Zespół Teoretycznego Modelowania Procesów Chemicznych

Wydział Chemii

Uniwersytet Wrocławski

Sprawozdanie za 2013 rok

Skład Zespołu:

prof. **dr hab. Zdzisław Latajka** - kierownik Zespołu
dr hab. Sławomir Berski - adiunkt
dr hab. Jerzy Moc – adiunkt
dr hab. Robert Wieczorek – adiunkt
dr Andrzej Bil – adiunkt
dr Przemysław Dopieralski – adiunkt
dr Piotr Durlak - adiunkt
dr Krzysztof Mierzwicki – adiunkt (do 30.09.2013)
dr Jarosław Panek – adiunkt

mgr Łukasz Fojcik – doktorant
mgr Akmaral Kussayeva – doktorantka
mgr Emilia Makarewicz - doktorantka
mgr Piotr Okrasiński – doktorant
mgr Grzegorz Mierzwa – doktorant
mgr Nuno Manuel Almeida Barbosa – doktorant
mgr Marek Szczepaniak – doktorant
mgr Paulina Krajewska - doktorantka

Temat grantu obliczeniowego:

Teoretyczne badania oddziaływań miedzycząsteczkowych

Realizowane zadania w ramach grantu:

- *teoretyczne badania układów z wiązaniem wodorowym,*
- *teoretyczna analiza natury wiązań chemicznych i reakcji chemicznych,*
- *teoretyczne badania oddziaływań w modelowych klasterach,*
- *teoretyczne badania nowych materiałów.*

Realizowane projekty badawcze

- **Badania kwantowomechaniczne tlenków i ozonków fulerenu C_{70} i ich modyfikowanych endohedralnie analogów.**

  Projekt badawczy własny, nr. N N204 2807 38

  Realizacja projektu: 29.03.2010 – 28.03.2013

  Kierownik: dr Andrzej Bil

- **Eksperymentalne i teoretyczne badania układów oddziaływujących z ksenonem oraz zmian struktury układów molekularnych indukowanych światłem podczerwonym w niskich temperaturach (XEPHOT).**

  Międzynarodowy projekt badawczy w ramach konkursu ERA Chemistry, Open Initiative 2009; nr. projektu: ERA-Chemistry-2009/01/2010

  Realizacja projektu: 25.01.2011 – 24.01.2014

  Kierownik: prof. dr hab. Zdzisław Latajka

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Wynik realizacji grantu obliczeniowego:

18 *prac opublikowanych w czasopismach międzynarodowych*

21 *wystąpień konferencyjnych na konferencjach międzynarodowych (w tym 7 wykładów na zaproszenie)*

1 *obroniona praca magisterska*

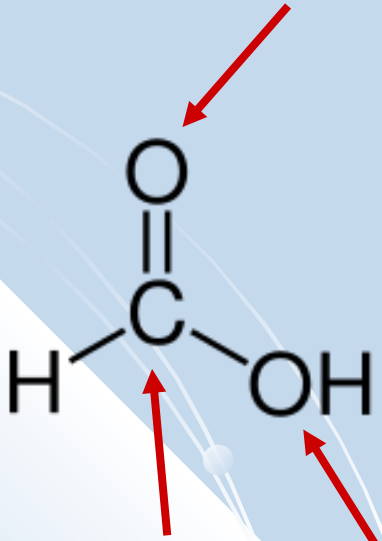
Teoretyczne badania oddziaływań międzycząsteczkowych

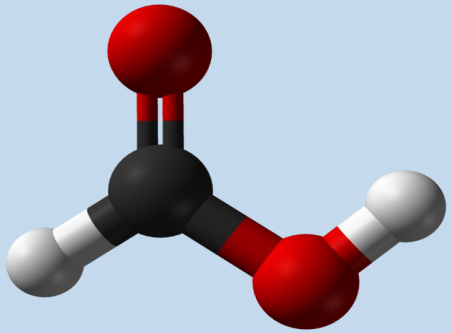
Reaction of atomic hydrogen with formic acid

$$H + HCOOH \rightarrow ?$$

Three possible different channels:

- reaction with the oxygen atom of the hydroxyl group (OH),
- reaction with the oxygen atom of the carbonyl group (C=O),
- reaction with the carbon atom.





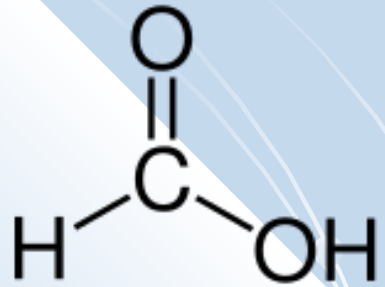
Experimental studies in Kr matrix.

HCOOH/HBr/Kr (1/2/1000) T = 4.3K

Calculations – UCCSD(T) and UMP2 with aug-cc-pVTZ

Reaction with the oxygen atom of the hydroxyl group (OH).

No minimum was found. Formation of a new H-O bond, the break of C-O bond and the formation of water molecule, which finally leads to the $HCO\ldots H_2O$ complex.



$$HCOOH \rightarrow CO\ldots.H_2O$$

$$HBr \rightarrow H + Br$$

$$H + CO\ldots H_2O \rightarrow HCO\ldots H_2O$$

$HCO\ldots H_2O$

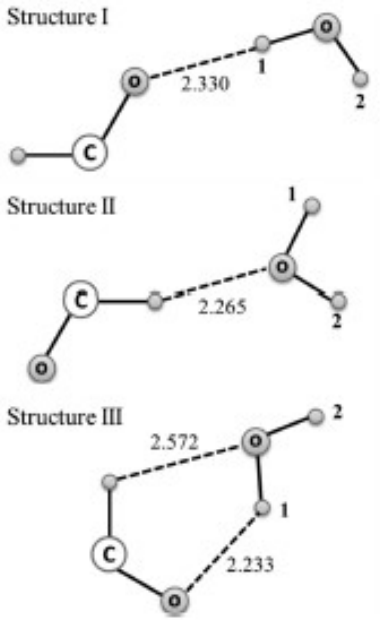


Figure 1. UCCSD(T)/aug-cc-pVTZ optimized structures of the $HCO\cdots H_2O$ complex with intermolecular bond lengths (in Å).

Table 1. Calculated Energies (in kcal mol^{-1}) of the $HCO\cdots H_2O$ and the $HCO\cdots HOD$ Complexes at the UCCSD(T)/aug-cc-pVTZ Level of Theory

	Structure I	Structure II	Structure III
	$HCO\cdots H_2O$		
ΔE_{tot} + ΔZPVE	0.75	0.00	0.04
E_{int}	−2.64	−2.92	−3.71
E_{int}^{CP}	−2.24	−2.62	−3.35
BSSE	0.40	0.30	0.36
E_{int}^{CP} + ΔZPVE	−0.83	−1.70	−1.61
ΔZPVE	1.41	0.92	1.74
	$HCO\cdots HOD$		
E_{int}^{CP} + ΔZPVE	−1.10[a]	−1.69[a]	−1.94[a]
	−0.96[b]	−1.70[b]	−1.79[b]
ΔZPVE	1.14[a]	0.93[a]	1.41[a]
	1.28[b]	0.92[b]	1.56[b]

[a]D atom in position 1 (Figure 1). [b]D atom in position 2 (Figure 1).

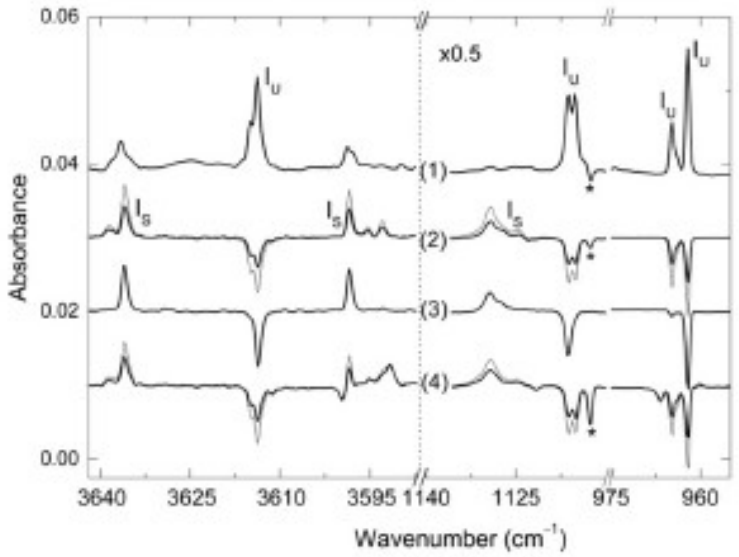
$HCOOH \rightarrow CO\ldots.H_2O$

$HBr \rightarrow H + Br$

$H + CO\ldots H_2O \rightarrow HCO\ldots H_2O$

Experimental studies in Kr matrix. HCOOH/HBr/Kr T = 4.3K

Fig. 2 Difference FTIR spectra of a HCOOH/HBr/Kr (1/2/1000) matrix



photolyzed at 193 nm showing the results of (1) annealing at 31 K (5 min); (2) 1 hour (thick line) and 2 hours (thin line) at 4.3 K under Globar irradiation after annealing; (3) narrow-band IR excitation at *ca.* 3614 cm^{-1} of the annealed matrix. Trace 4 shows the difference IR spectra of a photolyzed and annealed HCOOH/HCl/Kr (1/2/1000) matrix as a result of 1 hour (thick line) and 2 hours (thin line) at 4.3 K under Globar irradiation. The spectra were measured at 4.3 K. The bands marked by asterisks are tentatively assigned to a FA dimer (tt4).[39]

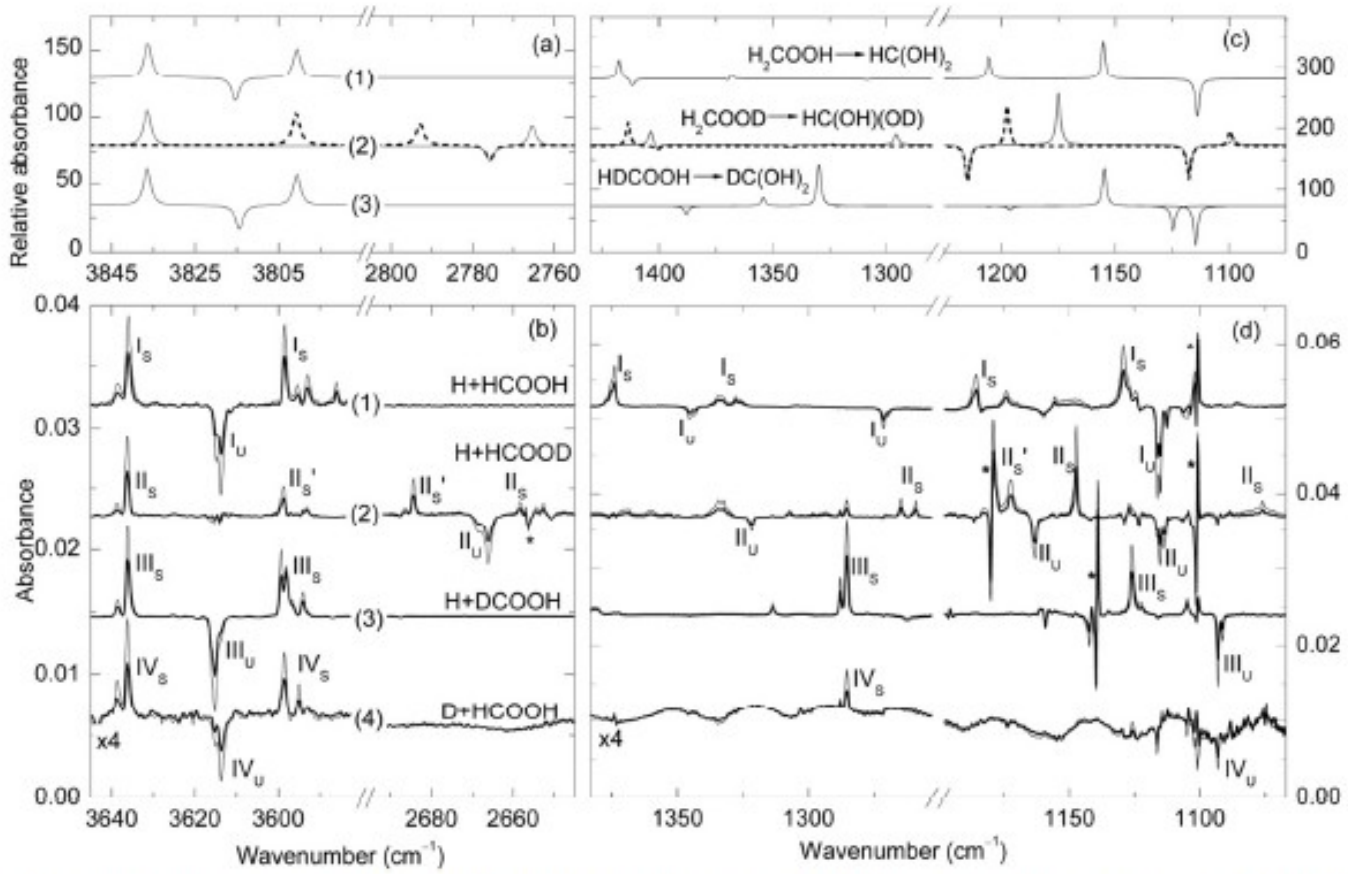


Fig. 4 (a and c) Calculated IR spectra of *trans*-H_2COOH (negative bands) and *trans-cis*-$HC(OH)_2$ (positive bands) and their deuterated analogous. The dashed line in the calculated spectrum (2) corresponds to *trans-cis*-HC(OH)(OD) with the *cis*-OD group. The splitting of the negative band in the calculated spectrum (3) of *trans*-HDCOOH is caused by different location of the CD group. (b and d) Difference IR spectra showing the conversion processes after different reactions: (1) H + HCOOH, (2) H + HCOOD, (3) H + DCOOH, (4) D + HCOOH. Thick and thin lines in the experimental spectra correspond to 4 and 8 hours in the dark at 4.3 K after annealing, respectively. Bands of FA are marked by asterisks. The FA/HBr (C_3D_2)/Kr matrices were first photolyzed at 193 nm and then annealed for 5 min at 31 K. The spectra were measured at 4.3 K. Notice the different absorbance scales in the left and right panels.

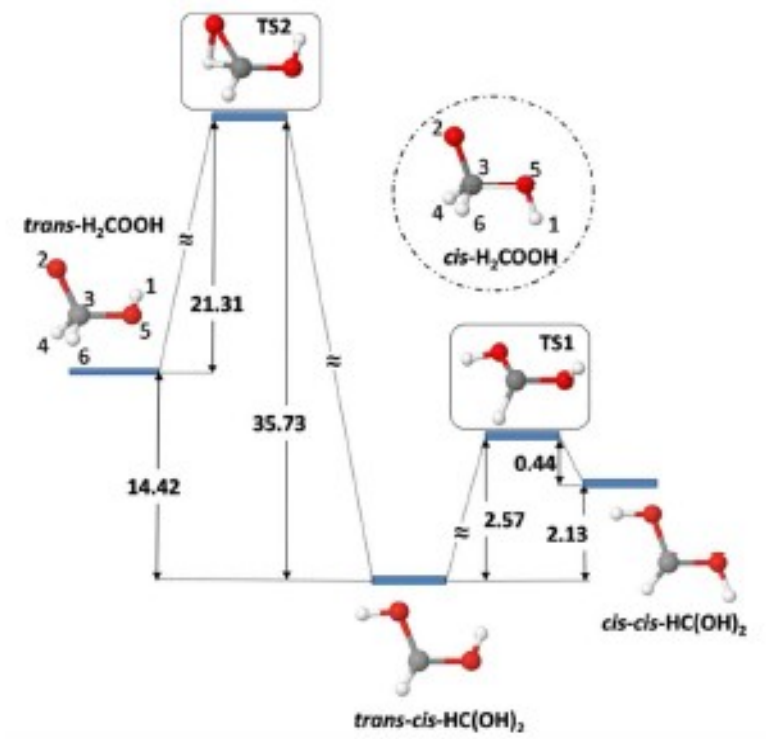


Fig. 1 Schematic potential energy diagram of the radicals that may be formed in the H+HCOOH reaction. The energy values (in kcal mol^{-1}) are calculated at the UMP2 level (for the UCCSD(T) energies of the optimized structures see Table 1). The structures shown in rectangles are transition states (TS1 and TS2); *cis*-H_2COOH (shown in a dashed circle) is energetically unfavourable. In *trans*-H_2COOH, H1 and H4 are on the same side of the heavy-atom skeleton.

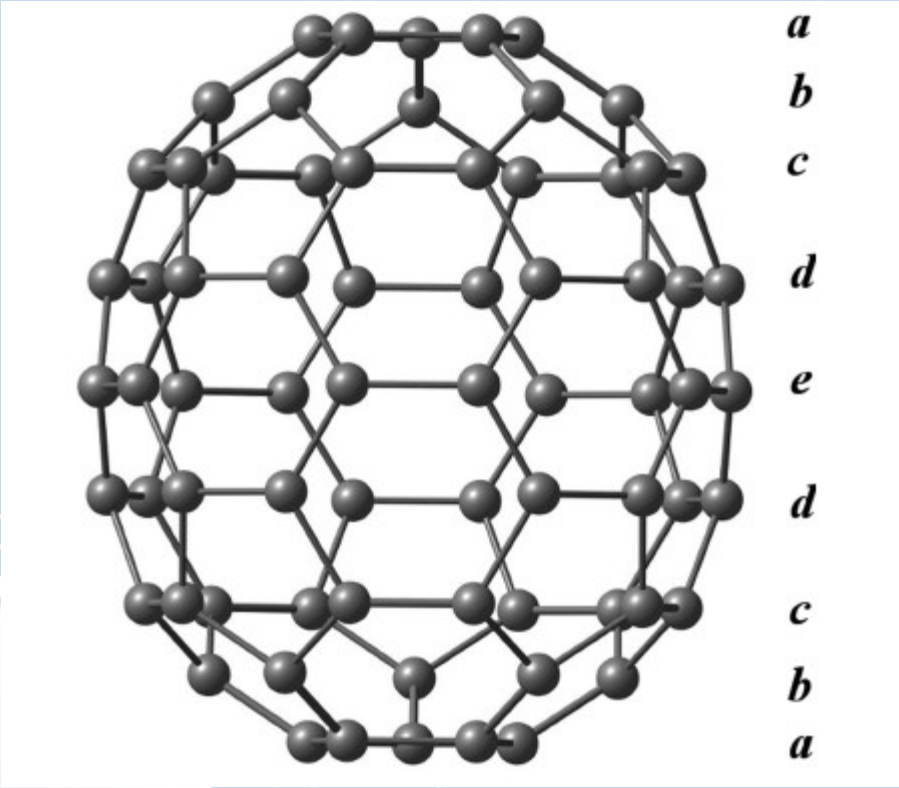
Table 1 Energetics (in kcal mol^{-1}) for the radicals that may be formed in the H + HCOOH reactions calculated at the UCCSD(T) and UMP2 (in parentheses) levels of theory.

	Relative energy (ΔE + ΔZPVE)		Reaction energy (ΔE_r + ΔZPVE)	
trans-cis-$HC(OH)_2$	0	(0)	−10.01	(−10.87)
cis-cis-$HC(OH)_2$	2.16	(2.13)	−7.85	(−8.74)
trans-H_2COOH	8.10	(14.42)	−1.91	(+3.55)
cis-H_2COOH	10.19	(16.61)	+0.17	(+5.74)

$$H + HCOOH \rightarrow HC(OH)_2$$

$$H + HCOOH \rightarrow H_2COOH$$

C_{70} and $C_{70}O_3$ doped with noble gas atoms and light molecules



Eight isomers of $C_{70}O_3$

a,b-$C_{70}O_3$ c,c-$C_{70}O_3$ (observed)

$C_{70}O_3 \rightarrow C_{70}O_3 + O_2$

BOMD, BLYP+D3, T = 298 K, NVT

Noble gas: He, Ne, Ar, Kr, Xe and Rn

Light molecules: BH_3, HCl, CH_4, H_2O, NH_3, CO_2, H_2 and $2H_2$

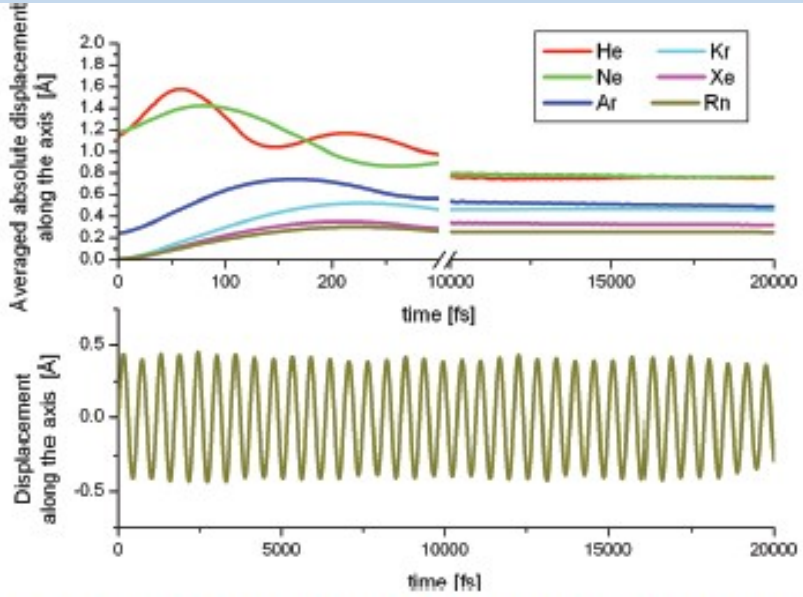


Figure 2. Time dependence of the displacement of the noble gas atom from the C_{70} mass center measured along the polar fullerene axis.

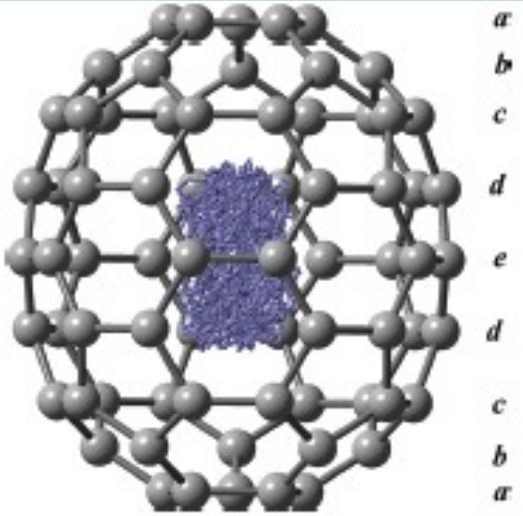


Figure 3. Trajectory (purple) arced by a He atom inside a C_{70} molecule during the course of a molecular dynamics simulation at 298 K.

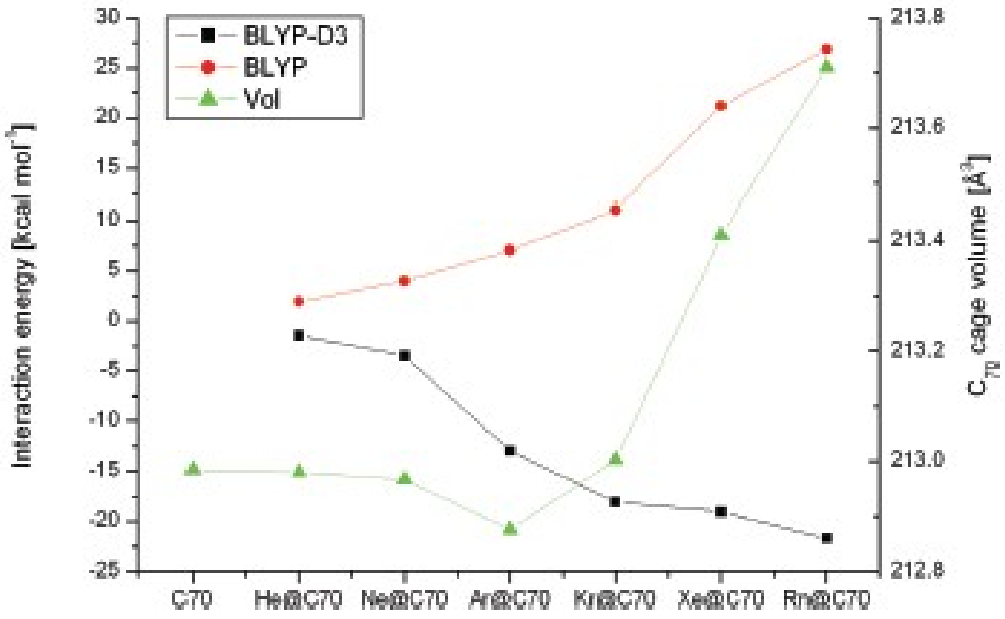


Figure 4. Left axis: calculated interaction energies between the C_{70} cage and the noble gas endohedral atom. Right axis: equilibrium volume of the carbon atom cage in C_{70} and $X@C_{70}$.

The change in the characteristic bond lengths [Å] in fullerenes with endohedral guests. The numbers characterize equilibrium structures of C_{70} and $X@C_{70}$.

	C_{70}	$He@C_{70}$	$Ne@C_{70}$	$Ar@C_{70}$	$Kr@C_{70}$	$Xe@C_{70}$	$Rn@C_{70}$
a,a	1.467	0.000	0.000	0.000	-0.001	-0.001	-0.001
a,b	1.416	0.000	0.000	0.000	-0.001	0.000	-0.001
b,c	1.463	0.000	0.000	0.000	0.000	0.000	+0.001
c,c	1.410	0.000	-0.001	-0.001	0.000	0.000	+0.001
c,d	1.461	0.000	0.000	0.000	0.000	+0.001	+0.001
d,d	1.454	0.000	-0.001	-0.001	+0.001	+0.002	+0.004
d,e	1.438	0.000	0.000	0.000	0.000	+0.001	+0.001
e,e	1.484	0.000	0.000	0.000	+0.001	+0.004	+0.006

	Vol.(0K) [Å^3]
C_{70}	213.0
$He@C_{70}$	213.0
$Ne@C_{70}$	212.0
$Ar@C_{70}$	212.9
$Kr@C_{70}$	213.0
$Xe@C_{70}$	213.4
$Rn@C_{70}$	213.7

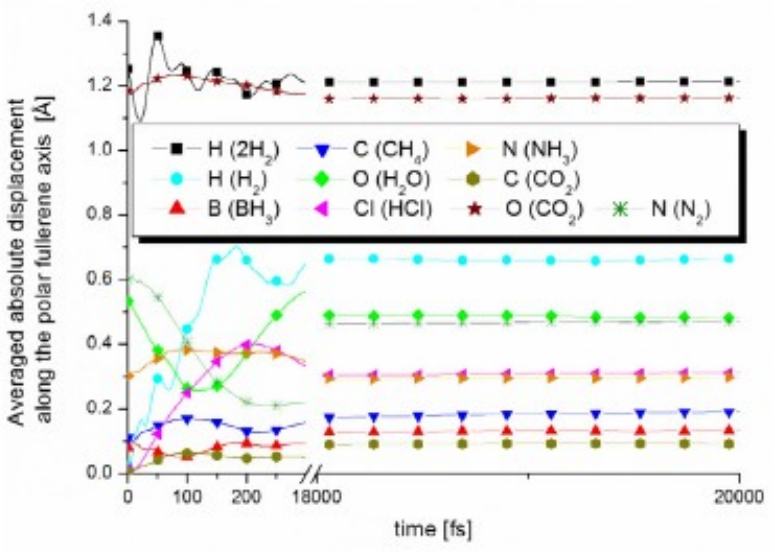


Fig. 1. Time dependence of the displacement of the heavy atom (in AH_n,CO_2,N_2) or a hydrogen atom (H_2, $2H_2$) from the C_{70} mass center measured along the polar fullerene axis.

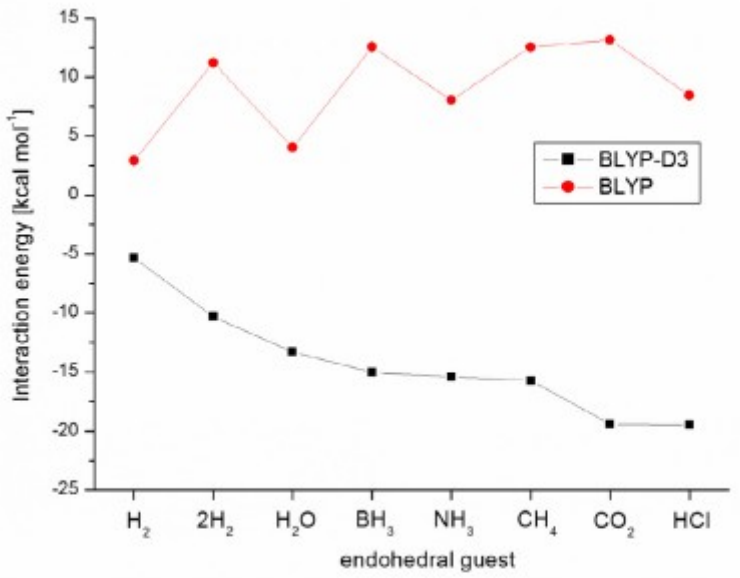


Fig. 4. Calculated interaction energies between the C_{70} cage and light endohedral molecules.

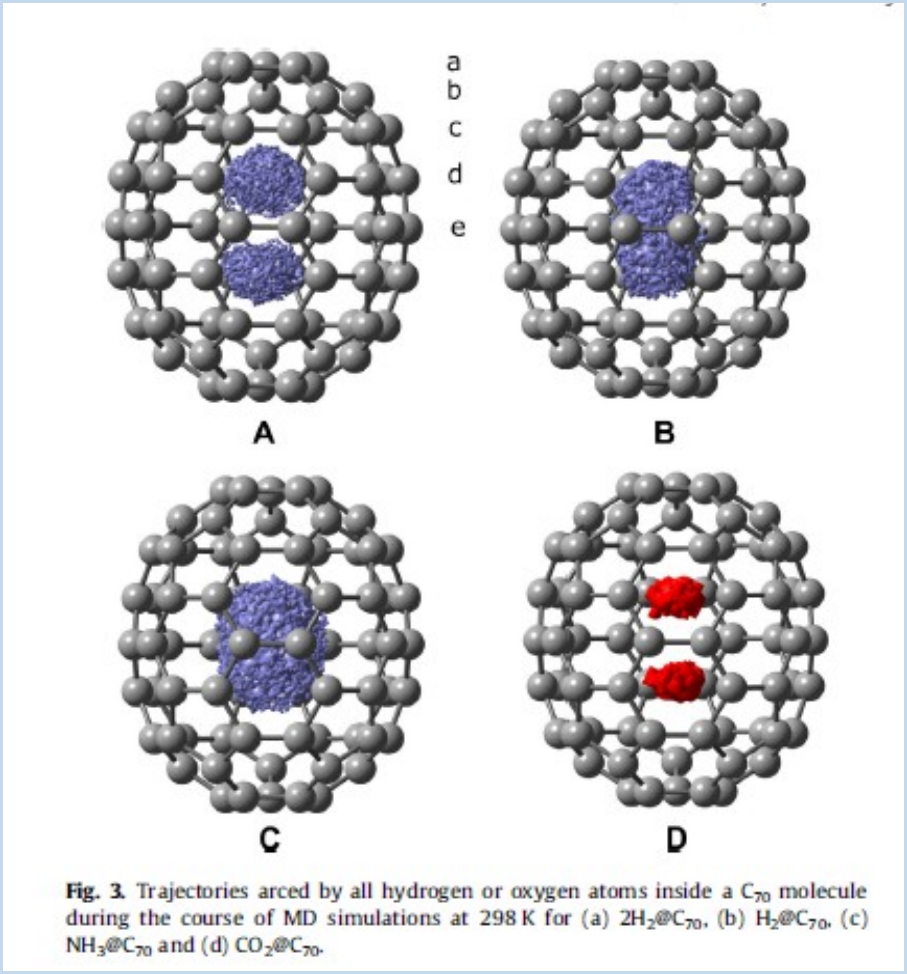


Fig. 3. Trajectories arced by all hydrogen or oxygen atoms inside a C_{70} molecule during the course of MD simulations at 298 K for (a) $2H_2@C_{70}$, (b) $H_2@C_{70}$, (c) $NH_3@C_{70}$ and (d) $CO_2@C_{70}$.

$Ar@C_{70}$ (-13.0 kcal/mol)

Kr@C70 (-18.1 kcal/mol)

He@C70 (-1.4 kcal/mol)

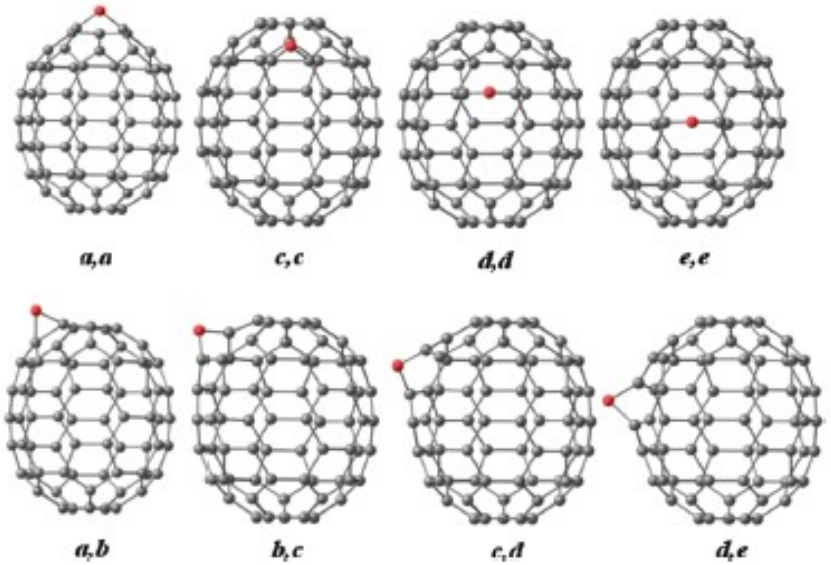


Figure 2. Scheme depicting the eight different possible isomers of $C_{70}O$.

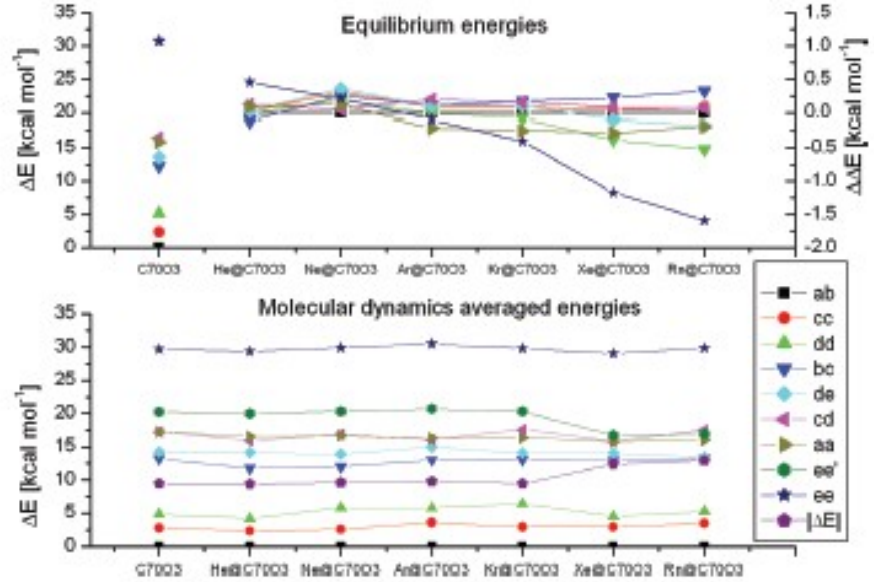


Figure 5. Total energies (upper panel) and average potential energies from MD trajectories (lower panel) of the $C_{70}O_3$ and $X@C_{70}O_3$ set of isomers, relative to the *a,b-* isomer. Due to small differences in relative energies for $X@C_{70}O_3$ (upper panel), we mark the differences (right axis) between actual results for a given $X@C_{70}O_3$ and the relative stabilities of the isomers of $C_{70}O_3$ (left axis).

Relative energy (kcal/mol)

	$C_{70}O_3$	He@ $C_{70}O_3$	Ne@ $C_{70}O_3$	Ar@ $C_{70}O_3$	Kr@ $C_{70}O_3$	Xe@ $C_{70}O_3$	Rn@ $C_{70}O_3$
a,b	0	0	0	0	0	0	0
c,c	2.3	2.3	2.6	2.4	2.4	2.4	2.4
a,a	15.9	16.0	16.0	15.7	15.6	15.6	15.7
d,d	5.2	5.2	5.4	5.2	5.1	4.8	4.7
b,c	12.3	12.2	12.5	12.4	12.4	12.5	12.6
c,d	16.4	16.5	16.5	16.6	16.6	16.5	16.5
d,e	13.6	13.7	13.9	13.7	13.7	13.5	13.5
e,e	30.8	31.2	31.0	30.7	30.4	29.6	29.2

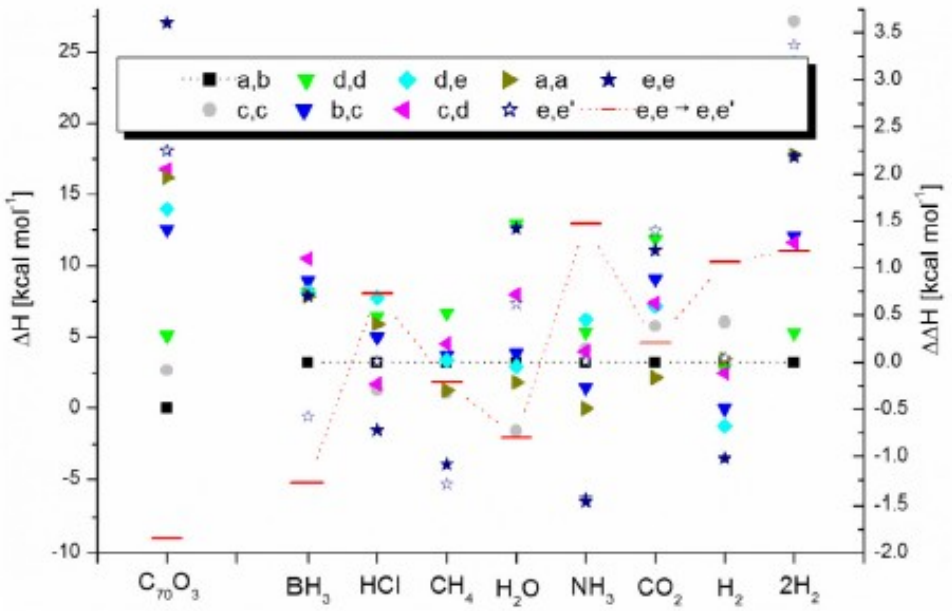


Fig. 5. Enthalpies of $C_{70}O_3$ and Im@$C_{70}O_3$ set of isomers, relative to a,b-$C_{70}O_3$/Im@a,b-$C_{70}O_3$ isomer. Due to small differences in relative energies for Im@$C_{70}O_3$, we mark the difference (right axis) between actual results for a given Im@$C_{70}O_3$ isomer and the relative stabilities of the isomer of $C_{70}O_3$ (left axis). Note e,e' denotes the product of the ozone ring opening reaction for e,e-$C_{70}O_3$ (illustrated in Fig. 6). The bar denotes the enthalpy of ozone ring opening for e,e-$C_{70}O_3$, calculated as the difference between the enthalpy of the open and closed form of the ozonide.

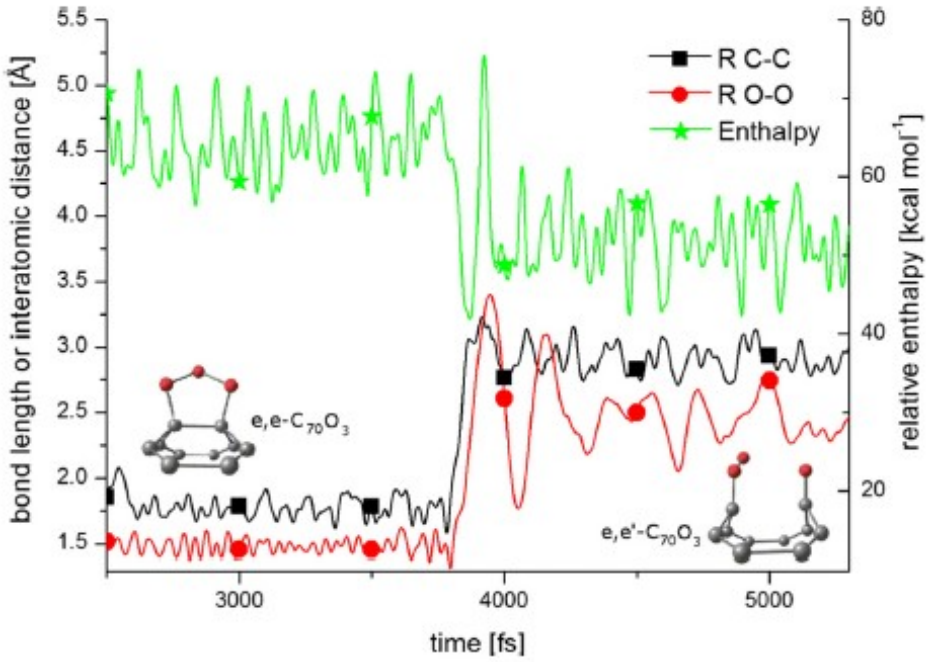


Fig. 6. Selected parameters obtained from a section of the MD run performed for $H_2O@e,e\text{-}C_{70}O_3$. The bond lengths C–C and O–O and the potential energy are depicted versus simulation time.

	ΔE (kcal/mol)	E^{TS} (kcal/mol)
a,b-$C_{70}O_3$	7.7	14.3
He@a,b-$C_{70}O_3$	7.7	14.3
Ne@a,b-$C_{70}O_3$	7.7	14.4
Ar@a,b-$C_{70}O_3$	7.8	14.4
Kr@a,b-$C_{70}O_3$	8.1	14.6
Xe@a,b-$C_{70}O_3$	8.8	14.8
Rn@a,b-$C_{70}O_3$	9.0	14.8
e,e-$C_{70}O_3$	-13.2	1.8
He@a,b-$C_{70}O_3$	-13.2	1.8
Ne@a,b-$C_{70}O_3$	-13.1	1.8
Ar@a,b-$C_{70}O_3$	-13.1	1.8
Kr@a,b-$C_{70}O_3$	-13.4	1.7
Xe@a,b-$C_{70}O_3$	-14.3	1.5
Rn@a,b-$C_{70}O_3$	-14.8	1.4

Main conclusion:

The presence and identity of the guest molecule influences only slightly the energy barriers an reaction energies of ozone ring opening process in:

Ng@a,b-$C_{70}O_3$, Ng@c,c-$C_{70}O_3$, and Ng@e,e-$C_{70}O_{3,}$

lm@a,b-$C_{70}O_3$, lm@c,c-$C_{70}O_3$, and lm@e,e-$C_{70}O_3$.

Dziękuję za uwagę