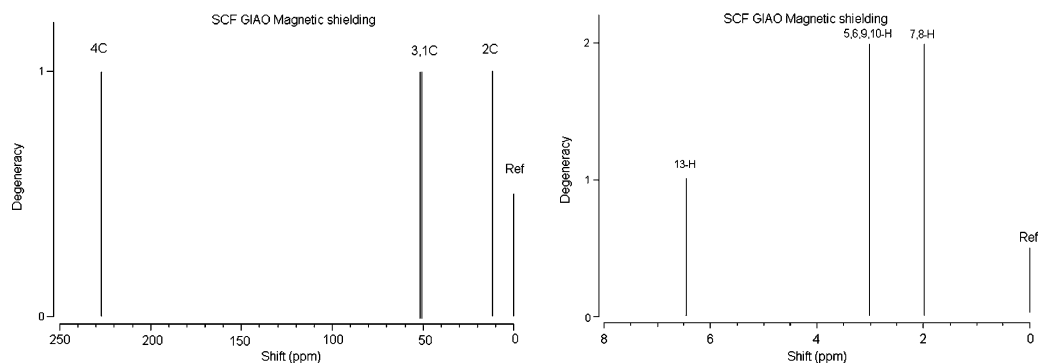
Computed B3LYP/6-311G\*\*  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR of the cyclobutanone and cyclobutanone complexes with HF and HCl referenced to tetramethylsilane (TMS):  $\delta$   $^1\text{H}$  and  $^{13}\text{C}$  ( $\text{CH}_3$ ) $_4\text{Si}$ =0.00 ppm are compared in Table 10. The trends of geometry and frequency changes from the corresponding monomer are similar in the results obtained with the MP2 and B3LYP methods. However, the influence of the method used is reflected in the intermolecular distances and frequency shifts, which are compared in Table 11. For the complex, the hydrogen bond O11...H13 distance calculated by the MP2 method is longer than that calculated by the B3LYP method with the same basis set, and this distance is longer for the cyclobutanone...HCl complex than for the cyclobutanone...HF complex.

## Conclusions

The geometric parameters, dipole moment, vibrational spectroscopic data and  $^1\text{H}$ ,  $^{13}\text{C}$  NMR chemical shifts of the cyclobutanone and cyclobutanone complexes with HF and HCl have been calculated at various levels of theory (B3LYP and MP2), using basis sets 6-311G, 6-311G\*\*, 6-311++G\*\*. The distances between the O atom of cyclobutanone and the H atom of HX were calculated to be 1.717 and 1.624 Å for the HF and HCl complexes, respectively. The C=O and H-X bonds participating in the hydrogen bond are elongated, while other bonds shrink. Calculated shifts of the C=O and HX stretching frequencies are -42.5, -39.9, -439 and -361  $\text{cm}^{-1}$  for the HF and HCl complexes, respectively. HX molecules are a good probe for the magnitude of the interaction; the longer the bond length, the lower the stretching frequency.

**Table 9** Scaled harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) of HF and HCl molecules

Parameter	B3LYP			MP2			Experimental <sup>a</sup>
	A	B	C	A	B	C	
$\nu_{\text{HF}}$	3,632.9	3,992.1	3,972.9	3,725.4	4,124.2	4,072.7	4,138
$\nu_{\text{HCl}}$	2,594.1	2,841.4	2,839.9	2,620.2	2,995.5	2,994.6	2,991

<sup>a</sup> From reference [1].**Fig. 11** Experimental and calculated variation in C=O stretching at different levels of calculation**Fig. 12** Calculated variation in HX stretching at different levels of calculation**Fig. 13** B3LYP/B  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the Cyc4 $\cdots$ HF complex**Fig. 14** B3LYP/B  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the Cyc4 $\cdots$ HCl complex

**Table 10** Calculated (B3LYP/6–311G, 6–311++G\*\*) <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts [ppm from tetramethylsilane (TMS), δTMS=0.00] for cyclobutanone and cyclobutanone complexes with HF and HCl

Atomic specific	CYC4		Cyc4–HF		CYC4–HCl	
	B3LY/C	B3LY/A	B3LY/C	B3LY/A	B3LY/C	B3LY/A
1 C	51.56	52.31	50.185	50.42	50.71	51.00
2 C	12.81	14.73	13.203	15.37	13.26	15.45
3 C	51.56	52.31	50.65	53.37	50.46	51.24
4 C	215.68	223.21	229.37	240.37	226.18	239.20
H5,6	3.10	3.23	3.10	3.30	3.10	3.38
H7,8	1.91	1.96	2.00	2.20	1.95	2.25
H9,10	3.10	3.23	3.10	3.60	3.10	3.50
H13			7.20	7.34	6.42	8.68

**Table 11** Intermolecular distances (Å), potential energy (Hartree) and frequency shifts (cm<sup>-1</sup>) of the cyclobutanone···HX complexes

	B <sub>3</sub> LYP/6–311G**					MP <sub>2</sub> /6–311G**				
	r <sub>x</sub> <sup>a</sup>	Δr <sub>H-X</sub> <sup>c</sup>	E <sup>b</sup>	Δν <sub>C=O</sub>	Δν <sub>HX</sub> <sup>c</sup>	r <sub>x</sub> <sup>a</sup>	Δr <sub>H-X</sub>	E	Δν <sub>C=O</sub>	Δν <sub>HX</sub>
HF	1.717	0.021	-331	-42.5	-439	1.753	0.006	-330	-21.7	-350
HCl	1.811	0.028	-692	-39.9	-361	1.858	0.019	-690		

<sup>a</sup> Distance between the O atom and the HX<sup>b</sup> Potential energy (Hartree)<sup>c</sup> Changes with respect to Cyc4

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