

Relativistic *ab initio* study on PtF and HePtF[†]

Wenli Zou, Yang Liu and James E. Boggs*

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The electronic structures and spectroscopic constants of the first three low-lying electronic states ($\Omega = 1/2, 3/2,$ and $5/2$) of the linear HePtF complex were investigated by highly accurate relativistic *ab initio* methods, in which the spin-orbit coupling was taken into account, and compared with the results of PtF. It shows that the complex is significantly different from the typical van der Waals systems because of short He–Pt bond distances (1.80–1.87 Å), large He–Pt stretching frequencies (500–600 cm⁻¹), considerable binding energies (1400–2500 cm⁻¹ with corrections), and a small electron transfer from helium (about 0.06). However, the topological analysis of the electron density distribution indicates that there is strong van der Waals interaction in the He–Pt bond instead of weak covalent one.

Introduction

Since xenon hexafluoroplatinate was experimentally prepared in 1962,¹ many neutral rare-gas compounds have been found.² However, for the compounds of He and Ne, nothing is known experimentally. Nevertheless, some neutral complexes of helium were theoretically predicted in the literature to be stable or metastable (*cf.* Ref.³ for summary). Most of them belong to the so-called “strong van der Waals complexes”. For these molecules, the calculated binding energies (BE) of helium only amount to a few kcal mol⁻¹ (1000–2000 cm⁻¹), and the topological analysis of the electron density distribution shows that there is no covalent bond formed on helium.³ The first example of a strong van der Waals complex is HeBeO.⁴

In a recent paper, we reported that there are considerable interactions between helium and metal atoms in HeCuF and HeAuF with the binding energies of 1632 and 1543 cm⁻¹, respectively.³ Inspired by these two species, we expected that HeNiF and HePtF should also be metastable. In this paper we report studies of HePtF using high-level *ab initio* methods. HeNiF is not discussed here because of the strong static-correlations in the nickel atom,^{5,6} although our preparatory computations show that the binding energy of its ground state ($\Omega = 3/2$) is about 1600 cm⁻¹.

Computational details

To account for the scalar relativistic effects, relativistic effective core potentials (RECPs) were used for Pt⁷ and F⁸ to replace the inner 60 and 2 core electrons, respectively. The valence basis of Pt was cc-pwCV5Z-PP,⁷ *i.e.*, (18s15p13d5f4g3h2i)/[9s9p8d5f4g3h2i]. The exponents of the valence basis of F were taken from all-electron cc-pV5Z⁹ by deleting the first five steep s-functions, and were recontracted at the internally contracted multi-reference configuration interaction with singles and doubles (MRCI)¹⁰ level of theory, leading to (9s8p4d3f2g1h)/[5s5p4d3f2g1h]. For He, the

standard cc-pV5Z basis set was used.¹¹ These basis sets have 5-zeta quality and are abbreviated later as V5Z. In order to approximate the complete basis set limit *via* complete basis set extrapolation (CBSE),¹² the corresponding basis sets with 4-zeta quality were used as well (denoted as VQZ).

Two kinds of calculations were performed in our research for the three low-lying scalar electronic states, *i.e.*, $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$. In the multi-reference calculations, PtF and HePtF were computed with state-averaged CASSCF followed by MRCI with Davidson's cluster correction (MRCI+Q).¹⁰ There were 9 active molecular orbitals corresponding to Pt 5d6s and F 2p, whereas the Pt 5s5p, F 2s, and He 1s orbitals were always doubly occupied and correlated. In the single-reference calculations, the restricted open-shell Hartree–Fock based spin-unrestricted open-shell CCSD and CCSD(T) methods^{13,14} were used, and all the electrons except the ones replaced by RECPs were correlated, as in MRCI+Q.

Unlike the computations of HeCuF and HeAuF, the spin-orbit coupling (SOC) could not be neglected for HePtF and PtF. SOC was treated *via* the state-interaction approach¹⁵ at the CASSCF level, where the diagonal elements of the spin-orbit matrix calculated with spin-orbit RECP were later replaced by the MRCI+Q, CCSD, or CCSD(T) energies. From $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$, five Ω states could be derived, *i.e.*, (I)1/2, (I)3/2, (I)5/2, (II)1/2, and (II)3/2 with an energy gap of about 7000 cm⁻¹ between the former three and the latter two spinor states. The cases of (II)1/2 and (II)3/2 are very complex since they cross with other higher excited states. In this research we focus only on the first three states.

At the minimum of each Ω state optimized with numerical gradients, the mass weighted second derivative matrix was numerically constructed for $^{195}\text{Pt}^{19}\text{F}$ or $^4\text{He}^{195}\text{Pt}^{19}\text{F}$ by hand in order to make maximum use of the symmetry and minimize the number of displacement coordinates. The matrix elements were obtained by the 3-point finite difference scheme with a displacement of 0.01 Å. Then, the harmonic vibrational frequencies were obtained by diagonalizing the matrix. The infrared (IR) intensities were computed from the dipole moment derivative matrix at the CASSCF level of theory.

All the *ab initio* calculations were performed using the MOLPRO program.¹⁶

Institute for Theoretical Chemistry, Chemistry and Biochemistry Department, The University of Texas at Austin, Austin, Texas 78712-0165, USA.
E-mail: james.boggs@mail.utexas.edu

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Table 1 Adiabatic excitation energies (T_e), equilibrium bond distances ($R_{\text{Pt-F}}$ and $R_{\text{He-Pt}}$), binding energies (BE), and vibrational frequencies (ν_1 , ν_2 , and ν_3) for PtF and HePtF

State	Method	T_e/cm^{-1}	$R_{\text{Pt-F}}/\text{\AA}$	$R_{\text{He-Pt}}/\text{\AA}$	BE ^a /cm ⁻¹	Frequency ^b /cm ⁻¹			Components ^c (%)
						ν_1	ν_2	ν_3	
PtF									
1/2	MRCI+Q	0	1.895					587	² Σ^+ (69) + ² Π (31)
	CCSD	0	1.894						² Σ^+ (69) + ² Π (31)
	CCSD(T)	177	1.891					590	² Σ^+ (66) + ² Π (34)
3/2	DFT ^d	855	1.894					597	
	MRCI+Q	205	1.878					590	² Π (83) + ² Δ (17)
	CCSD	111	1.878						² Π (82) + ² Δ (18)
	CCSD(T)	0	1.874					593	² Π (83) + ² Δ (17)
	DFT ^d	0	1.873					600	
5/2	Expt. ^e	0	1.874					580	
	MRCI+Q	1019	1.905					604	² Δ (100)
	CCSD	725	1.904						² Δ (100)
	CCSD(T)	747	1.905					594	² Δ (100)
DFT ^d	1347	1.915					587		
HePtF									
1/2	MRCI+Q	0	1.884	1.835	2290	381	543 (11)	632 (42)	² Σ^+ (74) + ² Π (26)
	CCSD	0	1.881	1.828	2432				² Σ^+ (73) + ² Π (27)
	CCSD(T)	0	1.881	1.828	2482		560 (13)	639 (65)	² Σ^+ (71) + ² Π (29)
3/2	MRCI+Q	500	1.866	1.873	2002	433	498 (7)	637 (48)	² Π (81) + ² Δ (19)
	CCSD	401	1.864	1.861	2143				² Π (81) + ² Δ (19)
	CCSD(T)	76	1.862	1.860	2229		524 (6)	645 (75)	² Π (82) + ² Δ (18)
5/2	MRCI+Q	546	1.901	1.801	2770	69	589 (14)	638 (30)	² Δ (100)
	CCSD	326	1.899	1.797	2832				² Δ (100)
	CCSD(T)	246	1.900	1.798	2807		597 (20)	641 (45)	² Δ (100)

^a Without corrections. ^b Numbers in parentheses are IR intensities (km/mole). The quantum numbers ν_1 , ν_2 , and ν_3 refer to bending, He–Pt stretching, and Pt–F stretching, respectively. ^c Computed at the corresponding equilibrium structures. ^d Reference¹⁷. ^e Reference¹⁸. $R_{\text{Pt-F}}$ corresponds to R_0 instead of R_e .

Results and discussion

To estimate the accuracy of the calculation methods for HePtF, the low-lying spinor states of PtF were first calculated at the same levels of theory. By using four-component relativistic density functional theory (DFT), Liu and Franke¹⁷ predicted that the ground state of PtF is $\Omega = 3/2$, and is different from that of PtH ($\Omega = 5/2$). This was further confirmed by a very recent microwave spectroscopy study.¹⁸ The published results as well as ours of PtF are summarized in Table 1.

It can be seen that the $\Omega = 5/2$ state is ² Δ dominant, and both $\Omega = 1/2$ and $3/2$ states are mixtures of ² Σ^+ + ² Π and ² Π + ² Δ , respectively. Among these states, CCSD(T) obtains $\Omega = 3/2$ as the ground state, being in agreement with the experimental and the DFT results, whereas MRCI+Q and CCSD erroneously give $\Omega = 1/2$ as the ground state. Obviously the higher-order correlations which are absent in MRCI+Q and CCSD are very important for the small energy gap between the $\Omega = 1/2$ and $3/2$ states of PtF. Nevertheless, the computed bond distances and vibrational frequencies by all the three methods are in good agreement with the DFT and available experimental values. It is expected that a similar accuracy can be achieved also for HePtF.

The spectroscopic constants of HePtF are listed in Table 1 as well. We can see that all of the methods support $\Omega = 1/2$ as the ground state. However, for the first excited state, MRCI+Q and CCSD(T) support $\Omega = 3/2$, being inconsistent with CCSD. Since MRCI+Q or CCSD(T) is more accurate than CCSD in the reference wavefunction or correlations, we can conclude that

the first excited state should be $3/2$. Similar to HeCuF and HeAuF,³ all the three spinor states of HePtF are computed to be linear, which are supported by the real bending vibrational frequencies (ν_1). Compared with PtF, the Pt–F distances in HePtF are significantly shortened by about 0.01 Å (for $1/2$ and $3/2$) or 0.005 Å ($5/2$). This phenomenon has also been found in HeCuF and HeAuF³ as well as other analogues.³ The short He–Pt distances (1.80–1.87 Å), the large He–Pt stretching frequencies (500–600 cm⁻¹), and the considerable binding energies of helium (2000–2800 cm⁻¹; uncorrected) also can be found from our results, which indicate that there is relatively strong interaction between the helium and platinum atoms in HePtF.

Since the binding energies are not sufficiently large, corrections must be included at the fixed geometries *via* the zero point energy (ZPE), basis set superposition error (BSSE),¹⁹ and CBSE,¹² as shown in Table 2. In the CCSD(T) calculations of HePtF, the bending modes in ZPE were taken from the results of MRCI+Q since the Hartree–Fock method can not describe the excited states properly. The basis sets used here are quite large, so both the BSSE and the CBSE corrections are quite small, and ZPE contributes the dominant corrections for the binding energies. After including these corrections, it can be seen in Table 2 that the states still have considerable binding energies, being 1400–2500 cm⁻¹ by the MRCI+Q and CCSD(T) methods.

For comparison, we may estimate the lower limit of the van der Waals distance and the standard covalent distance for the He–Pt bond by using the atomic van der Waals radius (R_{vdw}),²⁰ ionic radius (R_{ion}),²¹ and covalent radius (R_{cov})²² with the following

Table 2 Corrected binding energies of HePtF (cm⁻¹)

Methods ^a	1/2		3/2		5/2	
	MRCI+Q	CCSD(T)	MRCI+Q	CCSD(T)	MRCI+Q	CCSD(T)
uncorrected	2290	2482	2002	2229	2770	2807
ZPE (PtF)	+293	+295	+295	+297	+302	+297
ZPE (HePtF) ^b	-969	-981	-1000	-1017	-683	-688
BSSE	-36	-43	-35	-41	-41	-48
CBSE	+166	+123	+133	+83	+145	+118
Total	1745	1877	1395	1551	2493	2486

^a ZPE, BSSE, and CBSE represent the zero point energy, basis set superposition error, and complete basis set extrapolation, respectively. ^b Bending modes are taken from the MRCI+Q results.

Table 3 Mulliken charges for the scalar states of PtF and HePtF, computed by the MRAQCC method at the CCSD(T) optimized structures

	State	Pt	F	He
PtF	1/2 (² Σ ⁺)	+0.51	-0.51	
	3/2 (² Π)	+0.48	-0.48	
	5/2 (² Δ)	+0.51	-0.51	
HePtF	1/2 (² Σ ⁺)	+0.46	-0.52	+0.06
	3/2 (² Π)	+0.42	-0.48	+0.06
	5/2 (² Δ)	+0.47	-0.53	+0.06

formulae,²³ $R_{\text{vdW}}(\text{He-Pt}) = R_{\text{vdW}}(\text{He}) + R_{\text{ion}}(\text{Pt}^+) = 1.40 + 1.24 = 2.64 \text{ \AA}$, and $R_{\text{cov}}(\text{He-Pt}) = R_{\text{cov}}(\text{He}) + R_{\text{cov}}(\text{Pt}) = 0.46 + 1.23 = 1.69 \text{ \AA}$.

For different states the optimized $R_{\text{He-Pt}}$ values range in 1.80–1.87 Å (see Table 1) by different methods, being much shorter than $R_{\text{vdW}}(\text{He-Pt})$ and closer to $R_{\text{cov}}(\text{He-Pt})$.

At the structures optimized by CCSD(T) with SOC, the Mulliken charges were calculated for the dominant scalar state of each spinor state by the internally contracted multi-reference average quadratic coupled-cluster method (MRAQCC),^{24,25} which can be looked on as an approximation to multi-reference CCSD. The computed Mulliken charges are listed in Table 3. For the fluorine atom, we see that there is no significant change in the Mulliken charges, and a small electron transfer (about 0.06 charge for all the three states) takes place from the He atom to the Pt atom. Again, this implies the interaction between He and Pt.

Although the interaction between He and Pt is quite strong according to the above analysis, it does not necessarily imply a covalent He–Pt bond. To identify the covalent bond, the negative Laplacian [$\nabla^2\rho(r)$] at the critical point (r_c) is often used as an indicator, but fails for some covalent molecules (e.g., the Laplacian is positive for BeO^{4a} and F₂²⁶). So it is a necessary condition instead of a sufficient one.^{4a} Because of this reason, Cremer and Kraka²⁶ suggested the use of $H(r) = G(r) + V(r)$ (local kinetic energy density and local potential energy density, respectively) for this problem. Here we use a modified version of Bader's AIM-PAC program²⁷ to analyze the electron density distribution of the ground state. The wavefunction file was generated at the MRAQCC level of theory and the format was then converted by our Molden2WFN program. Because of the limitation of the AIM-PAC program, the all-electron relativistic ANO-RCC basis set²⁸ with 4-zeta quality was adopted for all the atoms. At the r_c point between He and Pt, it is found that the $\nabla^2\rho(r_c)$ values are positive (13.57, 10.84, and 14.27 e/Å⁵ for the scalar states ²Σ⁺, ²Π, and ²Δ, respectively) whereas the $H(r_c)$ values are negative but very small (−0.03, −0.08,

and −0.09 Hartree/Å³). Thus HePtF is a strong van der Waals complex with small covalent interaction. Perhaps it is difficult to define a clear borderline between strong van der Waals and weak covalent bonds.

In order to make clear the origin of the He–Pt bond, the natural bond orbital (NBO) analysis based on DFT(PBE0)/VQZ was carried out by the NBO program²⁹ via the PC-GAMESS/Firefly³⁰ interface. Since PC-GAMESS/Firefly cannot treat h -functions in the RECP and basis set, another RECP with 60 core electrons³¹ was used for Pt, and the valence basis set were recontracted accordingly. Similar to the case of HeAuF,³ NBO shows that the dominant interaction comes from the charge transfer from He 1s to a weakly-occupied antibonding orbital between F 2p_σ and Pt 6s with a certain amount of Pt 5d_σ. In addition, the analysis also gives a NBO charge of +0.07 on the helium atom, being very close to the Mulliken one (cf. Table 3), and a Wiberg bond index of 0.15 for the He–Pt bond.

Conclusions

The lowest three spinor states ($\Omega = 1/2, 3/2,$ and $5/2$) of the linear HePtF molecule have been investigated by highly accurate relativistic *ab initio* methods. All evidence, including the structures, vibrational frequencies, binding energies, and Mulliken charges, show that the He–Pt bond is much stronger than typical van der Waals interactions. However, no covalent contributions between He and Pt atoms can be found from the topological analysis of the electron density distribution, so HePtF is a kind of uncommonly strong van der Waals complex, similar to the case of HeCuF,³ HeAuF,³ and HeBeO.⁴

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