Electronic Supplementary Information

Metastable He–O bond inside a ferroelectric molecular cavity: $(HeO)(LiF)_2$

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Contents

S1. List of selected physical properties for which He exhibits the record value among all elements.

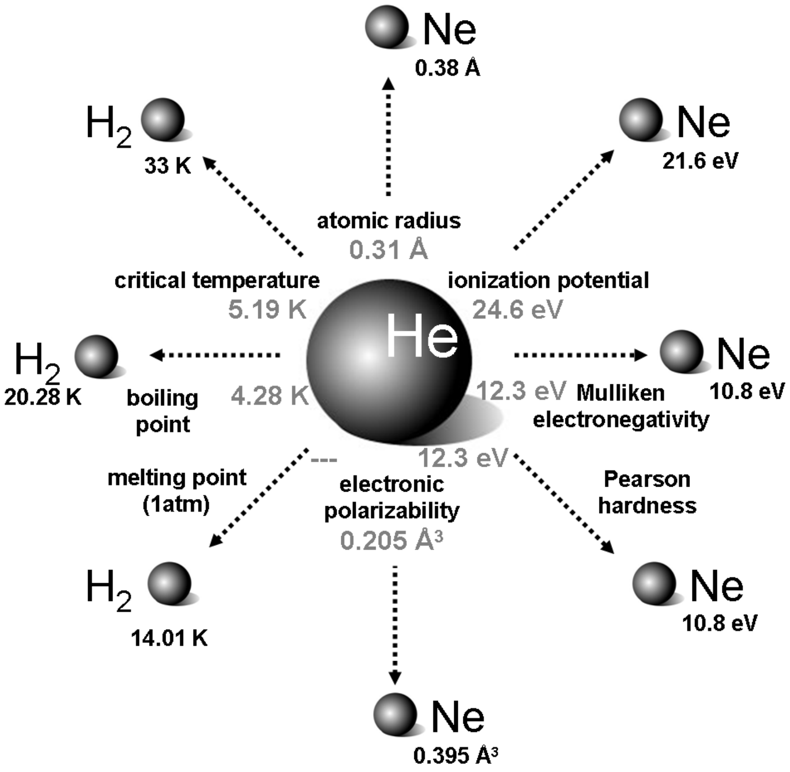
	Value for		
Property	**He**	**Element No.2**	**Unit**
Melting point	0.95*	14.01 (H_2)	K
Boiling point	4.22	20.28 (H_2)	K
Heat of fusion	0.0138	0.117 (H_2)	kJ mol^{-1}
Heat of vaporization	0.0829	0.904 (H_2)	kJ/mol
Critical temperature	5.19	33.20 (H_2)	K
van der Waals constant (a)	0.03457	0.2135 (Ne)	Å^2 atm mol^{-2}
Atomic radius	31	38 (Ne)	pm
Covalent radius	32	37 (H_2)	pm
Refractive index	1.000035	1.000067 (Ne)	[1]
1st ionization energy	2372.3	2080.7 (Ne)	kJ/mol
Solubility in water at RT	claimed to be the smallest of all gases	?	mg /l

***at 25 bar**

S2. List of selected physical properties for which He exhibits the second largest or the second smallest value among all elements.

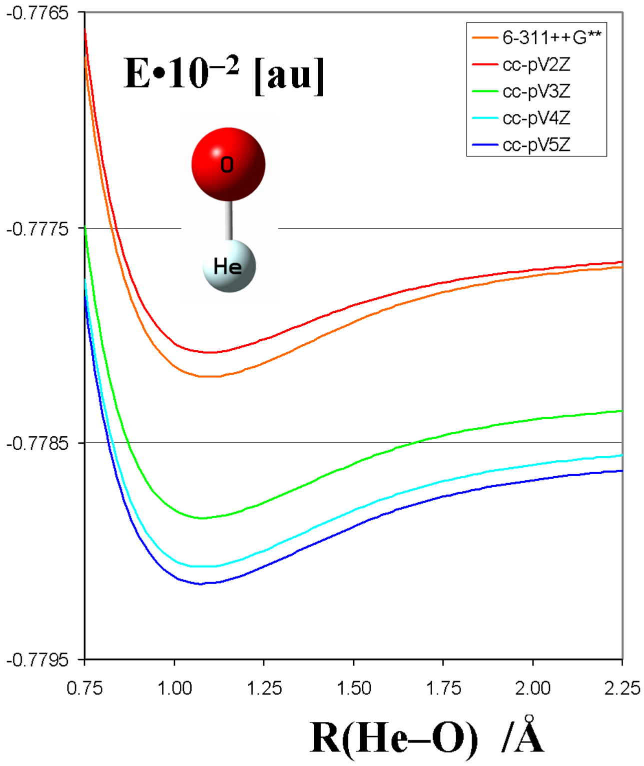
	Value for		
Property	**Element No.1**	**He**	**Unit**
Liquid range	2.51 (Ne)	3.27	K
Density (gas phase)	0.08988 (H_2)	0.1786	g L^{-1}
Specific heat	14.304 (H_2)	5.193	J g^{-1} K^{-1}
2nd ionization energy	7298.1 (Li)	5250.5	kJ mol^{-1}

S3. Illustration of selected physicochemical properties with the record-high- or record-low values for helium atom.

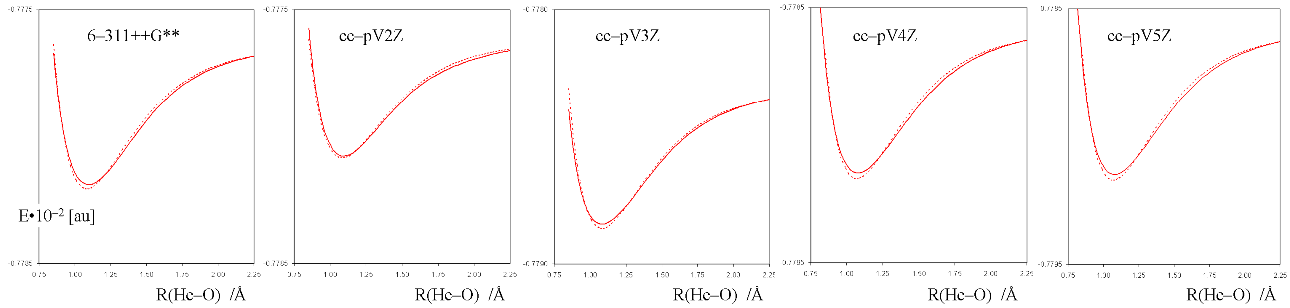


Helium and a handful of its important physicochemical properties with the record-high- or record-low values. Elements occupying the second position in each of the rankings, are also showed.

S4. Influence of the basis set on the on the PES of ^{1}HeO (E = 0.1 au). Graph shows energy, Ex10^{-2} (hartree) *vs.* the interatomic separation, R (Å) for several different basis sets.



S5. The fits of the PESs for ^{1}HeO (E = 0.1 au) with the Morse potential.

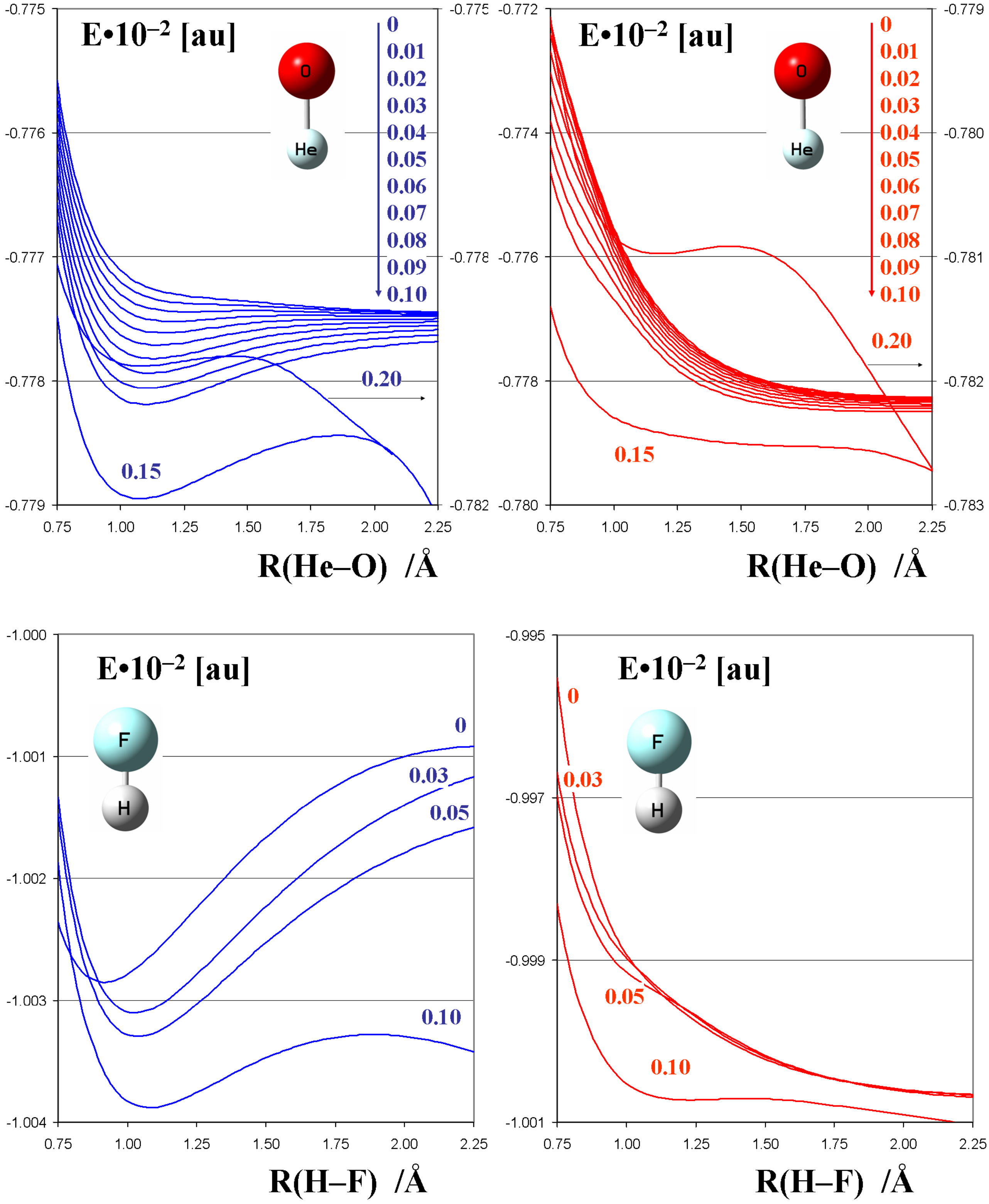


(solid line – the calculated PES, dotted line – the fitted curve)

Parameter/basis	6-311++G**	cc-pV2Z	cc-pV3Z	cc-pV4Z	cc-pV5Z
D_e [10^{-2} au]	0.000558	0.000457	0.000540	0.000540	0.000575
a [1]	2.9985	2.9985	2.9985	2.9978	2.9945
r_e [Å]	1.0833	1.0833	1.0832	1.0695	1.0688
$V(r_e)$ [10^{-2} au]	–0.7782	–0.7781	–0.7789	–0.7791	–0.7792

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2 + V(r_e)$$

S6. Impact of the strength of the external electric field, *E* (atomic units), on the lowest lying singlet (blue, $^1\Sigma$) and triplet (red, $^3\Pi$) potential energy surfaces of HeO and HF molecules. Graphs show energy, Ex10^{-2} (hartree) *vs.* the interatomic separation, R (Å) for several different values of electric field.



S7. Molecular orbital coefficients for ^{1}HeO (*E* = 0.1 au) and HF (*E* = 0 au).

^{1}HeO

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Orbital symmetries:
       Occupied  (SG) (SG) (SG) (PI) (PI)
       Virtual   (SG) (PI) (PI) (SG) (SG) (SG) (SG) (PI) (PI) (SG)
The electronic state is 1-SG.
 Alpha  occ. eigenvalues --  -20.67526  -1.43346  -0.94056  -0.57523  -0.57523
 Alpha virt. eigenvalues --   -0.09677   0.20098   0.20098   0.20506   0.29033
     Molecular Orbital Coefficients
                           1         2         3         4         5
                        (SG)--O   (SG)--O   (SG)--O   (PI)--O   (PI)--O
     EIGENVALUES --   -20.67526  -1.43346  -0.94056  -0.57523  -0.57523
   1 1   He 1S          0.00004   0.15448   0.19914   0.00000   0.00000
   2        2S          0.00025   0.28709   0.40471   0.00000   0.00000
   3        3S         -0.00001   0.10100   0.22954   0.00000   0.00000
   4        4S         -0.00010   0.00740  -0.06131   0.00000   0.00000
   5        5PX         0.00000   0.00000   0.00000   0.00000   0.02235
   6        5PY         0.00000   0.00000   0.00000   0.02235   0.00000
   7        5PZ         0.00020   0.04397   0.03325   0.00000   0.00000
   8 2   O  1S          0.55157  -0.09980   0.07349   0.00000   0.00000
   9        2S          0.47179  -0.16686   0.12446   0.00000   0.00000
  10        2PX         0.00000   0.00000   0.00000   0.00000   0.29951
  11        2PY         0.00000   0.00000   0.00000   0.29951   0.00000
  12        2PZ        -0.00173  -0.03249  -0.11754   0.00000   0.00000
  13        3S          0.00493   0.48622  -0.37397   0.00000   0.00000
  14        3PX         0.00000   0.00000   0.00000   0.00000   0.45926
  15        3PY         0.00000   0.00000   0.00000   0.45926   0.00000
  16        3PZ         0.00085  -0.05828  -0.18166   0.00000   0.00000
  17        4S         -0.00041   0.34296  -0.39206   0.00000   0.00000
  18        4PX         0.00000   0.00000   0.00000   0.00000   0.41684
  19        4PY         0.00000   0.00000   0.00000   0.41684   0.00000
  20        4PZ        -0.00030  -0.00160  -0.12406   0.00000   0.00000
  21        5S          0.00036  -0.02055   0.00818   0.00000   0.00000
  22        5PX         0.00000   0.00000   0.00000   0.00000   0.06449
  23        5PY         0.00000   0.00000   0.00000   0.06449   0.00000
  24        5PZ         0.00004   0.01272  -0.04153   0.00000   0.00000
  25        6D 0       -0.00053   0.01217   0.01917   0.00000   0.00000
  26        6D+1        0.00000   0.00000   0.00000   0.00000  -0.00673
  27        6D-1        0.00000   0.00000   0.00000  -0.00673   0.00000
  28        6D+2        0.00000   0.00000   0.00000   0.00000   0.00000
  29        6D-2        0.00000   0.00000   0.00000   0.00000   0.00000
                           6         7         8         9        10
                        (SG)--V   (PI)--V   (PI)--V   (SG)--V   (SG)--V
     EIGENVALUES --    -0.09677   0.20098   0.20098   0.20506   0.29033
   1 1   He 1S          0.04625   0.00000   0.00000   0.12508  -0.04887
   2        2S          0.04743   0.00000   0.00000   0.30858   0.00063
   3        3S          0.12621   0.00000   0.00000   0.71210  -0.62166
   4        4S          1.72341   0.00000   0.00000  -0.51061  -1.69364
   5        5PX         0.00000   0.00185   0.00000   0.00000   0.00000
   6        5PY         0.00000   0.00000   0.00185   0.00000   0.00000
   7        5PZ        -0.02315   0.00000   0.00000  -0.02808  -0.00911
   8 2   O  1S          0.02595   0.00000   0.00000   0.02828   0.02302
   9        2S          0.04222   0.00000   0.00000   0.05021   0.03674
  10        2PX         0.00000  -0.11293   0.00000   0.00000   0.00000
  11        2PY         0.00000   0.00000  -0.11293   0.00000   0.00000
  12        2PZ         0.01034   0.00000   0.00000   0.26467  -0.00902
  13        3S         -0.09364   0.00000   0.00000  -0.17778  -0.05724
  14        3PX         0.00000  -0.09049   0.00000   0.00000   0.00000
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  15        3PY          0.00000   0.00000  -0.09049   0.00000   0.00000
  16        3PZ          0.10856   0.00000   0.00000   0.35583  -0.04252
  17        4S          -0.45585   0.00000   0.00000  -0.22965  -0.83434
  18        4PX          0.00000  -0.56125   0.00000   0.00000   0.00000
  19        4PY          0.00000   0.00000  -0.56125   0.00000   0.00000
  20        4PZ         -0.37469   0.00000   0.00000   0.92553   0.05125
  21        5S          -0.68905   0.00000   0.00000   0.18480   3.06815
  22        5PX          0.00000   1.27562   0.00000   0.00000   0.00000
  23        5PY          0.00000   0.00000   1.27562   0.00000   0.00000
  24        5PZ          1.81233   0.00000   0.00000  -0.64897  -1.60770
  25        6D 0         0.00924   0.00000   0.00000   0.00727  -0.01855
  26        6D+1         0.00000   0.00251   0.00000   0.00000   0.00000
  27        6D-1         0.00000   0.00000   0.00251   0.00000   0.00000
  28        6D+2         0.00000   0.00000   0.00000   0.00000   0.00000
  29        6D-2         0.00000   0.00000   0.00000   0.00000   0.00000
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^{1}HF

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       Occupied  (SG) (SG) (SG) (PI) (PI)
       Virtual   (SG) (SG) (PI) (PI) (SG) (SG) (SG) (PI) (PI) (SG)
The electronic state is 1-SG.
 Alpha  occ. --  -26.29921  -1.60649  -0.77293  -0.65184  -0.65184
 Alpha virt. --    0.04303   0.20971   0.29879   0.29879   0.31232
     Molecular Orbital Coefficients
                           1         2         3         4         5
                        (SG)--O   (SG)--O   (SG)--O   (PI)--O   (PI)--O
     EIGENVALUES --    -26.29921  -1.60649  -0.77293  -0.65184  -0.65184
   1 1   H  1S          0.00015   0.09302  -0.17265   0.00000   0.00000
   2        2S          0.00011   0.06224  -0.24960   0.00000   0.00000
   3        3S         -0.00019   0.01778  -0.03671   0.00000   0.00000
   4        4S         -0.00009   0.00875  -0.00138   0.00000   0.00000
   5        5PX         0.00000   0.00000   0.00000   0.03483   0.00000
   6        5PY         0.00000   0.00000   0.00000   0.00000   0.03483
   7        5PZ         0.00009   0.03087  -0.04887   0.00000   0.00000
   8 2   F  1S          0.54767  -0.12142  -0.02972   0.00000   0.00000
   9        2S          0.47350  -0.20376  -0.05062   0.00000   0.00000
  10        2PX         0.00000   0.00000   0.00000   0.30763   0.00000
  11        2PY         0.00000   0.00000   0.00000   0.00000   0.30763
  12        2PZ        -0.00119  -0.02909   0.26034   0.00000   0.00000
  13        3S          0.00616   0.60160   0.15934   0.00000   0.00000
  14        3PX         0.00000   0.00000   0.00000   0.46755   0.00000
  15        3PY         0.00000   0.00000   0.00000   0.00000   0.46755
  16        3PZ         0.00044  -0.05070   0.39390   0.00000   0.00000
  17        4S         -0.00076   0.44246   0.23813   0.00000   0.00000
  18        4PX         0.00000   0.00000   0.00000   0.40071   0.00000
  19        4PY         0.00000   0.00000   0.00000   0.00000   0.40071
  20        4PZ        -0.00012  -0.01830   0.25887   0.00000   0.00000
  21        5S          0.00062  -0.03911   0.04272   0.00000   0.00000
  22        5PX         0.00000   0.00000   0.00000   0.05811   0.00000
  23        5PY         0.00000   0.00000   0.00000   0.00000   0.05811
  24        5PZ        -0.00005   0.01129   0.01762   0.00000   0.00000
  25        6D 0       -0.00011   0.00784  -0.01817   0.00000   0.00000
  26        6D+1        0.00000   0.00000   0.00000  -0.01152   0.00000
  27        6D-1        0.00000   0.00000   0.00000   0.00000  -0.01152
  28        6D+2        0.00000   0.00000   0.00000   0.00000   0.00000
  29        6D-2        0.00000   0.00000   0.00000   0.00000   0.00000
                           6         7         8         9        10
                        (SG)--V   (SG)--V   (PI)--V   (PI)--V   (SG)--V
     EIGENVALUES --     0.04303   0.20971   0.29879   0.29879   0.31232
   1 1   H  1S          0.00000   0.07831   0.00000   0.00000   0.02585
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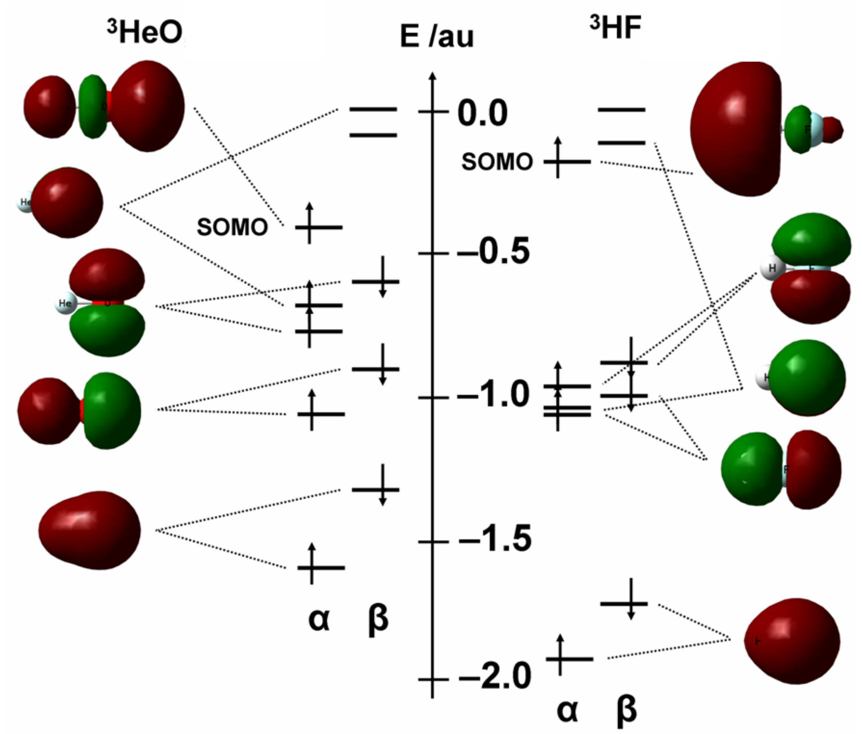
   2         2S           0.13786  -0.21882   0.00000   0.00000   0.08800
   3         3S          -0.17759   4.46174   0.00000   0.00000   1.11038
   4         4S           1.38881  -1.46322   0.00000   0.00000  -0.62091
   5         5PX          0.00000   0.00000   0.00000   0.01814   0.00000
   6         5PY          0.00000   0.00000   0.01814   0.00000   0.00000
   7         5PZ         -0.01584  -0.05769   0.00000   0.00000  -0.01319
   8 2   F   1S           0.01381   0.01450   0.00000   0.00000   0.02778
   9         2S           0.02442   0.02532   0.00000   0.00000   0.04577
  10         2PX          0.00000   0.00000   0.00000  -0.11339   0.00000
  11         2PY          0.00000   0.00000  -0.11339   0.00000   0.00000
  12         2PZ          0.03788   0.09996   0.00000   0.00000  -0.05052
  13         3S          -0.09183  -0.09070   0.00000   0.00000  -0.10343
  14         3PX          0.00000   0.00000   0.00000  -0.09472   0.00000
  15         3PY          0.00000   0.00000  -0.09472   0.00000   0.00000
  16         3PZ          0.05451   0.14380   0.00000   0.00000  -0.01136
  17         4S          -0.02786  -0.00665   0.00000   0.00000  -0.71103
  18         4PX          0.00000   0.00000   0.00000  -0.55521   0.00000
  19         4PY          0.00000   0.00000  -0.55521   0.00000   0.00000
  20         4PZ          0.10070   0.10868   0.00000   0.00000  -0.38648
  21         5S          -0.48614  -2.38385   0.00000   0.00000   0.53823
  22         5PX          0.00000   0.00000   0.00000   1.27543   0.00000
  23         5PY          0.00000   0.00000   1.27543   0.00000   0.00000
  24         5PZ         -0.01100   1.16118   0.00000   0.00000   1.34826
  25         6D 0        -0.00186   0.00820   0.00000   0.00000   0.00746
  26         6D+1         0.00000   0.00000   0.00000   0.00392   0.00000
  27         6D-1         0.00000   0.00000   0.00392   0.00000   0.00000
  28         6D+2         0.00000   0.00000   0.00000   0.00000   0.00000
  29         6D-2         0.00000   0.00000   0.00000   0.00000   0.00000
```

S8. Gross orbital populations for ^{1}HeO (E = 0.1 au) and HF (E = 0 au).

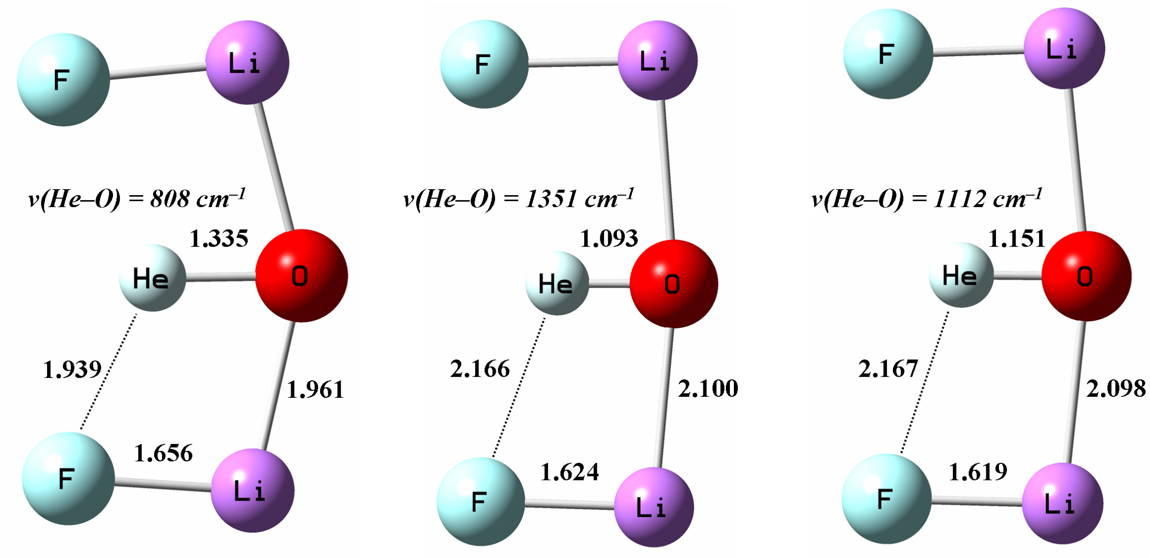
He	1S	**0.35131**	**H**	1S	**0.25628**
	2S	**0.90898**		2S	**0.31408**
	3S	**0.31499**		3S	0.03303
	4S	-0.00136		4S	0.00586
	5PX	0.01165		5PX	0.02463
	5PY	0.01165		5PY	0.02463
	5PZ	0.02406		5PZ	0.04194
O	1S	**1.08397**	**F**	1S	**1.0768**
	2S	**0.91182**		2S	**0.91983**
	2PX	**0.39976**		2PX	**0.41419**
	2PY	**0.39976**		2PY	**0.41419**
	2PZ	0.07797		2PZ	**0.31214**
	3S	**1.0567**		3S	**1.08269**
	3PX	**0.84691**		3PX	**0.86297**
	3PY	**0.84691**		3PY	**0.86297**
	3PZ	**0.22558**		3PZ	**0.69447**
	4S	**0.86572**		4S	**0.85874**
	4PX	**0.67928**		4PX	**0.64283**
	4PY	**0.67928**		4PY	**0.64283**
	4PZ	**0.16895**		4PZ	**0.43027**
	5S	-0.02872		5S	-0.04558
	5PX	0.06225		5PX	0.05493
	5PY	0.06225		5PY	0.05493
	5PZ	0.03147		5PZ	0.01579

S9. The molecular orbital structure of the HeO (E = 0.1 au) and HF (E = 0 au) molecules in their first excited triplet states (from the Hartree-Fock single-point calculation at geometries preoptimized with CCSD(T)).



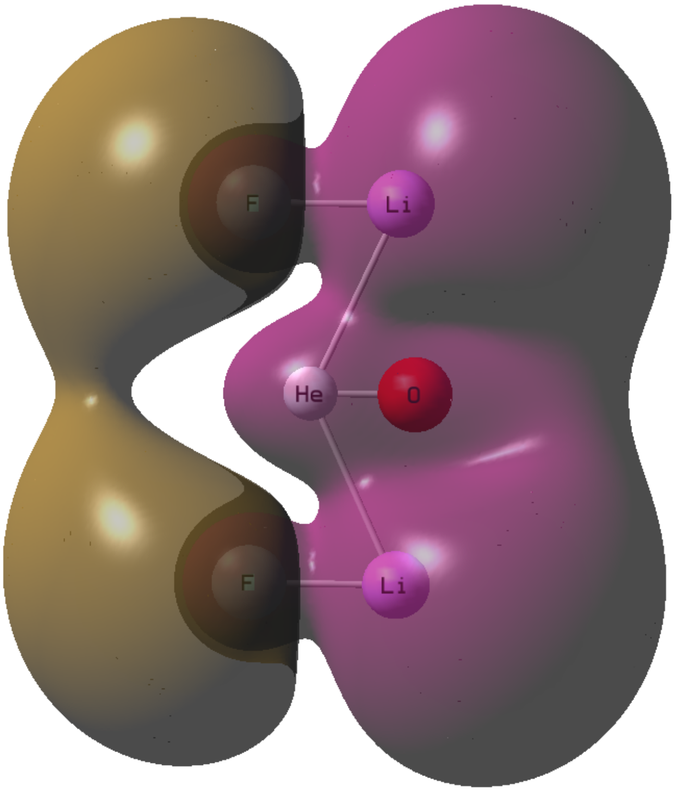
The α and β orbitals with similar spatial functions are linked with dotted lines to orbital image.

S10. Molecular geometry and He–O stretching frequency of (HeO)(LiF)$_2$ as optimized at B3LYP, MP2 and CCSD(T) levels of theory. Distances in Å.



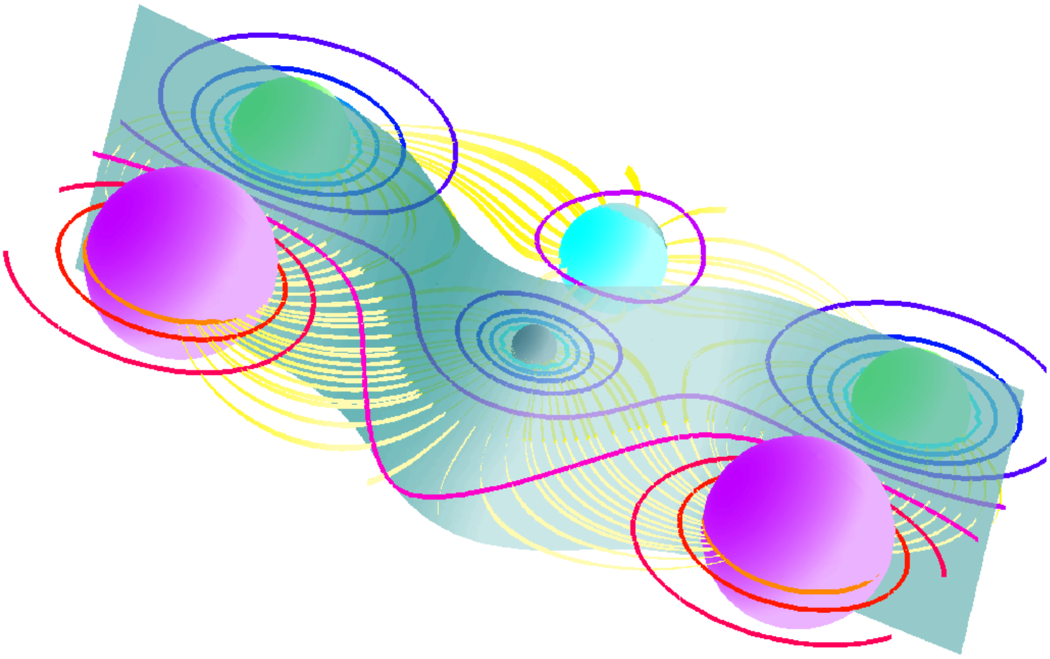
B3LYP **MP2** **CCSD(T)**

S11. The electrostatic potential of the (HeO)(LiF)$_2$ molecule in its lowest bound singlet state.



Isosurfaces drawn at ±0.05 au.

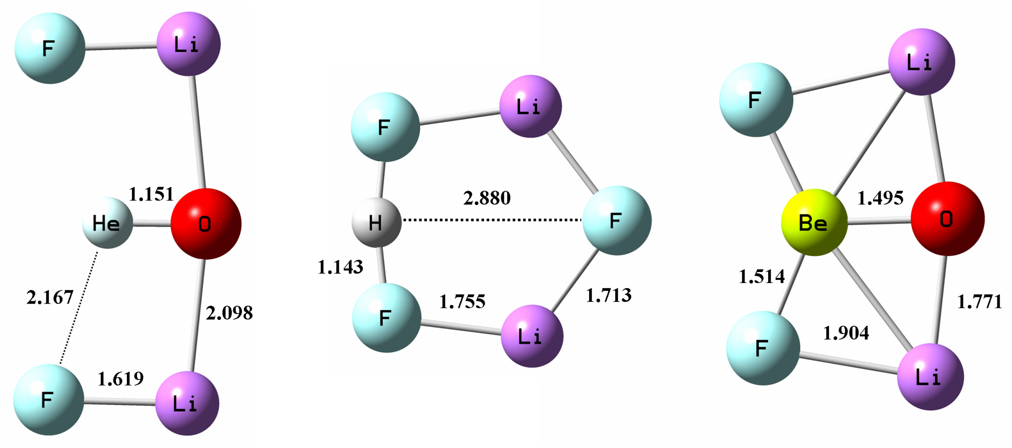
S12. The lines of electric field around the (HeO)(LiF)$_2$ molecule in its lowest bound singlet state.



Projection on the plane of the molecule (lines of electric field – yellow; isolines of electric potential – red, violet; isosurface of null potential – green).

S13. He *vs.* Be: the Group 2 elements?

In section 3 of the main paper we have discussed possible isoelectronic relation between HeO and HF. We suggested that too many important features of these two, formally 8-electron systems, indicate that they do *not* behave as isoelectronic species. But it is instructive to compare now more complex $(HeO)(LiF)_2$ species to its HF–homologue, *i.e.* $(HF)(LiF)_2$, as well as to related $(BeO)(LiF)_2$. We have optimized geometry for these molecules (Figure 10) as well as calculated their vibrational spectra and selected physicochemical features.



*Optimized molecular geometry of the planar $(HeO)(LiF)_2$, $(HF)(LiF)_2$ and $(BeO)(LiF)_2$ molecules (C_{2v}) in their lowest singlet state (CCSD(T) /6-311++G** results). No imaginary vibrational modes were detected or any of these species. Distances are in Å.*

The optimized geometry of $(HF)(LiF)_2$ differs substantially from that of $(HeO)(LiF)_2$; the major difference is that the [HF] unit is dissociated, similarly to the HF molecule in the electric field of 0.10 au (section 2 of the main paper). Thus, formula of $(HF)(LiF)_2$ should rather be written as $(Li_2F^+)(HF_2^-)$. Analogous description of $(Li_2O)(HeF_2)$ as $(HeO)(LiF)_2$ is definitely incorrect, taking into account the values of He–O and He–F bond lengths predicted for this molecule. The dissimilarity between [HeO] and [HF] is apparent again.

On the other hand, $(BeO)(LiF)_2$ is characterized by the presence of the Be–O bond at 1.495 Å, similarly to the He–O bond predicted for $(HeO)(LiF)_2$. The difference of the Be–O and He–O bond lengths is ~0.35 Å, which is much smaller than the diference of atomic radii of Be and He atoms, ~0.74 Å. This can be traced back to a much larger ionic character of chemical bonding in the BeO unit than for HeO. This is additionally seen in very short Be–F distances, large absolute values of Mulliken charge on Be and O atoms, and a small dipol moment of 3.9 D for Be system. Obviously, the $2s^2$ shell of Be may be depopulated more easily than the $1s^2$ shell of He. Still, [HeO] moiety seems to be resemble [BeO] better than [HF]. Thus, could helium, in agreement with its $1s^2$ electronic configuration but in disagreement with a more traditional view, be actually labeled as a Group 2 and not a Group 18 element?

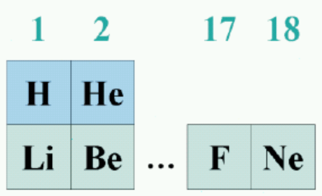
S14. He or Ne – which element is more noble?

Having studied $(HeO)(LiF)_2$ we have scrutinized its heavier noble gas analogues. However, neither $(NeO)(LiF)_2$ nor $(NeO)(NaF)_2$ could be detected as minima on the singlet PES. This stability difference is interesting since electronegativity and many other chemical properties of elements change quite monotonically when one goes down any of the Groups 13–18. For example, O is more electronegative than S, F than Cl, Ne than Ar, etc. Hence, He should be more electronegative and as such less prone to chemical bonding than Ne.

The atypical behaviour of He *vs.* Ne (*i.e.* reversal of stability for their theorized chemical connections) which obviously contrasts with the trend for the 1st ionization potentials of these elements (He > Ne), has been noticed before.[1,2,3,4,5,6,7] Various explanations were provided from electrostatic arguments[2] to increased Pauli repulsion from the filled 2p orbital on Ne[1]. We think that a relatively large reactivity of He with respect to Ne may be understood simply in terms of substantial charge density which appears at a small He center when its $1s^2$ shell is even partially depopulated. The incrased charge density obviously leads to stronger electrostatic and dispersive interactions with ligands.

S15. Position of He in the Periodic Table of Elements.

The combined picture of chemical bonding and physicochemical properties for small neutral and anionic species containing atoms of the lightest noble gas elements, He and Ne, as well as the proposed isoelectronic He~Be analogy, jointly suggest that He should be best placed in the 2nd Group of the periodic table of chemical elements, just above beryllium.[4] Neon is second to none as far as chemical inertness is considered, and the last true ‘noble gas’ in Group 18. Our analysis based on others’ and our own theoretical results, strongly supports what Bent and Scerri have been advocating for years.[8]



The suggested position of He in the periodic table of elements, which emerges from theoretical studies of small neutral and anionic species containing atoms of the lightest noble gas elements, He and Ne, and from the He~Be analogy. Modified by permission of the Polish Society of Chemistry after Ref.4.

He neighbouring H within the s block would reflect the electronic configurations and emphasize similarity of these nonmetallic elements (both are gaseous at ambient conditions).[4] Placement of He above Be is supported by a larger affinity of these elements to O than to F, as well as by the monotonic decrease of the first ionization potential down the Group 2, and down the Group 18, and by the null electron affinity of elements from these groups.[4] Identical trends of the ionization potential hold in the neigbouring Groups 1 and 17, respectively.

Neon now emerges as the most noble element known.

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