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PAPER

A metastable He–O bond inside a ferroelectric molecular cavity: $(HeO)(LiF)_2$†‡

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Elemental helium is a prototypical noble gas and its atom sets the records for many physicochemical properties. With its two electrons in the closed 1s shell, He is the smallest, the least polarizable, the most difficult to ionize, the hardest (in Pearson's sense) and the most electronegative atom known. Helium gas is considered to be as close to an 'ideal gas' as possible and used as a standard of compressibility and pressure. As a consequence of its closed-shell electronic configuration, helium also exhibits chemical inertness: non-charged species which contain chemically bound helium have not been synthesized to date. Here we are able to predict, using quantum mechanical methods, a small neutral molecule, $(HeO)(LiF)_2$, which contains a helium atom chemically bound to oxygen. The molecule is planar with the polarized $He^{\delta+}O^{\delta-}$ unit embedded anti-parallel in-between two co-aligned LiF dipoles. We calculate its selected physicochemical properties as well as suggest possible decomposition and synthesis pathways. Successful preparation of neutral species, $(HeO)(LiF)_2$ or related molecules, would break down the paradigm of helium's inertness.

Introduction

The chemistry of noble gases underwent remarkable development[1–4] since its birth half a century ago.[5] The heaviest among these elements, Xe, forms chemical connections in a formidable range of oxidation states varying from 0,[6] *via* +2, +4, and +6 up to +8.[7] Oxidation states up to +8 have also been theoretically predicted for Kr[8] and Ar,[9–11] but up to now only the divalent state has been achieved in isolable compounds of these elements.[12–14]

Helium has been viewed as the most reluctant to bonding amongst all elements. And justifiably so. With its record, a small atomic radius of *ca.* 0.31 Å, concomitant huge ionization potential (24.6 eV) and null electron affinity, a helium atom exhibits remarkably large values of Mulliken electronegativity and Pearson hardness, $EN_M = \eta_P = 12.3$ eV, as well as a negligible electronic polarizability of $\alpha = 0.205$ Å^3 *i.e.* small 'electronic softness' (*cf.* Fig. S3 in ESI‡). These values validate description of a He atom as a small and hard ball, a spherical electron cloud which does not interact with other atoms. Helium gas is considered to be as close to an 'ideal gas' as possible and used as a standard of compressibility and pressure, while the He atom serves for tests of extremely precise quantum chemical calculations.[15] Our subconscious perception of elemental helium is shaped by images of a colourless cryo-coolant, an ultra-cold and easy boiling-off liquid, which never freezes at ambient pressure[16] but (rather costly!) disappears into a gas phase and once lost – inevitably leaves the gravitational field of the planet Earth.

With the fully occupied 1s orbital (closed shell), the huge 1s–2s gap, and the 2p orbitals (responsible for deformation of spherically symmetric electron density in the external electric field of approaching atoms) even higher on the energy scale, helium does not engage in chemical bonding with neutral molecules.[17] Nevertheless, a number of interesting theoretical predictions exist of novel uncharged species containing He.

Previous theoretical explorations

In 1986 Koch *et al.* have suggested that the He atom could bind to an isolated BeO molecule at its metal site, with a short predicted He···Be separation of 1.538 Å, but rather soft He···Be stretching mode at 450 cm^{-1} (despite low reduced mass of the oscillator) and an energy of He detachment of a mere 0.14 eV (ZPE- and BSSE-corrected).[18] The helium atom was computed to borrow some of Be's cationic character with a small positive charge on He of +0.09 *e* (according to Mulliken population analysis). Here, Be^{2+} bound to just one anionic

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partner may be considered as a 'naked cation' which attempts to fulfill its need for linear coordination (sp hybridization) by attaching any Lewis base, even as a weak one as a He atom. Interestingly, attachment of He to BeO results in slight stiffening of the BeO bond, which shrinks by about 0.01 Å; the associated Be–O stretching frequency increases by $\sim$100 cm^{-1}. Albeit small, this effect is clearly inverse to a '*trans* influence' which is common in the chemistry of transition and post-transition elements. Somewhat more precise calculations performed over two decades later by Takayanagi *et al.* have confirmed the most important features of the He···BeO adduct; these authors gave the dissociation energy of 0.19 eV and the He···Be stretching mode at 510 cm^{-1}.[19]

Extending their findings, Frenking *et al.* have explored adducts of the He atom to isolated BN, LiF and LiH molecules (the first two being isoelectronic with BeO) and they found that the binding energy of these species is either marginally small ($<$0.1 kcal mol^{-1}) or even negative.[20]

More recently, Antoniotti *et al.* have studied a few systems related to He···BeO, namely He···BeNR where R = H, CH_3, OH and F, and they found that they exhibit a similar degree of stability as the parent He···BeO molecule.[21] The related He···BeS species is less strongly bound than its oxygen analogue, as it could be expected from a normal *trans* effect.[22] Grandinetti and his team have also suggested an alternative chemically-sound way to enhance the dissociation energy of He from BeO *via* attachment of the Lewis acid at the O end of the BeO molecule (corresponding to a 'normal' *trans* effect). The He···Be separation of 1.512 Å and the dissociation energy of a quarter eV have been predicted for the He···BeO → BH_3 molecule.[23] This simple strategy may be pursued further (for example by the use of SbF_5 or related strong Lewis acids) but it seems that the He → Be^{2+} interaction can hardly be much stronger than 0.3 eV in any neutral molecules of this type. Dimerization of BeO into a rhombic dimer (BeO_2Be) obviously leads to an increase of coordination number of Be^{2+}, a decrease of its 'acidic' (*i.e.* acceptor) character, hence to decrease of He's binding energy as compared to a BeO monomer.[24]

It is important to note that He···BeO and related species are predicted to dissociate off the He atom without any dramatic change in the electronic distribution; a singlet ground state of He···BeO yields two isolated singlet state species: He and BeO. Thus, moderate stability of a He···Be link is rather due to an unusually strong dispersive interaction (which for some could be insufficient to be considered a 'true' dative or covalent chemical bond). The situation is not much different in adducts of He with the isolated MF molecules, where M = Cu, Ag and Au. The largest calculated binding energy does not exceed 0.20 eV for He···CuF.[25]

Slightly different systems – but conceptually related to He···BeO – were studied by Rzepa.[26] The neutral molecules he considered (aside from a range of charged species) consist of an aromatic cyclobutadienyl dianion (with various substituents) which coordinates either to Be^{2+} or to B^{3+}. The shortest predicted He–Be and He–B bond lengths are 1.466 Å and 1.355 Å, respectively, with dissociation energies not exceeding 0.3 eV.

A completely different strategy of stabilizing chemical bonds to helium was used in the study of hypothetical hypervalent HHeF, which may be viewed as a product of insertion of He into a sigma bond of HF.[27,28] HHeF is a local minimum at the potential energy surface with the short He–H and He–F separations of 0.822 Å and 1.385 Å, respectively. Unfortunately, it exhibits tiny barriers towards decomposition either *via* simultaneous bond stretching or *via* bending;[29] as a consequence HHeF in the gas phase would not be a stable molecule but an extremely short lived species, with a lifetime in the picosecond range.[29] The presence of light hydrogen facilitates tunneling: HHeF is predicted to decay by tunneling even in its lowest vibrational state; the H → D substitution has a beneficial effect for the lifetime pushing it to the nanosecond range.[29] Despite all its discouraging features HHeF contains 'real' chemical bonds – dissociation of this reactive species along the lowest energy pathway leads to huge rearrangement of electron density: two chemical bonds are broken and a new one (H–F) is formed. Recent calculations predict that complexation with alkali metal cations and various small molecules also does not lead to sufficient stabilization of HHeF.[30]

M(I)FHeO (M = Cs, NMe_4) described by Grochala are two more candidates for neutral He-containing molecules.[31] These are derivatives of the metastable $^{-}$FHeO anion, first theorized by Hu *et al.* in 2005.[32] The anion itself is predicted to exhibit a very short He–O bond of 1.152 Å which is quite close to the sum of covalent radii of He and O (0.94 Å); the He···F distance is large (1.653 Å) while pointing to anionic character of F.[31] Simultaneously, He is quite positively charged, with the Mulliken charge exceeding +0.2 *e*. Attachment of large cations of small Lewis acidity to the anion seems to preserve metastability of the species but the energy of dissociation along the He–O stretching coordinate decreases substantially, from 0.55 eV for $^{-}$FHeO to 0.19 eV for CsFHeO.[31] This is not far from the energy of the zero-point He–O vibration (1117 cm^{-1} or 0.14 eV) suggesting that CsFHeO would be a chemically fragile species. Moreover, crossing of the singlet–triplet potential energy surfaces takes place for the He···O internuclear separation of 1.36 Å, at an energy of 0.115 eV above the minimum of the singlet surface; only the ground vibrational level is located below the crossing point (at 0.07 eV). The bending channel offers another pathway for dissociation, now to CsOF and He (the lowest energy products).

Although CsFHeO may seem to be an exotic local minimum, yet it contains real short chemical bonds to helium. The hole of over +0.2 *e* in the $1s^2$ manifold is probably the largest ever computed for the He atom in a neutral molecule. Disintegration of these species is a true chemical reaction, with the He–O bond being broken and the O–F bond being formed. The related NMe_4FHeO is calculated to exhibit a very short He–O bond length of *ca.* 1.1 Å (at the MP2 level only, due to system size) which is over 0.2 Å shorter than that for its Cs^+ sibling (also MP2).[31] NMe_4FHeO, which most probably has very similar stability to that of the $^{-}$FHeO anion, now awaits reexamination with more advanced quantum mechanical treatments.

The theoretical predictions described here are exciting; regretfully, none of these systems have been synthesized to date. In the current contribution we aim to enlarge the pool of the species containing chemically bound helium, so that they could be searched for in experiments. First we report the results of our calculations for the HeO molecule in the external electric field; the outcome of these calculations guided us towards $(HeO)(LiF)_2$ and several related molecular systems. We found that $(HeO)(LiF)_2$, which exhibits a short He–O chemical bond, is a true local minimum on the potential energy surface at the CCSD(T) computational level, and we discuss selected properties of this intriguing species.

Theoretical calculations

We have used various levels of theory, ranging from Density Functional Theory (DFT) with the B3LYP functional for initial screening, *via* Hartree–Fock (HF) calculations followed by a Møller–Plesset correlation energy correction truncated at the second or fourth order (MP2, MP4), to the coupled cluster calculations using double or single and double substitutions from the Hartree–Fock determinant, CCD and CCSD, respectively, as well as including triple excitations non-iteratively, CCSD(T). All optimizations were followed by harmonic frequencies calculations for the most abundant isotopes (^{4}He, ^{7}Li).

While studying the HeO molecule in the electric field with the CCSD(T) method we have noticed that choice of the basis set (Pople's triple-zeta 6-311++G** *vs.* Dunning's correlation consistent cc-pv2Z, cc-pv3Z, cc-pv4Z, cc-pv5Z) has little effect on the position of the minimum on the potential energy surface (PES), as well as on the dissociation energy (*cf.* ESI‡), and we have proceeded with calculations using Pople's basis also for more complex chemical systems.[32]

Dissociation energies (eqn. (2)) are given with zero-point energy correction but without taking of the basis set superposition error into account.

The calculations were performed with Gaussian'09[33] (most results) and VASP[34] (only for the ELF function from the DFT/GGA calculation for a molecule inside the 10 × 15 × 13 Å *Pmm*2 unit cell which enables a 10 Å separation between molecules; molecular geometry taken from the CCSD(T) calculation; cutoff 600 eV).

Results and discussion

1 General strategy for stabilizing He–O chemical bonding

Early on, it was realized that – since the He atom has an appreciable ionization potential of 24.6 eV but null electron affinity – a partial depletion of its 1s^2 electron density is required to stabilize chemical connections of He. The He atom must become *positively* charged while serving as a Lewis base towards an appropriate acid; energy of an empty orbital of an acid should fall reasonably close to the energy of a 1s^2 shell of He to facilitate bonding. Spatial extent of acid's orbitals should also be similar to that of the 1s^2 function of He; acid's orbitals should be compact to promote good overlap within a chemical bond.

A singlet oxygen atom (2s^{2}2p^4) has been selected as helium's counterpart in this study due to the presence of one empty ('acidic') low-lying 2p orbital (at −13.6 eV) as well as of the formally occupied 2s function (at −32.3 eV). The energy of an sp hybrid at an O atom (taken tentatively as an average of 2s and 2p orbital energies), equals *ca.* −23 eV and thus falls close to the energy of a 1s^2 pair at He, which in turn could lead to bonding. But to achieve this, an O atom should first be either excited or polarized in the electric field so that a significant depopulation of its 2s^2 shell could be achieved. This is why we will first take a look at the HeO molecule placed in an external electric field.

2 The HeO molecule in an external electric field

Inspection of the potential energy surface (PES) of the lowest lying singlet and triplet states of the HeO molecule in the absence of an external electric field reveals that the molecule is not bound (Fig. 1), in agreement with the previously published results.[35] The situation changes dramatically, however, upon application of the external electric field oriented parallel to the molecular axis and in the direction which corresponds to electron flow from He to O. The field, *E*, of 0.02 au (1 atomic unit = 514.22 GV m^{-1}) induces the appearance of the small yet chemically meaningful minimum at the singlet PES (at 1.31 Å). The He–O separation is somewhat longer than the sum of the covalent radii of O and He atoms (0.94 Å) yet much shorter than the sum of the corresponding van der Waals radii (2.92 Å). The equilibrium bond length, *R*(He–O), shifts progressively to smaller values as the external electric field increases, and reaches a value as small as 1.09 Å for $E = 0.10$ au. An energy of dissociation of the HeO molecule (measured *at the singlet PES*) under these conditions is as large as 1.52 eV (CCSD(T)/6-311++G** result) or 1.57 eV (CCSD(T)/aug-cc-pV5Z result).[33] Interestingly, the internuclear separation calculated here agrees well with that of 1.07 Å derived from single bond additive covalent radii of He and O.[36]

Clearly, a true chemical bond between He and ^{1}O is born in the external electric field.[37] The bond is polarized; an appreciable positive Mulliken charge of +0.39 *e* resides on the He atom for $E = 0.10$ au, and the molecule is a source of a dipole moment of 3.2 D; appreciable mixing of valence functions of He and O takes place for the occupied σ orbitals (ESI‡).

At all values of the electric field the triplet PES crosses the singlet surface and the crossing distance shifts up as the electric field increases. The crossing occurs at 1.33 Å for $E = 0.10$ au, and the dissociative triplet is located as much as 2.2 eV below singlet for *R*(He–O) of 2.25 Å. The rupture of the He–O bond *via* singlet–triplet crossing is naturally associated with formation of an oxygen atom in its ground triplet state. Metastability with respect to the ^{3}O product is, as we will

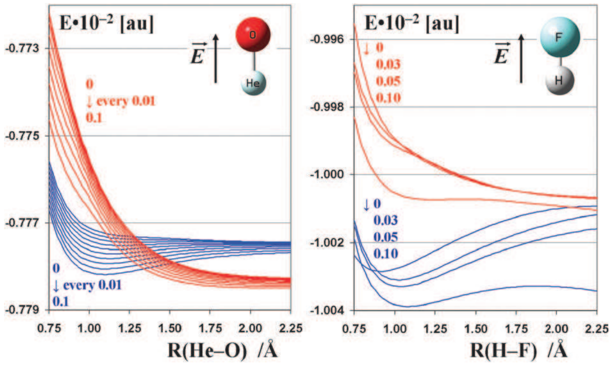

Fig. 1 Impact of the strength of the external electric field, *E* (atomic units), on the lowest singlet (blue, $^1\Sigma$) and triplet (red, $^3\Pi$) potential energy surfaces of HeO and HF molecules. Graphs show energy, $E \times 10^{-2}$ (hartree) *vs.* the interatomic separation, (Å) for ten (HeO) and four (HF) different values of electric field from 0.0 up to 0.1 au.

see later, the characteristic feature of all species containing the He–O bond.

A subsequent increase of the electric field from the value of 0.10 au does not lead to a further improvement of stability of the ^{1}HeO molecule. Instead, the PESs of both the singlet and triplet states substantially bend down at large interatomic separations thus heralding full ionization of a molecule to free He^+ and O^- ions for $E = 0.15$–0.20 au (ESI‡). Thus, the electric fields required for formation of the metastable He–O bond are quite substantial, and not far from the values which result in a dielectric catastrophy. The electric field of *ca.* 5 GV m^{-1} may seem vast at first, yet it is comparable to local electric fields generated in the vicinity of small ions. For example, an electric field generated by a point charge of 1 *e* at the distance of 2 Å is as large as 135 GV m^{-1}. Real ions having a finite size and diffuse electron distribution, such as for example F^- or Cl^-, generate smaller yet still substantial fields. This is why attachment of light halide anions at the He end of the HeO molecule yields hypothetical metastable ($X^- \cdots HeO$) anions which are protected from decomposition by energy barriers.[31,32]

3 HeO *vs.* HF: isoelectronic or not?

With its eight valence electrons the fragile ^{1}HeO molecule formed at an electric field of 0.10 au might formally be considered isoelectronic to a much more stable ^{1}HF (and also to the $^1HeF^+$ cation). But are HeO and HF molecules really isoelectronic?

Indeed, similarities may be noticed in the nature of the ground and excited states of HeO and HF. For example, both molecules exhibit a single σ-type bond (*cf.* the molecular orbital diagram, Fig. 2) while their first vertically excited dissociative triplet state has *Π* symmetry. The corresponding σ, σ* and lone pair π MOs of both species may be easily matched (Fig. 2). Secondly, the dipole moment for ^{1}HeO is oriented similarly as for ^{1}HF at comparable Mulliken charges for He (+0.38 *e*) and for H (+0.30 *e*). However, there are also substantial qualitative and quantitative differences in chemical bonding for these species:

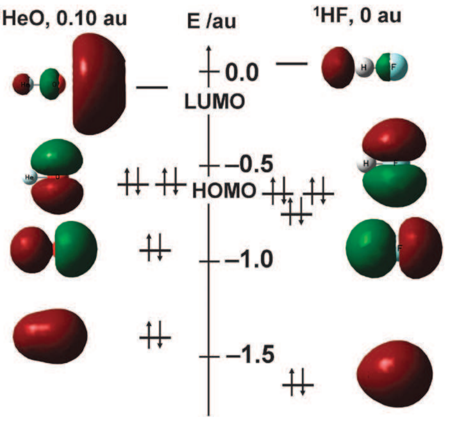

Fig. 2 The molecular orbital structure of the HeO ($E = 0.1$ au) and HF ($E = 0$ au) molecules in their lowest singlet states (from the B3LYP single-point calculation at geometries preoptimized with CCSD(T)). The low-lying occupied Kohn–Sham MOs corresponding mostly to 1s of O and F have not been shown.

1 The first excited triplet state is always found above the ground singlet state for HF but for HeO at large internuclear separations the triplet state has lower energy for singlet (Fig. 1).

2 An increase of the electric field from 0 to 0.10 au leads to elongation of the H–F bond, but the He–O bond shortens.

3 The electric field required for dielectric breakdown of the HF molecule (*i.e.* dissociation to H^+ and F^-) is substantially smaller than for the HeO molecule, due to a more ionic nature of the former.

4 The bond dissociation energy of the HeO molecule (at the field of 0.10 au) is lesser than a quarter of the dissociation energy of HF (at zero field).

5 Spin density in the vertically excited π state is centered predominantly on the p-block atom for HeO (1.60 *e* at O) yet on the s-block atom for HF (1.35 *e* at H) (ESI‡).

6 The lowest unoccupied molecular orbital (LUMO) is usually centered on a less electronegative element in the system. For HF this corresponds to the H atom, but for HeO this is not He but rather the O atom.

7 The splitting on the energy scale between the σ and σ* MOs is larger for HF than for HeO testifying to larger stability of the single bond or HF.

8 The Pearson's hardness (estimated as half of the HOMO/LUMO gap) is larger for HF than for HeO showing that the former molecule is harder and less reactive than the latter.

The differences between HeO and HF come largely from remarkably different valence bond descriptions of these molecules: in the case of HF it is formally the F^- base which coordinates the H^+ acid ($F^- \rightarrow H^+$), while an analogous description of HeO (*i.e.* O^{2-} base coordinating He^{2+}) is far from realistic; it is more fair to say that the weak He^0 base weakly coordinates with the ^{1}O acid ($He^0 \rightarrow O$). The reversal of acid/base functions of s- and p-block elements is apparent. In terms of the electron count, HeO would be genuinely isoelectronic to HF only if the latter species were best described by an unusual $H^- \rightarrow F^+$ valence bond structure, which is obviously far from true.

4 $(HeO)(LiF)_2$: ^{1}HeO inside a molecular ferroelectric cavity

Stabilization of ^{1}HeO in an external electric field as well as in the vicinity of a point charge – resembling small X^- anions (in ($X^- \cdots HeO$) where X = F and Cl[31,32]) suggest that other more complex systems could be found where atomic constituents provide electrostatic potential required for formation of the He–O bond. One such possibility is offered by a pair of parallel electric dipoles with an empty space between them ready to host the HeO molecule (Fig. 3). The orientation of electric dipoles pictured in Fig. 3 is obviously energetically disfavoured. Nevertheless, it is sometimes observed (as a collective and complex phonon-related phenomenon) for numerous extended solid state materials: ferroelectrics, where even a macroscopic dielectric polarization is achieved. This is why an empty space between two dipoles pictured in Fig. 3 could be provisionally referred to as a *molecular ferroelectric cavity*.[38,39]

$(HeO)(LiF)_2$ (Fig. 4 and Table 1) provides the first example of a hypothetical metastable molecule where bond polarization of the central $He^{\delta+}O^{\delta-}$ unit is achieved by attachment of two LiF dipoles. This species turned out to be a genuine minimum

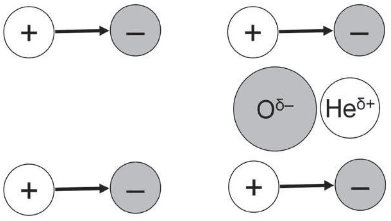

Fig. 3 A molecular ferroelectric cavity composed of two non-collinear parallel molecular dipoles: empty cavity (left) and one filled with a polarized HeO molecule forming an antiparallel electric dipole (right).

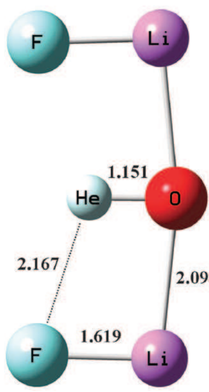

Fig. 4 Optimized molecular geometry of the planar $(HeO)(LiF)_2$ molecule (C_{2v}) in its lowest singlet state (CCSD(T)/6-311++G** results). Distances are in Å.

on the singlet PES, with a very short He–O separation of 1.151 Å at the CCSD(T) level. This value is identical within the error margin to the one calculated for ($F^{-}\cdots HeO$) with the same method and basis set, and simultaneously not much longer than 1.09 Å calculated for the most strongly bound HeO molecule in the optimum electric field (Section 2). The behaviour of $(HeO)(LiF)_2$ is in strong contrast with the situation encountered for (HeO)(LiF) (with one LiF unit), which we have found to be essentially unbound. The lack of stability of (HeO)(LiF) has been noticed before also by Li *et al.*[32] Clearly, there are substantial many-body effects in operation, as typical for mutual polarization phenomena. Certainly, the presence of the $He^{\delta+}O^{\delta-}$ dipole separating the LiF dipoles of the $(LiF)_2$ sandwiched in antiparallel orientation helps to stabilization of the otherwise unstable empty cavity.

The symmetry-unconstrained geometry optimizations for $(HeO)(LiF)_2$ have yielded the planar molecule of C_{2v} symmetry for all computational methods applied (Table 1). The calculated He–O bond length progressively elongates from 1.093 Å to 1.151 Å in the series: MP2 < MP4 < CCD < CCSD < CCSD(T) but the difference between the CCSD and CCSD(T) result is as small as 0.002 Å.[32] Interestingly, the standard B3LYP density functional theory is incapable of reproducing a short He–O bond; this signifies a strongly correlated nature of $(HeO)(LiF)_2$.

Charge distribution for $(HeO)(LiF)_2$ departs from what is expected for three dipole moments interacting in a purely electrostatic manner. Mulliken population analysis suggests some degree of charge transfer occurring between (LiF) and (HeO) units, with the (HeO) unit attaining a partial positive (+0.18 *e*) and the (LiF) unit a partial negative charge (−0.09 *e*, CCSD(T)).

Table 1 The values of the He–O and Li–F bond lengths (R/Å), the harmonic frequencies of the He–O stretching and Li–F stretching modes and of the softest mode detected (ν/cm^{-1}), Mulliken charges on atoms (q/e), electric dipole moment (μ/D) and the relative energies of the first vertically excited triplet state at the optimized geometry of the singlet state (^3E–^1E/eV), and as obtained at various levels of theory for the $(HeO)(LiF)_2$ molecule. The 6-311++G(d,p) basis set was always used. Excitation energies are given without the ZPE correction

Property	MP2	MP4	CCD	CCSD	CCSD(T)	B3LYP
R(He–O)	1.093	1.130	1.143	1.149	1.151	1.335
R(Li–F)	1.624	1.626	1.611	1.615	1.619	1.656
ν(HeO)	1351	1231	1084	1102	1112	809
ν(LiF)	833	827	857	849	838	682
	835	831	860	851	842	763
ν_{min}	79	76	75	78	78	92
q(He)	+0.237	+0.221	+0.216	+0.213	+0.208	+0.193
q(O)	−0.059	−0.042	−0.036	−0.033	−0.029	−0.191
q(Li)	+0.598	+0.599	+0.595	+0.596	+0.597	+0.515
q(F)	−0.688	−0.689	−0.685	−0.685	−0.685	−0.516
μ	11.40	11.58	11.03	10.96	11.60	8.89
^3E–^1E	+3.12	+3.18	+2.18	+2.17	+2.24	+0.57

The molecule possesses a huge dipole moment of ~11 D, due to the fact that small dipole moment of the HeO unit cannot compensate for two larger ones of the LiF units. The electrostatic potential of the molecule resembles a butterfly (ESI‡).

$(HeO)(LiF)_2$ exhibits no imaginary vibrational modes at all tested levels of theory (Fig. 5 and Table 2). The softest modes at 78 cm^{-1} correspond to out-of-plane deformations of a molecule, with the entire LiF units moving against the HeO unit. The group theory predicts 12 non-degenerate vibrational modes:

$$\Gamma_{vib} = 5A_1 + 1A_2 + 2B_1 + 4B_2 \tag{1}$$

All modes are Raman active, and all modes except for A2 are IR active. The modes which significantly alter the molecule's dipole moment (symmetric stretching of the Li–F units, at 838 cm^{-1}, and in-plane bending of the Li–F···He angles) are predicted to yield the most intense IR absorption bands.

A stiff He–O vibron at 1112 cm^{-1} may be compared to the 1146 cm^{-1} one calculated for the ($F^{-}\cdots HeO$) anion at the same level of theory (CCSD(T)) testifying to the comparable strength of He–O bonds in both molecules, as far as Badger's rule is considered.[40] It is interesting that mutual interaction of LiF oscillators is rather weak, since the in-phase (A1) and out-of-phase (B2) Li–F stretching modes are split by a mere 4 cm^{-1}. The Li–O oscillators share the central O atom, so they

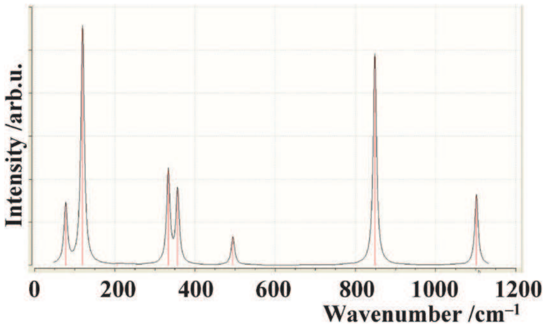

Fig. 5 The calculated IR spectrum of the $(HeO)(LiF)_2$ molecule in its lowest bound singlet state (CCSD(T)/6-311++G** result). See Table 2 for assignment.

Table 2 The harmonic frequencies, their group symmetry label (sym.), infra-red activity (IR), and character of vibration as calculated for $(HeO)(LiF)_2$ at the CCSD(T)/6-311++G(d,p) level. All modes are Raman-active. v – very, s – strong, m – medium, w – weak, ip – in plane, oop – out of plane, s – symmetric, as – antisymmetric

No.	ν/cm^{-1}	Sym.	IR	Description
1	78	B1	(m)	oop Li–HeO–Li deformation
2	78	A2	(silent)	oop $(LiF)_2$ deformation (butterfly)
3	79	A1	(vw)	ip Li–He–Li bending
4	104	B2	(vs)	ip as F–Li–He bending
5	213	A1	(vw)	ip s Li–He–Li bending + s Li–O–Li bending
6	331	A1	(vw)	ip s Li–O–Li stretching + s Li–He–Li stretching
7	340	B2	(s)	ip as Li–O–Li stretching + as Li–He–Li stretching
8	369	B1	(m)	oop Li–He–Li deformation
9	477	B2	(w)	ip as Li–He–Li stretching
10	838	A1	(vs)	ip s Li–F stretching
11	842	B2	(vw)	ip as Li–F stretching
12	1112	A1	(m)	ip He–O stretching

interact more strongly: the in-phase (A1) and out-of-phase (B2) Li–O stretching modes are split by 9 cm^{-1}.

It is instructive to analyze the molecular orbital structure of $(HeO)(LiF)_2$. Inspection of the MOs (Fig. 6) confirms the mixing between He(1s) and O(2s,2p) functions. The He atom is small enough to penetrate into the 2s orbital of O and forms a bond (*cf.* MOs at $E \approx -1$ au, Fig. 7); in addition, the O(2p) function also shows good overlap with He(1s) (*cf.* MO at $E \approx -0.75$ au, Fig. 6); we recall that such scenario has served as an inspiration for this study (Section 1). Although the F(2s) orbitals seem to mix well with the He(1s) one, yet the net bonding is weak because some occupied orbitals are He–F bonding, but others are He–F antibonding, and both effects largely cancel out.

As expected, the donor function of the molecule (HOMO, B2) is composed mostly of the combination of (2p) orbitals of F, which are perpendicular to the axis of the LiF unit; the same situation is found in a free LiF molecule. The acceptor function (LUMO) is He–O but also He–F antibonding. Occupation of LUMO with even 1 electron must lead to the decomposition into LiF, He and O fragments. Clearly, the He–O bond constitutes the weakest link of the molecule.

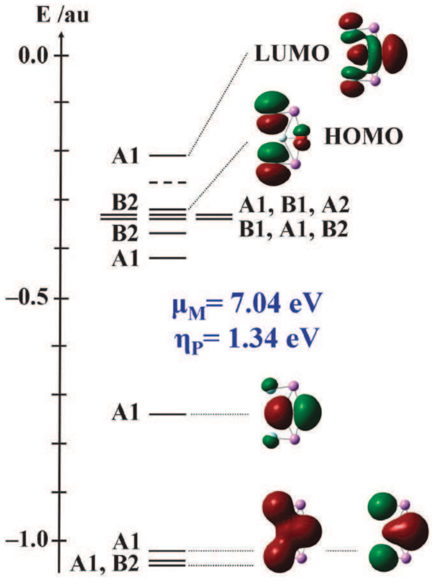

Fig. 6 Selected Kohn–Sham orbitals (shown at 0.02 *e* Å^{-3}) of the $(HeO)(LiF)_2$ molecule in its lowest bound singlet state (from the B3LYP single-point calculation at geometries preoptimized with CCSD(T)). Note the involvement of the He(1s) orbital in σ bonding to both oxygen and fluorine atoms. The thermodynamic Fermi level of the molecule is marked with the dotted line. He – white, F – pink ball.

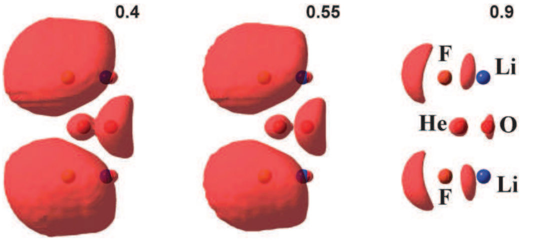

Fig. 7 The electron localization function for the $(HeO)(LiF)_2$ molecule in its lowest bound singlet state. Isosurfaces drawn at 0.40, 0.55 and 0.90.

The Fermi level of the molecule is at a large binding energy, corresponding to a large value of the Mulliken electronegativity, μ_M, of 7.04 eV,[41] which is comparable to the experimental value for Cl radical (8.3 eV). This feature renders $(HeO)(LiF)_2$ a strong oxidizer. Depopulation of the $1s^2$ shell of He is responsible for the oxidizing nature of the He compound. The calculated HOMO/LUMO gap is small, leading to Pearson's hardness, η_P, of just 1.34 eV.[42] The true band gap is certainly larger as DFT tends to underestimate it. Still, $(HeO)(LiF)_2$ is certainly reactive and fragile. As we will see in Section 6, the molecule may readily lower its energy by decomposing to harder fragments.[43]

The electron localization function (ELF)[44] for $(HeO)(LiF)_2$ calculated for electron density derived from DFT calculations, is shown in Fig. 7 for three different ELF values. Three types of regions may be distinguished corresponding to well-localized electron pairs (ELF = 0.9), one kind at F atoms (2 regions), another at the Li–F bonds (2 regions), and one at the O atom (1 region). The maximum value of ELF at the He–O bond is 0.55, not much more than 0.50 corresponding to the electron gas. Clearly, the He–O bond is not covalent but rather it arises due to anomalously strong polarization of the spherical electron cloud at the He atom. In view of the above, the bonding may be better described as a donor–acceptor interaction $He^0 \rightarrow O^0$ enforced by an electric field; nevertheless, it would be interesting to perform analysis of $(HeO)(LiF)_2$ within the framework of the valence bond method, and elucidate % contributions of various resonance structures (including ionic structure $He^{2+} \leftarrow O^{2-}$). The Bader analysis of electron density[45] is also worth performing to more precisely calculate charges assigned to various atomic pools, derive components of electric dipole (and higher) moments and to partition other properties to individual atoms.

5 Possible metastability of $(HeO)(LiF)_2$

Substantial energetic or at least kinetic stability is crucial for a molecule to exhibit long half-life thus giving researchers chance to observe it in experiment. We first examine energetic stability.

Six chemically reasonable decomposition reactions of $(HeO)(LiF)_2$ together with their calculated energies are given below (eqn (2a–f)):

$$(HeO)(LiF)_2 \rightarrow {}^1O + 2LiF + He\ (+0.43\ eV) \quad (2a)$$

$$(HeO)(LiF)_2 \rightarrow {}^3O + 2LiF + He\ (-1.86\ eV) \quad (2b)$$

$$(HeO)(LiF)_2 \rightarrow LiOF + LiF + He\ (-2.10\ eV) \quad (2c)$$

$$(HeO)(LiF)_2 \rightarrow Li_2O + F_2 + He\ (+1.\ 39\ eV) \quad (2d)$$

$$(HeO)(LiF)_2 \rightarrow {}^1O + (LiF)_2 + He\ (-2.31\ eV) \quad (2e)$$

$$(HeO)(LiF)_2 \rightarrow {}^3O + (LiF)_2 + He\ (-4.60\ eV) \quad (2f)$$

Only unimolecular reactions have been considered corresponding to $(HeO)(LiF)_2$ in isolation; obviously, bimolecular reactions would be more facile since both clustering of LiF molecules into larger clusters, and pairing of oxygen atoms in a molecule, are energetically favourable.

Dissociation of $(HeO)(LiF)_2$ along the He–O stretching coordinate (yielding 2 LiF molecules, He and ^1O) on the singlet PES requires an energy of 0.43 eV. This is twice more than for analogous reaction for CsFHeO (0.19 eV).[31] Simultaneously, the first vertically excited triplet state of $(HeO)(LiF)_2$ is located at 2.24 eV above the singlet (Table 1), again more than for CsFHeO (2.04 eV).[31] At the same time the zero-point He–O vibration has nearly identical energy for both systems (1112 cm^{-1} or 0.14 eV for $(HeO)(LiF)_2$, 1117 cm^{-1} for CsF(HeO)[31]). All features combined suggest that the singlet–triplet crossing should take place at sufficiently large He···O internuclear separation to ensure kinetic stability of $(HeO)(LiF)_2$ at low temperatures with respect to decomposition (eqn (2b)). Recall, for CsF(HeO) the crossing of the singlet–triplet PESs takes place at the He···O distance of 1.36 Å,[46] at an energy of 0.115 eV above the minimum at the singlet surface; only the ground vibrational level is located below the crossing point (at 0.07 eV). $(HeO)(LiF)_2$ is expected to behave similarly, but to be slightly more kinetically stable.

A bending channel (mostly along the B2 mode at 340 cm^{-1} or 0.04 eV) offers another important pathway for dissociation, now yielding LiOF, LiF and He. This is similar to CsFHeO where bending leads to the most stable products: He and Cs(I) hypofluorite. We have been able to detect an actual transition state (TS) for this process in the case of $(HeO)(LiF)_2$ but only at the MP4 level of theory (probably the PES is too shallow to pin down the transition state with the CCSD(T) calculation). The geometry of the transition state is shown in Fig. 8 together with the one for the undistorted molecule. The TS is at +0.04 eV with respect to the minimum; obviously, this is not much, but the ZPE of the bending mode is half of this value (0.02 eV), so one or even two anharmonic vibrational energy levels could fit into the PES along this coordinate.

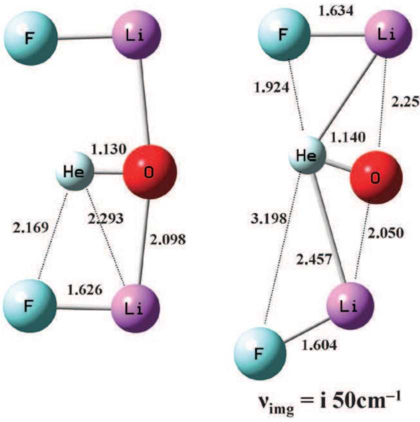

Fig. 8 The transition state geometry (right) for decomposition of the $(HeO)(LiF)_2$ molecule (left) *via* bending mode, yielding He, LiF and LiOF as products (the MP4 results). Distances are in Å.

$(HeO)(LiF)_2$ could also be viewed as a bent HeF_2 molecule with unusually long He···F contacts, which interacts with Li_2O. Thus, the last decomposition pathway could consist of expulsion of the He atom away from the cavity with concomitant formation of Li_2O and F_2 molecules (eqn (2d)). Interestingly, this route is predicted to lead to products which are less stable than the substrate by ~1.4 eV.

Clustering of dipolar LiF molecules in dimers would obviously decrease energy of the products and facilitate decomposition of $(HeO)(LiF)_2$ (compare eqn (2e) and (f) *vs.* eqn (2a) and (b). Indeed, a true energy minimum of the system of $HeOLi_2F_2$ stoichiometry corresponds to an antiferroelectric $(LiF)_2$ dimer, and He and ^3O atoms. However, LiF molecules are separated by a HeO unit in the substrate and they also need to rotate 180° to couple to their ionic counterparts. Thus, early stages of decomposition of $(HeO)(LiF)_2$ (crucial for overall kinetics of disintegration) cannot benefit from LiF···LiF dimerization.

In conclusion of this section we would like to stress that the CCSD(T) calculations predict that $(HeO)(LiF)_2$ would be dynamically stable, with no imaginary oscillation modes, and with at least one vibrational level of each type sitting inside the potential energy well.

6 Could $(HeO)(LiF)_2$ be prepared?

Synthesis of $(HeO)(LiF)_2$ would necessarily be a challenging task. First, the molecule has huge uncompensated dipole moment, so it will likely be unstable in the presence of anything but He or Ne atoms. Second, synthesis pathways towards this species are not straightforward. One of the possible substrates, the empty $(LiF)_2$ cavity is obviously unstable in ferroelectric configuration. However, synthesis from ^1O + 2LiF + He (eqn (2a)) or from Li_2O + F_2 + He (eqn (2d)) is downhill in the energy landscape, so it could be pursued. Photochemical insertion of He into the OF bond of LiOF (in the presence of LiF) is another possibility.

Obviously, any realistic attempt to synthesize fragile He-containing molecules must be carried out at very low temperatures (~10 K), where entropy effects (which diminish stability of $(HeO)(LiF)_2$) are minimized.

7 Other related systems containing the He–O bond

Prompted by remarkable features of $(HeO)(LiF)_2$ we have considered homologous systems of this kind, *viz.* $(HeO)(MF)_2$ (M = H, Na and Cs), and $(HeO)(MO)_2$ (M = Be and Mg). For none of these systems we have detected a $(HeO)(LiF)_2$-resembling minimum at the PES. Either the bond polarization of MF (or MO) units is too small (HF and BeO), or the M–F (M–O) distance is too long to accommodate the small HeO unit inside the ferroelectric cavity. Some of these systems hold together in the DFT calculations but they disintegrate already when MP2 or CC methods are applied.

Results of additional calculations for systems containing Be or Ne instead of He, discussion of similarities between He and Be and contrast between He and Ne, and considerations about possible placement of helium in Group 2 of the Periodic Table, are contained in ESI.‡

Conclusions and prospect

Large sensitivity of the singlet [HeO] molecule to electric polarization has prompted us to theoretically investigate a (HeO) unit inserted into a ferroelectric cavity composed of two parallel LiF dipoles. The CCSD(T)/6-311++G** calculations suggest that $(HeO)(LiF)_2$ is a genuine minimum on the singlet PES. Inspection of the calculated equilibrium geometry of this exotic species, its vibrational modes, and energy barriers surrounding the minimum reveals that $(HeO)(LiF)_2$ is a candidate for the neutral compound of helium. Calculations suggest that at least one vibrational state of each kind (but not more!) can be safely placed in the potential energy well surrounding the minimum so the species could be sufficiently long-lived to be detected at temperatures close to 0 K.

$(HeO)(LiF)_2$ arises from strong nonadditive polarization (many-body) effects and itself is a host of strong electronic correlation. As our exploratory study shows, the He–O bond length and some other calculated properties are quite sensitive to the basis set and the computational method applied. Although the CCD → CCSD → CCSD(T) calculations seem to reveal the converged stability of the local minimum, yet the multireference configuration interaction calculations with much larger basis sets are needed to correctly account for polarization effects, assess the shape of the PES surrounding the minimum, calculate anharmonic frequencies, and predict nuclear dynamics and lifetime of this unusual molecule with large precision. It would also be worthwhile to extend out theoretical screening to other systems, based on a similar molecular engineering principle.

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