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## Nature and role of the weak intermolecular bond in enantiomeric conformations of H<sub>2</sub>O<sub>2</sub>-Noble gas adducts: a chiral prototypical model

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In this work the role of the weak intermolecular interaction between hydrogen peroxide molecule (H<sub>2</sub>O<sub>2</sub>) and noble gas atoms Ng (Ng = He, Ne, Ar, Kr, Xe and Rn) was investigated. This is mainly important to determine spectroscopic features of two-body interacting systems found in bulks under temperature confined in the thermal range. The stability of the formed adducts was inferred by their lifetime evaluated as a function of temperature. The lifetime analysis suggests that only H<sub>2</sub>O<sub>2</sub>-He complex is unstable in the 200-500K temperature range. Moreover, exploiting the combination of several advanced theoretical methods, particular attention has been addressed to characterize nature and anisotropy of related intermolecular interaction, focusing the attention on selected and representative conformations of the H<sub>2</sub>O<sub>2</sub>-Ng systems that were obtained in a previous study of our research group. Such conformations involve two basic structures of the enantiomeric H<sub>2</sub>O<sub>2</sub> moiety and the other refer to the barriers between the two chiral structures. The interaction analysis was performed using Charge Displacement (CD), Natural Bond Orbitals (NBO), and Symmetry-Adapted Perturbation Theory (SAPT). For the selected conformations, it was observed that the polarization effects were more pronounced in complexes involving Xe and Rn atoms. CD analysis shows, especially in the cis-barrier conformation, a small but not negligible charge transfer (CT) from Ng to H<sub>2</sub>O<sub>2</sub>, suggesting that the CT is enhanced by the two symmetrical interactions between the two hydrogens of H<sub>2</sub>O<sub>2</sub> and Ng. This stimulates the formation of a weak intermolecular hydrogen bond. The NBO analysis confirms the CD results, further showing that the largest electronic donation occurs from Ng's valence lone pair orbitals to the two O-H antibonding orbitals. The selectivity of CT is expected to appreciably reduce the adiabatic energy barrier height due to the torsional mode of H<sub>2</sub>O<sub>2</sub> moiety within the complex, making the torsion slightly favored with respect to the case of isolated molecule. Finally, SAPT and NCI analysis indicate that all systems are essentially van der Waals complexes, where the dispersion forces determines the most important attractive contribution to the interaction.

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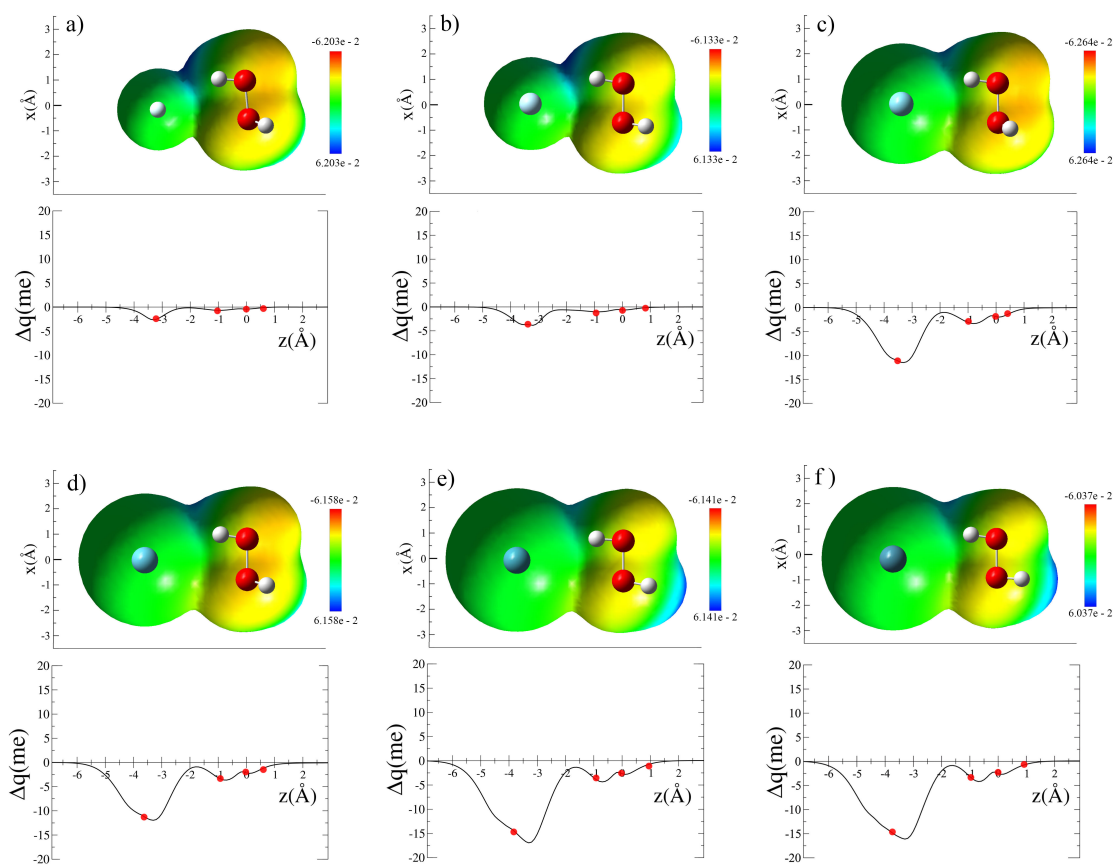
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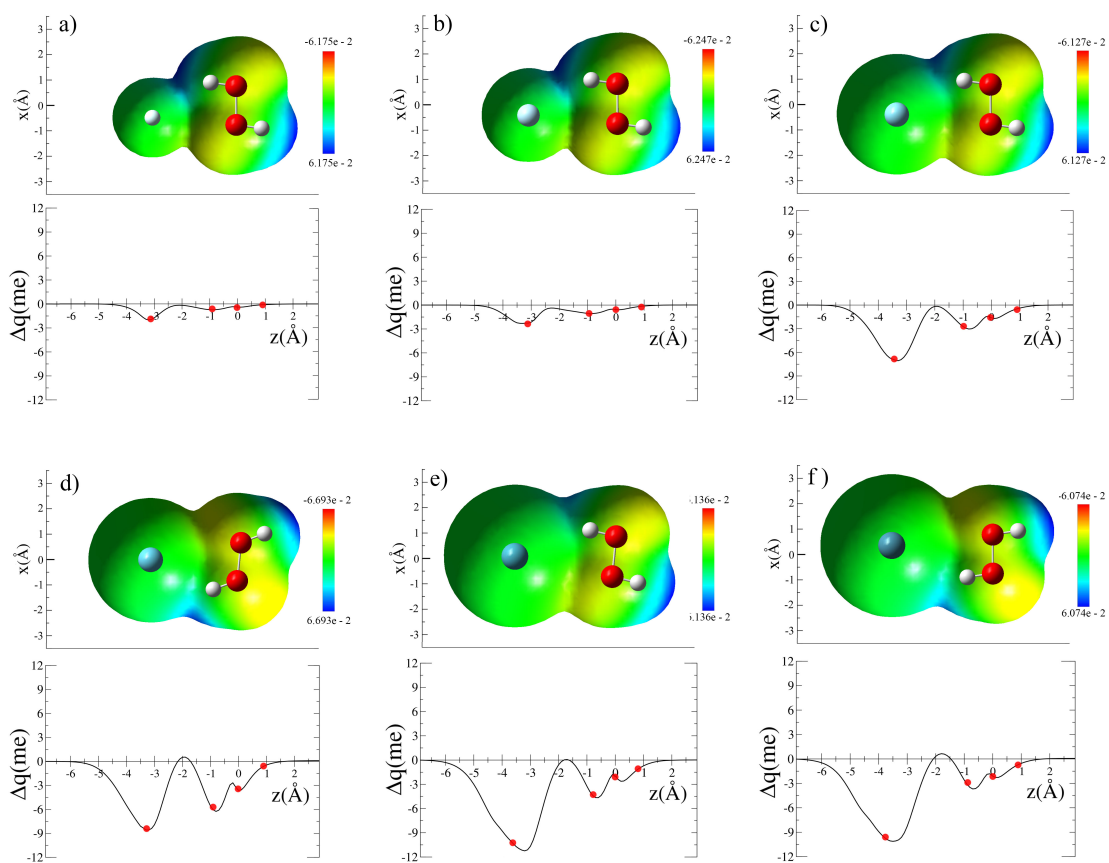
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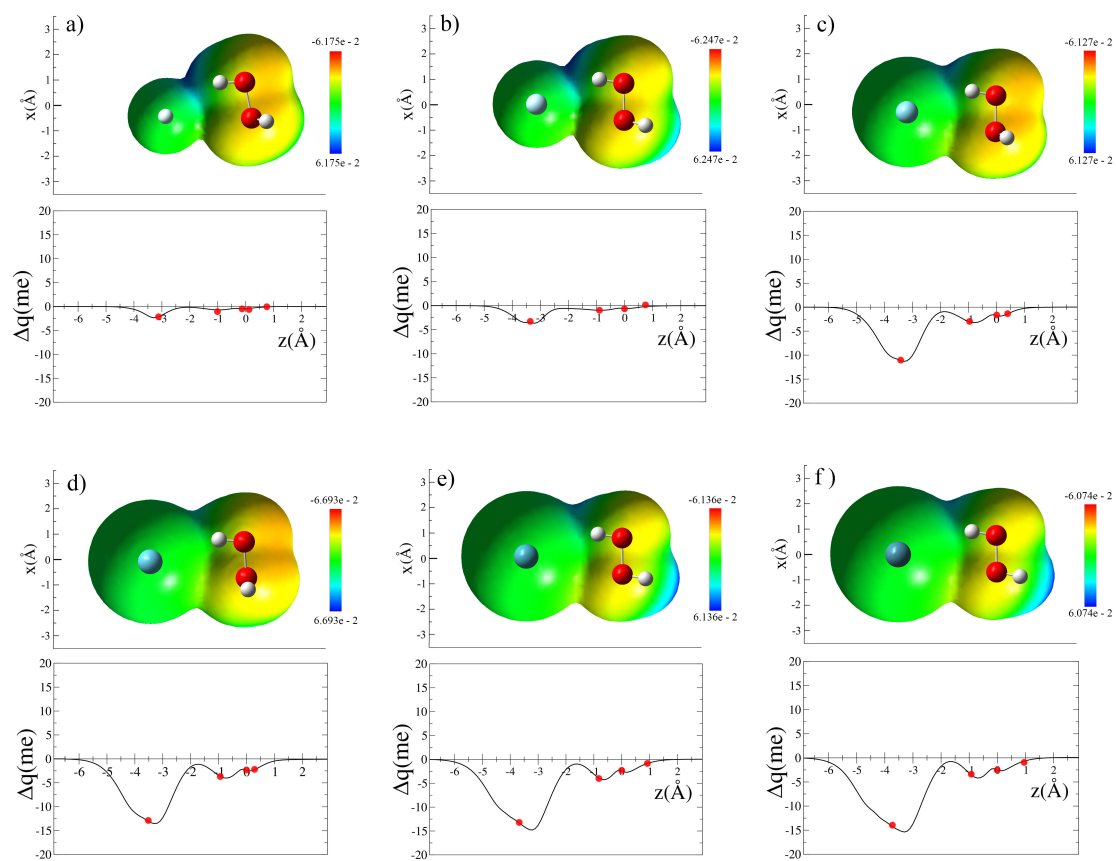
† There is a supplementary material attached to this study where additional information regarding the cis-well, trans-barrier and trans-well configurations is provided.



**Fig. 1** CCSD(T)/aug-cc-pVTZ electron density change representation (upper panels) and charge-displacement ( $\Delta q$  curves) for cis-well configuration for the a)  $H_2O_2$ -He, b)  $H_2O_2$ -Ne, c)  $H_2O_2$ -Ar, d)  $H_2O_2$ -Kr, e)  $H_2O_2$ -Xe, and f)  $H_2O_2$ -Rn compounds. The red circles on the  $\Delta q$  curves represent the projection of the nuclear position of the O, H and Ng atoms on the  $z$  axis. The origin of the axis was defined at the center of mass of  $H_2O_2$  molecule.

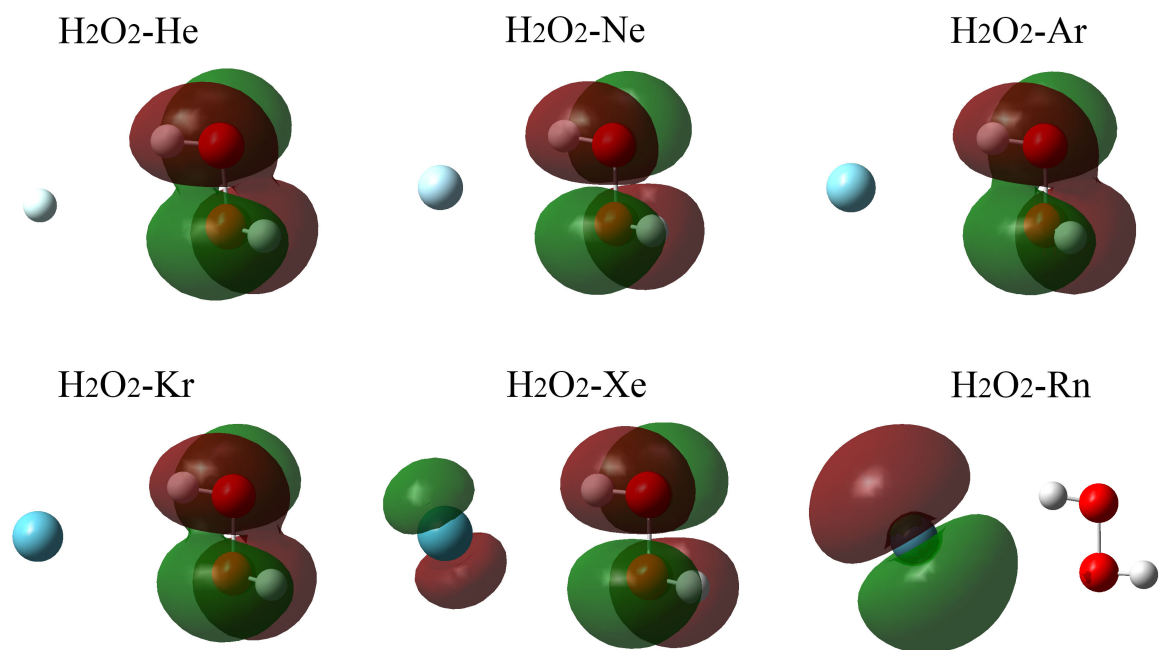


**Fig. 2** CCSD(T)/aug-cc-pVTZ electron density change representation (upper panels) and charge-displacement ( $\Delta q$  curves) for trans-barrier configuration for the a)  $\text{H}_2\text{O}_2$ -He, b)  $\text{H}_2\text{O}_2$ -Ne, c)  $\text{H}_2\text{O}_2$ -Ar, d)  $\text{H}_2\text{O}_2$ -Kr, e)  $\text{H}_2\text{O}_2$ -Xe, and f)  $\text{H}_2\text{O}_2$ -Rn compounds. The red circles on the  $\Delta q$  curves represent the projection of the nuclear position of the O, H and Ng atoms on the  $z$  axis. The origin of the axis was defined at the center of mass of  $\text{H}_2\text{O}_2$  molecule.

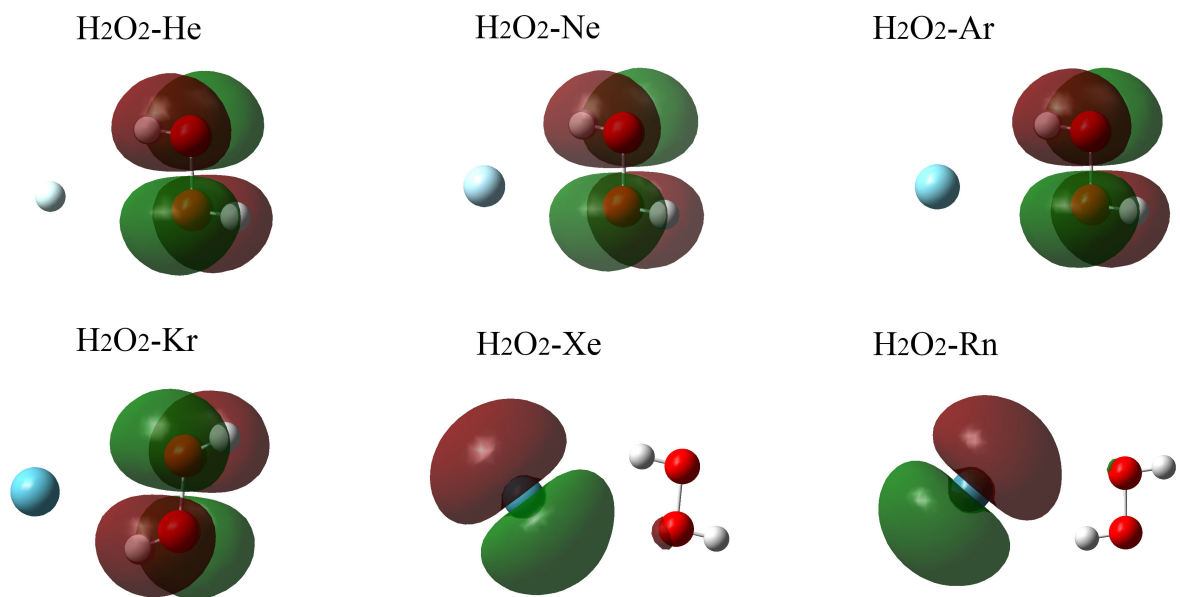


**Fig. 3** CCSD(T)/aug-cc-pVTZ electron density change representation (upper panels) and charge-displacement ( $\Delta q$  curves) for trans-well configuration for the a)  $\text{H}_2\text{O}_2$ -He, b)  $\text{H}_2\text{O}_2$ -Ne, c)  $\text{H}_2\text{O}_2$ -Ar, d)  $\text{H}_2\text{O}_2$ -Kr, e)  $\text{H}_2\text{O}_2$ -Xe, and f)  $\text{H}_2\text{O}_2$ -Rn compounds. The red circles on the  $\Delta q$  curves represent the projection of the nuclear position of the O, H and Ng atoms on the  $z$  axis. The origin of the axis was defined at the center of mass of  $\text{H}_2\text{O}_2$  molecule.

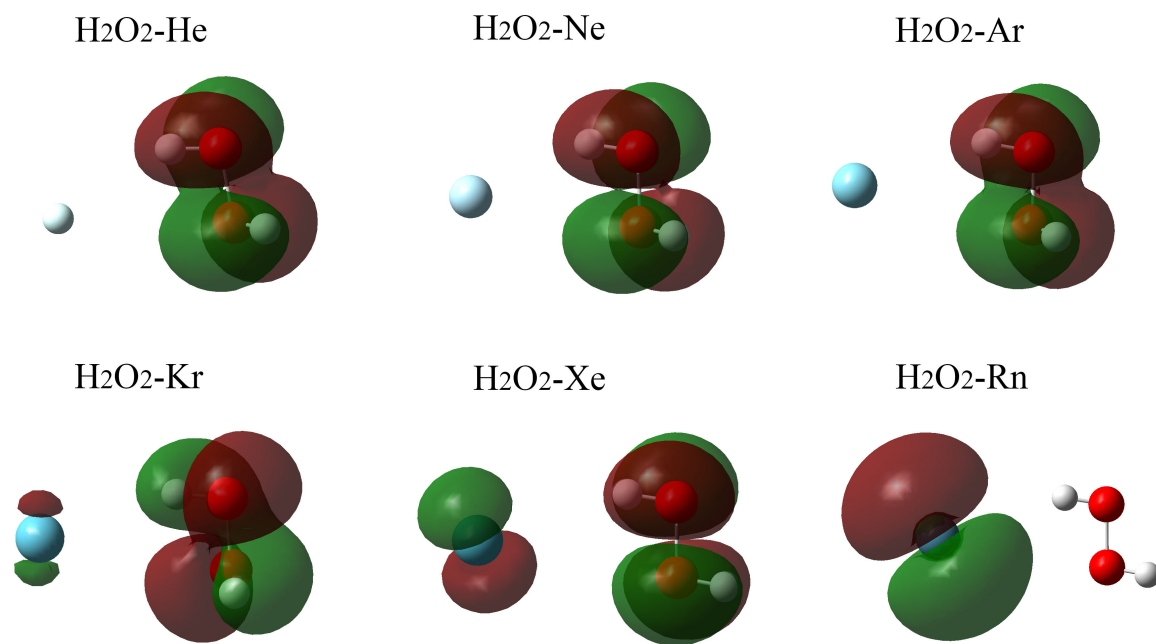




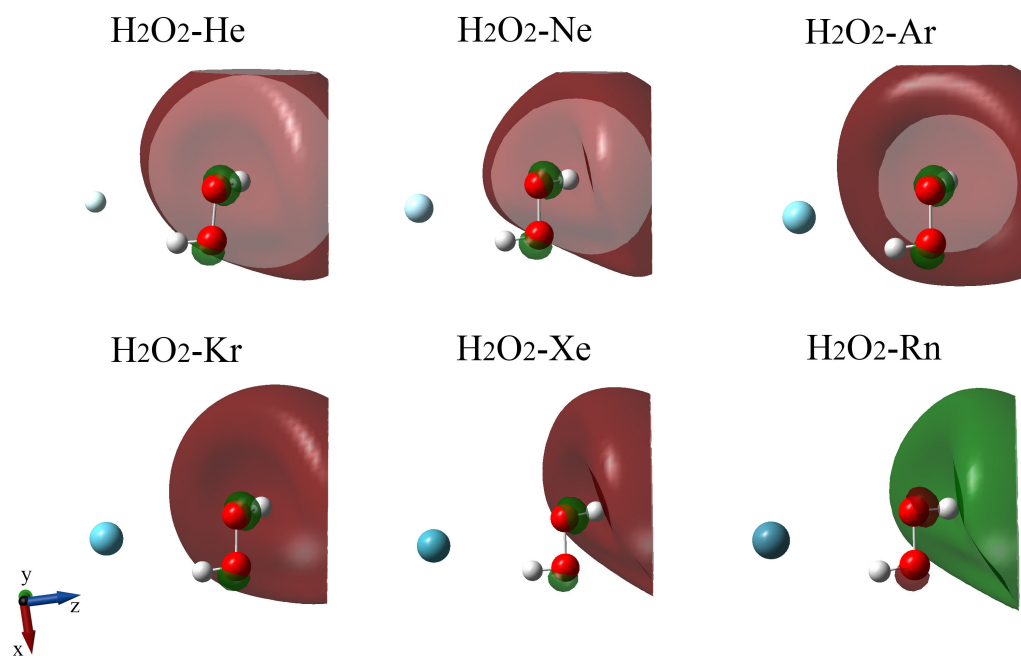
**Fig. 4**  $\text{H}_2\text{O}_2\text{-Ng}$  frontier molecular orbital (HOMO) for the cis-well conformation obtained with CCSD(T)/aug-cc-pVTZ level of theory. The positive and negative phases are represented by claret and green colors, respectively.



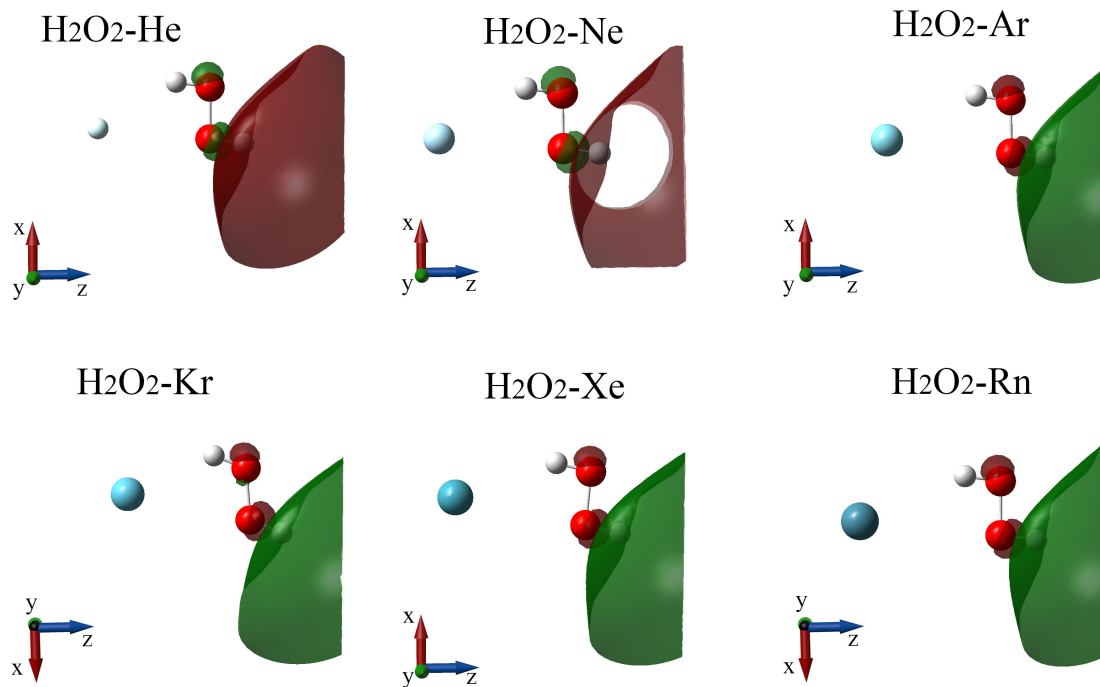
**Fig. 5**  $\text{H}_2\text{O}_2\text{-Ng}$  frontier molecular orbital (HOMO) for the trans-barrier conformation obtained with CCSD(T)/aug-cc-pVTZ level of theory. The positive and negative phases are represented by claret and green colors, respectively.



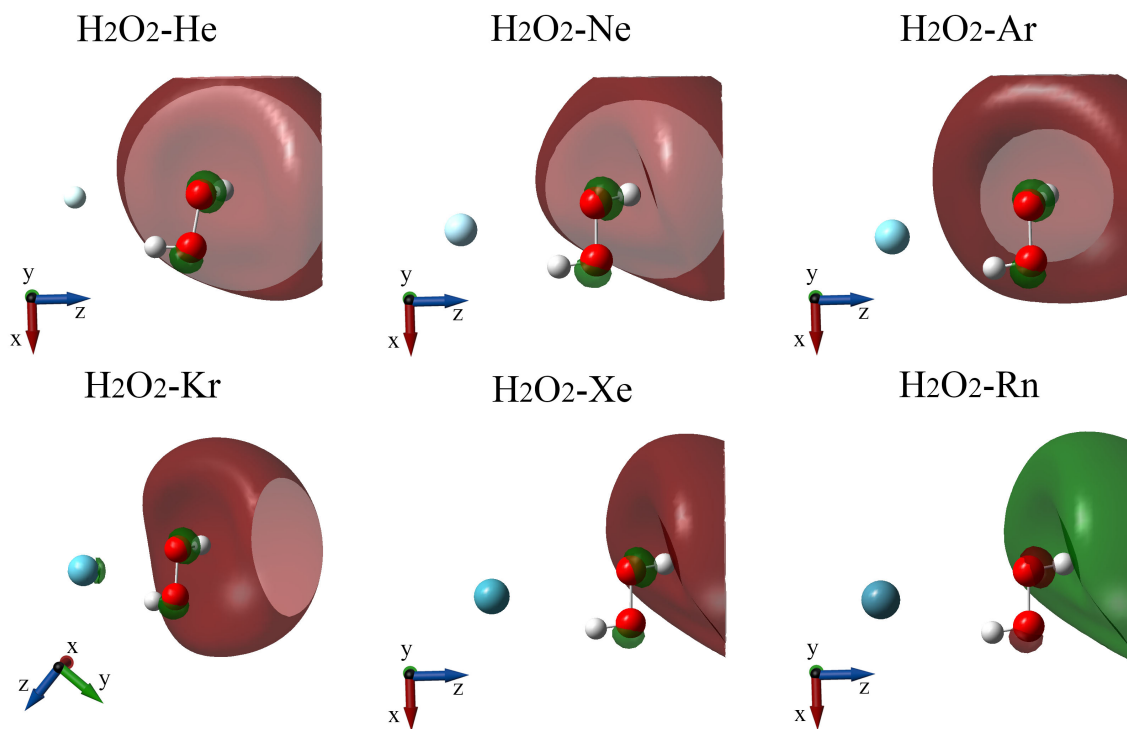
**Fig. 6** H<sub>2</sub>O<sub>2</sub>-Ng frontier molecular orbital (HOMO) for the trans-well conformation obtained with CCSD(T)/aug-cc-pVTZ level of theory. The positive and negative phases are represented by claret and green colors, respectively.



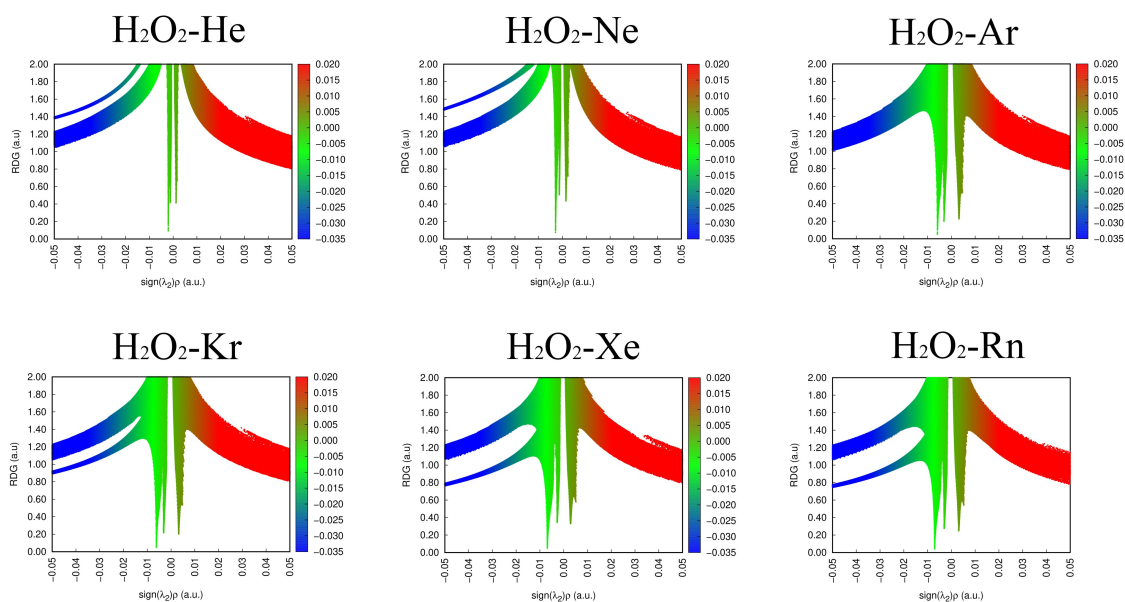
**Fig. 7** H<sub>2</sub>O<sub>2</sub>-Ng frontier molecular orbital (LUMO) for the cis-well conformation obtained with CCSD(T)/aug-cc-pVTZ level of theory. The positive and negative phases are represented by claret and green colors, respectively.



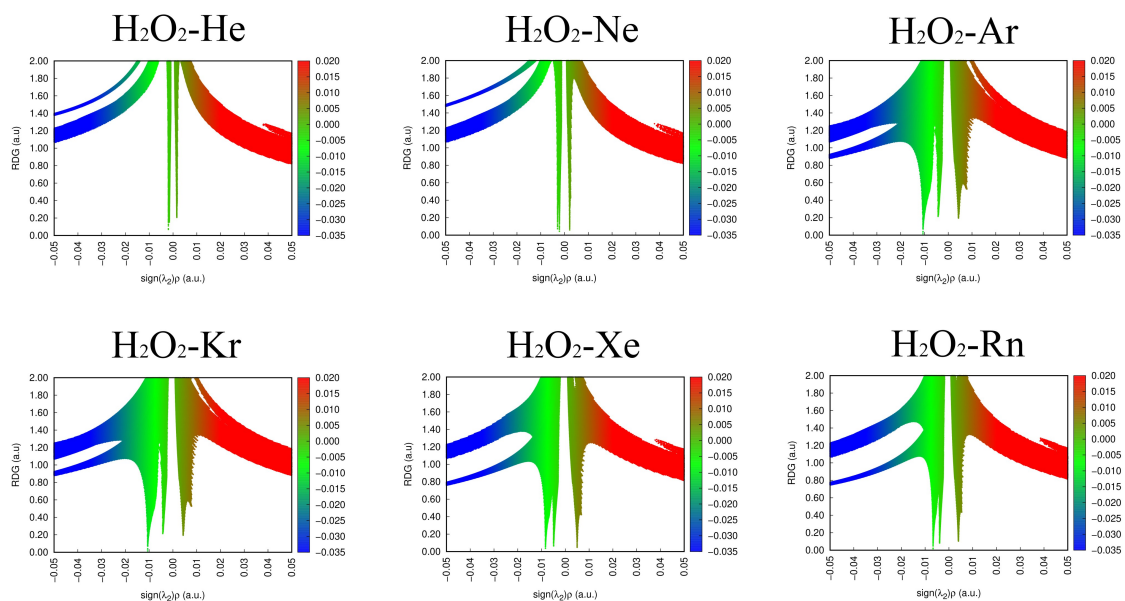
**Fig. 8** H<sub>2</sub>O<sub>2</sub>-Ng frontier molecular orbital (LUMO) for the trans-barrier conformation obtained with CCSD(T)/aug-cc-pVTZ level of theory. The positive and negative phases are represented by claret and green colors, respectively.



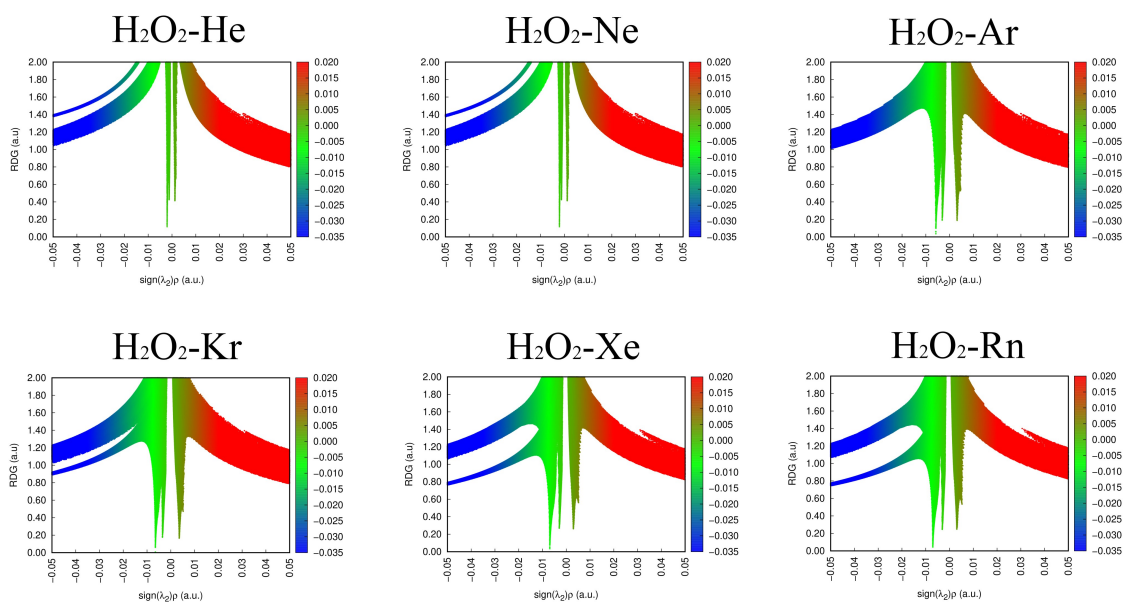
**Fig. 9**  $\text{H}_2\text{O}_2\text{-Ng}$  frontier molecular orbital (LUMO) for the trans-well conformation obtained with CCSD(T)/aug-cc-pVTZ level of theory. The positive and negative phases are represented by claret and green colors, respectively.



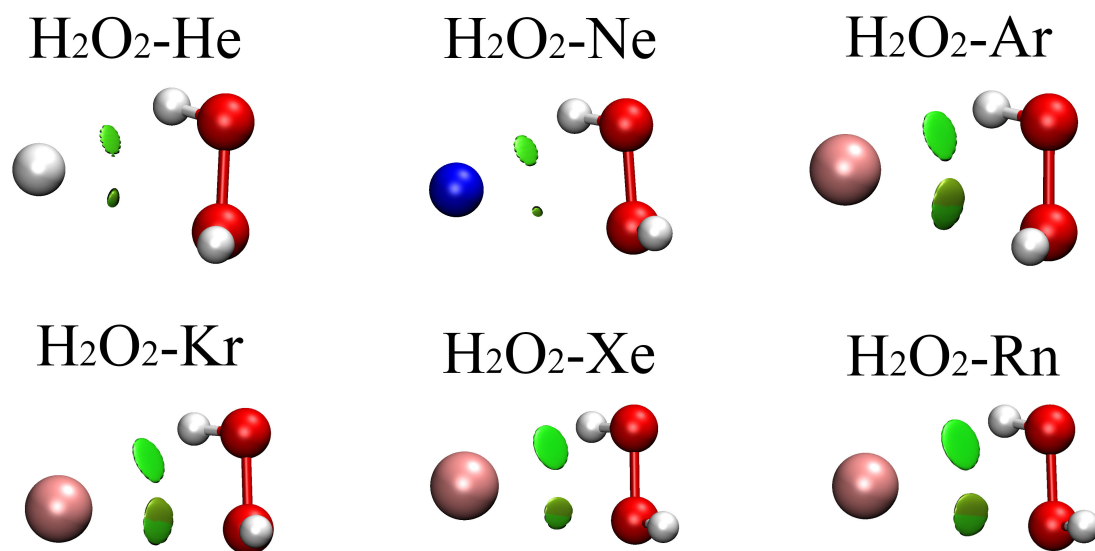
**Fig. 10**  $\text{H}_2\text{O}_2\text{-Ng}$  reduced density gradient (RDG) as a function of electron density ( $\rho$ ) multiplied by the sign of the second eigenvalue of the hessian matrix ( $\lambda_2$ ) for cis-well configuration. The  $(\lambda_2)\rho$  sign function is represented by three colors: Red color to indicate the strong repulsion region ( $\rho > 0$  and  $\lambda_2 > 0$ ), blue color to denote the strong attraction region ( $\rho > 0$  and  $\lambda_2 < 0$ ), and green color to designate van der Waals interaction ( $\rho \approx 0$  and  $\lambda_2 \approx 0$ ).



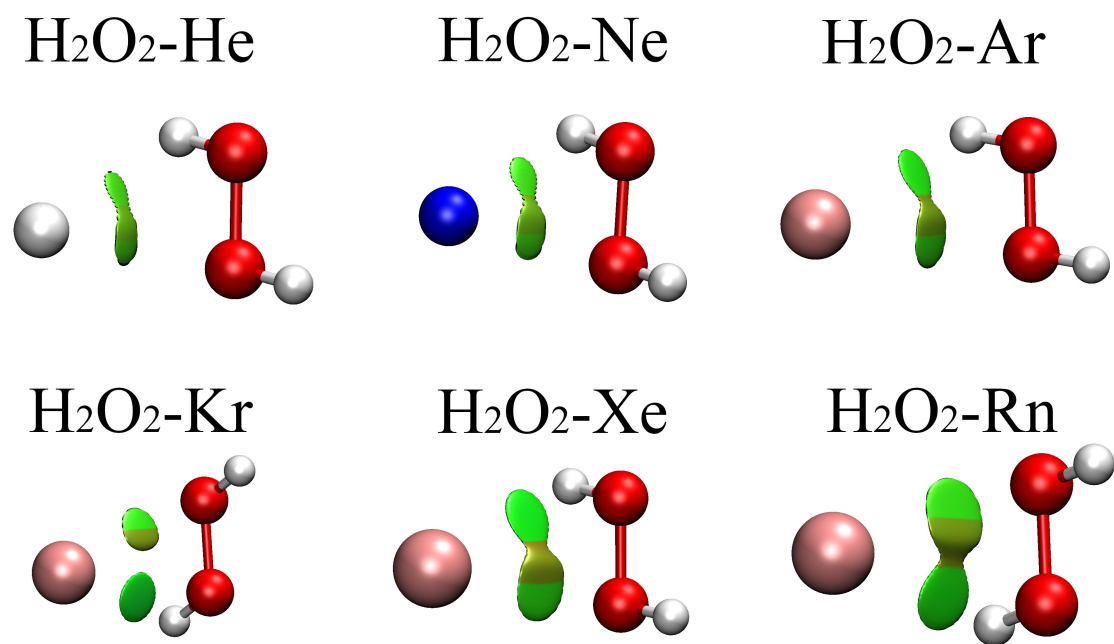
**Fig. 11**  $\text{H}_2\text{O}_2\text{-Ng}$  reduced density gradient (RDG) as a function of electron density ( $\rho$ ) multiplied by the sign of the second eigenvalue of the hessian matrix ( $\lambda_2$ ) for trans-barrier configuration. The  $(\lambda_2)\rho$  sign function is represented by three colors: Red color to indicate the strong repulsion region ( $\rho > 0$  and  $\lambda_2 > 0$ ), blue color to denote the strong attraction region ( $\rho > 0$  and  $\lambda_2 < 0$ ), and green color to designate van der Waals interaction ( $\rho \approx 0$  and  $\lambda_2 \approx 0$ ).



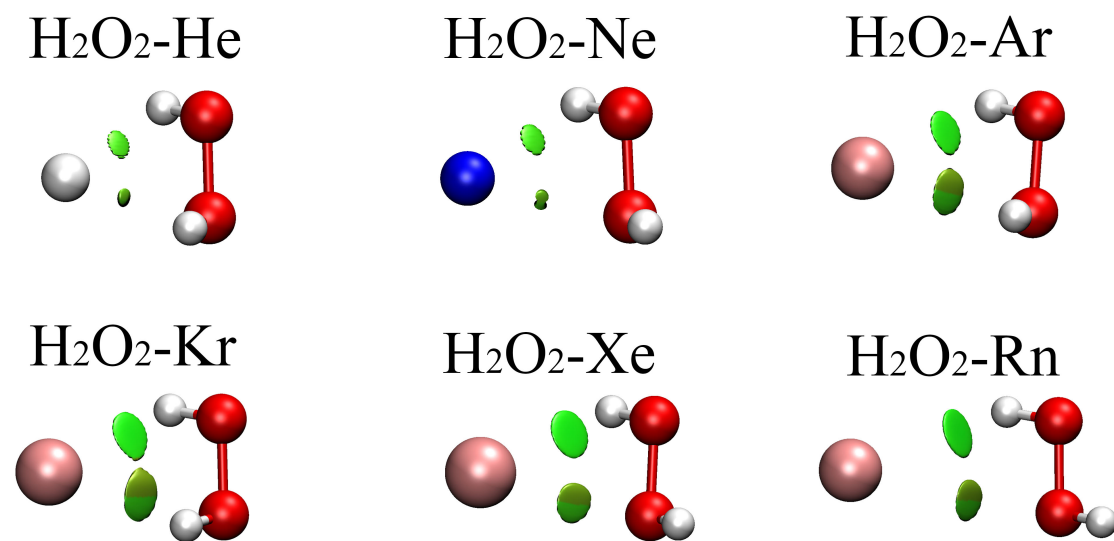
**Fig. 12**  $\text{H}_2\text{O}_2\text{-Ng}$  reduced density gradient (RDG) as a function of electron density ( $\rho$ ) multiplied by the sign of the second eigenvalue of the hessian matrix ( $\lambda_2$ ) for trans-well configuration. The  $(\lambda_2)\rho$  sign function is represented by three colors: Red color to indicate the strong repulsion region ( $\rho > 0$  and  $\lambda_2 > 0$ ), blue color to denote the strong attraction region ( $\rho > 0$  and  $\lambda_2 < 0$ ), and green color to designate van der Waals interaction ( $\rho \approx 0$  and  $\lambda_2 \approx 0$ ).



**Fig. 13**  $\text{H}_2\text{O}_2\text{-Ng}$  three-dimensional isosurfaces of reduced density gradient for cis-well configuration represented by a greenish region between the  $\text{H}_2\text{O}_2$  molecule and Ng atom of isovalues equal to 0.5 a.u. The existence of this isosurface confirms that the  $\text{H}_2\text{O}_2\text{-Ng}$  interaction is dominated by the van der Waals component (non covalent nature).



**Fig. 14**  $\text{H}_2\text{O}_2\text{-Ng}$  three-dimensional isosurfaces of reduced density gradient for trans-barrier configuration represented by a greenish region between the  $\text{H}_2\text{O}_2$  molecule and Ng atom of isovalues equal to 0.5 a.u. The existence of this isosurface confirms that the  $\text{H}_2\text{O}_2\text{-Ng}$  interaction is dominated by the van der Waals component (non covalent nature).



**Fig. 15**  $\text{H}_2\text{O}_2\text{-Ng}$  three-dimensional isosurfaces of reduced density gradient for trans-well configuration represented by a greenish region between the  $\text{H}_2\text{O}_2$  molecule and Ng atom of isovalues equal to 0.5 a.u. The existence of this isosurface confirms that the  $\text{H}_2\text{O}_2\text{-Ng}$  interaction is dominated by the van der Waals component (non covalent nature).



**Table 1** Cis-well main NBO population donation at CCSD(T)/aug-cc-pVTZ level for H<sub>2</sub>O<sub>2</sub> complexes. Second-order perturbation energies (E<sup>2</sup>) obtained via NBO analysis (expressed in kJ/mol) are shown in parentheses.

complexes	Donor	Acceptor	E <sup>2</sup> (kcal/mol)
H <sub>2</sub> O <sub>2</sub> -He	-	-	-
H <sub>2</sub> O <sub>2</sub> -Ne	LP (4)Ne	BD*(1) O- H	0.06 (0.25)
H <sub>2</sub> O <sub>2</sub> -Ar	BD (1) O-H	RY*(1)Ar	0.05 (0.21)
	LP (2) O	RY*(1)Ar	0.06 (0.25)
	LP (4)Ar	BD*(1) O-H	0.51 (2.13)
H <sub>2</sub> O <sub>2</sub> -Kr	BD (1) O-O	RY*(1)Kr	0.06 (0.25)
	BD (1) O-H	RY*(1)Kr	0.07 (0.29)
	LP (4)Kr	BD*(1) O-H	0.66 (2.76)
H <sub>2</sub> O <sub>2</sub> -Xe	BD (1) O-O	RY*(1)Xe	0.07 (0.29)
	BD (1) O-O	RY*(2)Xe	0.06 (0.25)
	BD (1) O-H	RY*(1)Xe	0.09 (0.38)
	LP (4)Xe	BD*(1) O-H	1.15 (4.81)
H <sub>2</sub> O <sub>2</sub> -Rn	BD (1) O-O	RY*(1)Rn	0.08 (0.33)
	BD (1) O-O	RY*(2)Rn	0.06 (0.25)
	BD (1) O-H	RY*(1)Rn	0.09 (0.38)
	LP (4)Rn	BD*(1) O-H	1.20 (5.02)

**Table 2** Trans-barrier main NBO population donation at CCSD(T)/aug-cc-pVTZ level for H<sub>2</sub>O<sub>2</sub> complexes. Second-order perturbation energies (E<sup>2</sup>) obtained via NBO analysis (expressed in kJ/mol) are shown in parentheses.

complexes	Donor	Acceptor	E <sup>2</sup> (kcal/mol)
H <sub>2</sub> O <sub>2</sub> -He	-	-	-
H <sub>2</sub> O <sub>2</sub> -Ne	BD (1) O-O	RY*(1)Ne	0.06 (0.25)
H <sub>2</sub> O <sub>2</sub> -Ar	BD (1) O-O	RY*(1)Ar	0.07 (0.29)
	LP (4)Ar	BD*(1) O-H	0.41 (1.72)
H <sub>2</sub> O <sub>2</sub> -Kr	BD (1) O-H	RY*(1)Kr	0.08 (0.33)
	LP (1) O	RY*(1)Kr	0.08 (0.33)
	LP (1) O	RY*(1)Kr	0.07 (0.29)
	LP (4)Kr	RY*(3) H	0.12 (0.50)
H <sub>2</sub> O <sub>2</sub> -Xe	LP (4)Kr	BD*(1) O-H	1.31 (5.48)
	BD (1) O-O	RY*(1)Xe	0.11 (0.46)
	BD (1) O-H	RY*(1)Xe	0.09 (0.38)
	LP (4)Xe	RY*(5) H	0.06 (0.25)
	LP (4)Xe	BD*(1) O-H	1.40 (5.86)
H <sub>2</sub> O <sub>2</sub> -Rn	LP (4)Xe	BD*(1) O-H	0.10 (0.42)
	BD (1) O-O	RY*(1)Rn	0.09 (0.38)
	BD (1) O-H	RY*(1)Rn	0.08 (0.33)
	LP (4)Rn	BD*(1) O-H	1.02 (4.27)
H <sub>2</sub> O <sub>2</sub> -Rn	LP (4)Rn	BD*(1) O-H	0.07 (0.29)
	LP (4)Rn	BD*(1) O-H	0.07 (0.29)

**Table 3** Trans-well main NBO population donation at CCSD(T)/aug-cc-pVTZ level for H<sub>2</sub>O<sub>2</sub> complexes. Second-order perturbation energies (E<sup>2</sup>) obtained via NBO analysis (expressed in kJ/mol) are shown in parentheses.

complexes	Donor	Acceptor	E <sup>2</sup> (kcal/mol)
H <sub>2</sub> O <sub>2</sub> -He	-	-	-
H <sub>2</sub> O <sub>2</sub> -Ne	LP (4)Ne	BD*(1) O-H	0.05 (0.21)
H <sub>2</sub> O <sub>2</sub> -Ar	BD (1) O-H	RY*(1)Ar	0.05 (0.21)
	LP (2) O	RY*(1)Ar	0.06 (0.25)
	LP (4)Ar	BD*(1) O-H	0.49 (2.05)
H <sub>2</sub> O <sub>2</sub> -Kr	BD (1) O-O	RY*(1)Kr	0.05 (0.21)
	BD (1) O-O	RY*(2)Kr	0.07 (0.29)
	BD (1) O-H	RY*(1)Kr	0.07 (0.29)
	BD (1) O-H	RY*(3)Kr	0.05 (0.21)
	LP (2) O	RY*(1)Kr	0.08 (0.33)
	LP (4)Kr	BD*(1) O-H	0.71 (2.97)
H <sub>2</sub> O <sub>2</sub> -Xe	BD (1) O-O	RY*(1)Xe	0.07 (0.29)
	BD (1) O-H	RY*(1)Xe	0.09 (0.38)
	LP (4)Xe	BD*(1) O-H	1.06 (4.44)
H <sub>2</sub> O <sub>2</sub> -Rn	BD (1) O-O	RY*(1)Rn	0.07 (0.29)
	BD (1) O-H	RY*(1)Rn	0.10 (0.42)
	LP (4)Rn	BD*(1) O-H	1.18 (4.94)

**Table 4** SAPT2+(CCD)- $\delta$ MP2/aug-cc-pVTZ (for H<sub>2</sub>O<sub>2</sub>-Ng=He, Ne, Ar, Kr, and Xe) and SAPT2+3/aug-cc-pVTZ (H<sub>2</sub>O<sub>2</sub>-Rn) interaction energies for cis-well configuration (all values are in kJ/mol). E<sub>elect</sub>, E<sub>exch</sub>, E<sub>ind</sub>, and E<sub>disp</sub> refer to attractive electronic, repulsive exchange, induction, and attractive dispersion terms of interaction energy, respectively.

Energy term	H <sub>2</sub> O <sub>2</sub> -He	H <sub>2</sub> O <sub>2</sub> -Ne	H <sub>2</sub> O <sub>2</sub> -Ar	H <sub>2</sub> O <sub>2</sub> -Kr	H <sub>2</sub> O <sub>2</sub> -Xe	H <sub>2</sub> O <sub>2</sub> -Rn
E <sub>elect</sub>	-0.08	-0.22	-1.02	-1.36	-1.54	-1.93
E <sub>exch</sub>	0.55	0.97	4.34	5.35	6.74	7.97
E <sub>ind</sub>	-0.14	-0.23	-1.17	-1.50	-2.31	-2.75
E <sub>disp</sub>	-0.85	-1.47	-4.62	-5.50	-6.53	-7.51
%E <sub>elect</sub>	7.48	11.46	14.98	16.27	14.84	15.83
%E <sub>ind</sub>	13.08	11.98	17.18	17.94	22.25	22.56
%E <sub>disp</sub>	79.44	76.57	67.84	65.79	69.91	61.61
SAPT2 energies	-0.52	-0.95	-2.47	-3.01	-3.64	-4.22

**Table 5** SAPT2+(CCD)- $\delta$ MP2/aug-cc-pVTZ (for H<sub>2</sub>O<sub>2</sub>-Ng=He, Ne, Ar, Kr, and Xe) and SAPT2+3/aug-cc-pVTZ (H<sub>2</sub>O<sub>2</sub>-Rn) interaction energies for trans-barrier configuration (all values are in kJ/mol). E<sub>elect</sub>, E<sub>exch</sub>, E<sub>ind</sub>, and E<sub>disp</sub> refer to attractive electronic, repulsive exchange, induction, and attractive dispersion terms of interaction energy, respectively.

Energy term	H <sub>2</sub> O <sub>2</sub> -He	H <sub>2</sub> O <sub>2</sub> -Ne	H <sub>2</sub> O <sub>2</sub> -Ar	H <sub>2</sub> O <sub>2</sub> -Kr	H <sub>2</sub> O <sub>2</sub> -Xe	H <sub>2</sub> O <sub>2</sub> -Rn
E <sub>elect</sub>	-0.10	-0.27	-1.09	-3.70	-3.07	-2.32
E <sub>exch</sub>	0.61	1.17	4.52	13.85	11.52	8.69
E <sub>ind</sub>	-0.13	-0.23	-1.12	-2.73	-2.97	-2.66
E <sub>disp</sub>	-0.95	-1.70	-4.84	-8.83	-8.89	-7.97
%E <sub>elect</sub>	8.47	12.27	15.46	24.25	20.56	17.91
%E <sub>ind</sub>	11.02	10.45	15.89	17.89	19.89	20.54
%E <sub>disp</sub>	80.51	77.27	68.65	57.86	59.54	61.54
SAPT2 energies	-0.57	-1.03	-2.53	-1.41	-3.41	-4.26

**Table 6** SAPT2+(CCD)- $\delta$ MP2/aug-cc-pVTZ (for H<sub>2</sub>O<sub>2</sub>-Ng=He, Ne, Ar, Kr, and Xe) and SAPT2+3/aug-cc-pVTZ (H<sub>2</sub>O<sub>2</sub>-Rn) interaction energies for trans-well configuration (all values are in kJ/mol).  $E_{elect}$ ,  $E_{exch}$ ,  $E_{ind}$ , and  $E_{disp}$  refer to attractive electronic, repulsive exchange, induction, and attractive dispersion terms of interaction energy, respectively.

Energy term	H <sub>2</sub> O <sub>2</sub> -He	H <sub>2</sub> O <sub>2</sub> -Ne	H <sub>2</sub> O <sub>2</sub> -Ar	H <sub>2</sub> O <sub>2</sub> -Kr	H <sub>2</sub> O <sub>2</sub> -Xe	H <sub>2</sub> O <sub>2</sub> -Rn
$E_{elect}$	-0.08	-0.21	-1.01	-1.54	-1.69	-1.93
$E_{exch}$	0.56	0.92	4.29	5.89	7.08	8.00
$E_{ind}$	-0.14	-0.22	-1.14	-1.62	-2.29	-2.73
$E_{disp}$	-0.86	-1.44	-4.59	-5.82	-6.71	-7.50
% $E_{elect}$	7.41	11.23	14.98	17.15	15.81	15.87
% $E_{ind}$	12.96	11.76	16.91	18.04	21.42	22.45
% $E_{disp}$	79.63	77.00	68.10	64.81	62.77	61.68
SAPT2 energies	-0.52	-0.95	-2.45	-3.09	-3.61	-4.16