Argon matrix effect on the geometry and infrared spectrum of $H_2C=MH_2$ (M = Ti, Zr, Hf): A theoretical study

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Abstract

Within the framework of polarizable continuum model with integral equation formalism (IEF-PCM), an argon matrix effect on the geometry and infrared frequencies of the agostic $H_2C=MH_2$ (M = Ti, Zr, Hf) methylidene complexes was investigated at B3LYP level of theory with the 6-311++G(3df,3pd) basis set for C, H, and Ti atoms and Stuttgart/Dresden ECPs MWB28 and MWB60 for the Zr and Hf atoms. At the B3LYP/IEF-PCM level of theory, $H_2C=TiH_2$ was optimized to an energy minimum having a pyramidal structure. The calculated dipole moment of this structure is 3.06 D. The B3LYP/IEF-PCM simulations gave the three complexes' agostic angle $\angle HCM$ (°), distance $r(H \cdots M)$ (Å), and C=M bond length $r(C=M)$ (Å) as follows: $\angle HCTi = 87.4$, $r(H \cdots Ti) = 2.079$, $r(C=Ti) = 1.803$; $\angle HCZr = 89.3$, $r(H \cdots Zr) = 2.243$, $r(C=Zr) = 1.956$; $\angle HCHf = 94.7$, $r(H \cdots Hf) = 2.343$, $r(C=Hf) = 1.972$. As a comparison, the B3LYP simulations gave the values as follows: $\angle HCTi = 91.5$, $r(H \cdots Ti) = 2.150$, $r(C=Ti) = 1.811$; $\angle HCZr = 92.9$, $r(H \cdots Zr) = 2.299$, $r(C=Zr) = 1.955$; $\angle HCHf = 95.6$, $r(H \cdots Hf) = 2.352$, $r(C=Hf) = 1.967$. As far as the MH_2 symmetric and asymmetric stretching and CH_2 wagging frequencies are concerned, the IEF-PCM calculated values are in better agreement with the experimental argon matrix ones than those calculated based on a gas phase model.
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1. Introduction

Agostic interactions, which play important roles in the activation of alkane C–H bond and elimination of α- and β-hydride, have been found in a number of transition metal alkylidene complexes containing a carbon–metal double bond [1–3]. These complexes are useful for developing catalysts in alkene metathesis and alkane activation reactions. Recently, the simplest agostic alkylidene complexes $H_2C=MH_2$ (M = Ti, Zr, Hf) were identified by comparing their neon and/or argon matrix infrared spectra to the density functional theory (DFT) frequency calculations [4–6]. However, these calculations were based on a gas-

phase model and the rare gas matrix effect was not modeled. Previous experiments have demonstrated that the rare gas matrix has an evident effect on the infrared spectrum of a complex and that the matrix-induced frequency shift is remarkable for some fundamental vibrational modes [7–13]. Cho et al. have modeled the argon matrix effect on the geometry and infrared frequencies of $H_2C=HfH_2$ by supermolecule method at MP2 level of theory [6]. Their investigations indicate that, (i) one single argon atom complexation results in only slight distortion of the complex and +5 to −9 cm^{-1} shifts in the most intense infrared absorbing modes; (ii) two argon atoms complexation with one above and one below the $H_2C=HfH_2$ plane also results in little change of the molecular structure (agostic angle still 81.6°) and the Hf–H stretching modes continue to red shift while the other strong modes blue shift. However, worthy to note is that,

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it is the DFT rather than the MP2 results that were used to compare with the experimental frequencies.

As a matter of fact, the matrix isolation infrared spectroscopic experiments [5,6] have already demonstrated an apparent matrix effect for the complexes $H_2C=ZrH_2$ and $H_2C=HfH_2$. For example, the symmetric and asymmetric H_3ZrH_4 (see Fig. 1 for atoms numbering) stretching frequencies are 1581.0 and 1546.2 cm^{-1}, respectively, in the Ne matrix while they become 1553.9 and 1504.3 cm^{-1} in the Ar matrix [5]. The Ne to Ar matrix shifts are -27.1 and -41.9 cm^{-1}. On the other hand, the Ar matrix C=Zr stretching and H_1CH_2 (see Fig. 1 for atoms numbering) wagging frequencies are 747.1 and 630.2 cm^{-1}, which are red-shifted rather than blue-shifted as compared to the Ne matrix values (757.0 and 634.5 cm^{-1}) [5]. Thus it may be necessary to model the matrix effect again so as to understand better the matrix infrared spectrum and molecular structure of the three complexes.

Recently, we have simulated the Ar matrix effect on the infrared fundamental frequencies of nitric acid [14] and *trans*-nitrous acid [15] molecules using polarizable continuum model with integral equation formalism (IEF-PCM). Most of the simulated matrix-induced frequency shifts are in reasonable agreement with the experimental ones. In addition to these two single molecules, we have also simulated the argon matrix effect on the $\nu_s(X–H)$ (X = F, Cl) of seven hydrogen-bonded complexes within the framework of IEF-PCM. The agreement between simulation and experiment is fairly good for five of the seven complexes [16,17]. In this paper, we will also use the IEF-PCM method to simulate Ar matrix effect on the geometry and infrared spectrum of the $H_2C=MH_2$ complexes. The simulated frequencies will be compared to the experimental ones as possible. The Ne matrix effect is not selected for modeling because the solvent neon should be defined (such as the designation of solvent dielectric constant and radius) first by ourselves while the solvent argon has already been well defined by the available Gaussian programs.

Finally, it's necessary to recall the previous B3LYP calculation results obtained from a gas-phase model before considering an argon matrix effect on the $H_2C=MH_2$ complexes. The singlet $H_2C=TiH_2$ complex was optimized to a planar C_s structure by the basis set 6-311++G(2d,p) or 6-311++G(3df,3pd) [4]. The triplet $H_2C–TiH_2$ state is less stable than the singlet state by 14 kcal/mol when the 6-311++G(2d,p) basis set was applied [4]. Using the MWB28 effective core potential (ECP) for Zr and 6-311++G(3df,3pd) for C and H, the global minimum of $H_2C=ZrH_2$ is found to have a C_1 structure far from planar (the C, Zr, H_3, and H_4 atoms form a pyramid and the

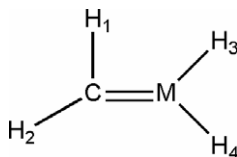dipole moment of the molecule is 3.59 D) [5]. Using the LANL2DZ ECP for Zr and the same basis set for C and H, the lowest triplet $H_2C–ZrH_2$ state is 17.0 kcal/mol higher in energy than the singlet state [5]. Using the MWB60 ECP for Hf and 6-311++G(2d,p) for C and H, the singlet $H_2C=HfH_2$ is almost planar at carbon but clearly pyramidal at hafnium [6]. Using the MDF10, MWB28, and MWB60 ECPs for Ti, Zr, and Hf, respectively, and 6-311++G(3df,3pd) for C and H, all the three complexes demonstrate an agostic C–H_1···M interaction. The interaction decreases following the increase of the atomic number of the metals [6,18].

On the other hand, Grunenberg et al. have evaluated the agostic bond of $H_2C=TiHF$ (the geometry of which is very similar to that of $H_2C=TiH_2$) using various theoretical methods and found that the B3LYP is in line with the CCSD(T) level of theory, as far as the agostic bond strength and the sign of the out-of-plane mode are concerned [19]. Roos et al. have studied the agostic interaction of the methylidene metal dihydride complexes $H_2C=MH_2$ (M = Y, Zr, Nb, Mo, Ru, Th, or U) using the CASSCF/CASPT2 and the B3LYP methods, and concluded that, in general, both the methods give the same description of the agostic effects in these complexes, even if they differ in details [20]. More importantly, they pointed out that the experimental vibrational frequencies have been accurately predicted by the harmonic B3LYP frequency calculations within the limits expected [20].

2. Computational details

All quantum chemical calculations were performed with the GAUSSIAN 03 programs [21]. The density functional theory applied is B3LYP (Becke's three parameter hybrid functional [22] in conjunction with Lee, Yang, and Parr's correlation functional [23]). An argon matrix effect on the geometry and infrared fundamental frequencies of the singlet $H_2C=MH_2$ (M = Ti, Zr, Hf) complexes was simulated by IEF-PCM [24–26] with designating the *Solvent* option as *argon* (Eps = 1.43, RSolv = 1.875). Here, Eps and RSolv refer to the dielectric constant and radius (in Angstroms) of the solvent argon. The applied atomic radii come from the UA0 model and an individual sphere is placed on the agostic hydrogen atom (using the SPHEREONH = N option of the IEF-PCM keyword). For C, H, and Ti atoms, the 6-311++G(3df,3pd) [27] basis set is used. For Zr and Hf atoms, the Stuttgart/Dresden ECPs MWB28 and MWB60 and the GTO valence basis sets (8s7p6d)/[6s5p3d] and (8s7p6d)/[6s5p3d] [28] are applied. In geometry optimizations of the three singlet complexes, tight convergence criteria were applied to reduce the computational errors and thus to ensure significance of small bond length differences (the convergence criterion for the "Maximum displacement" is 6.0×10^{-5} a.u., i.e. 3.2×10^{-5} Å) and reliability of frequencies computed subsequently. The modified GDIIS (Geometry optimization using Direct Inversion in the Iterative Subspace) algorithm [29] was

Fig. 1. Atoms numbering of the $H_2C=MH_2$ (M = Ti, Zr, Hf) complexes.

applied in the optimizations. The optimized stationary points were confirmed to be true minima rather than transition states or higher-order saddle points by followed harmonic frequency calculations.

For the singlet $H_2C=TiH_2$ complex similar calculations have been repeated at the BPW91 [30,31] and the MP2 [32–34] levels of theory for comparing with the results calculated at the B3LYP level of theory.

3. Results and discussions

Geometric parameters as well as infrared frequencies and intensities of the singlet $H_2C=MH_2$ (M = Ti, Zr, Hf) complexes calculated at the B3LYP level of theory are listed in Table 1 (columns labeled as "Gas"). These calculation results correspond to the *gas-phase* molecules. For the two complexes $H_2C=ZrH_2$ and $H_2C=HfH_2$ the geometric parameters optimized by the tight convergence criteria, as shown in Table 1, have little difference from those optimized by the default convergence criteria, as shown in Fig. 7 of Ref. [6]. For the $H_2C=TiH_2$ complex the present calculations show that the stationary planar C_s structure is a transition state rather than a true minimum,

which is different from the B3LYP result of Andrews et al. [4]. The imaginary frequency ($-51.5 \, cm^{-1}$) corresponds to the H_3TiH_4 wagging vibration. Distorting the complex along the H_3TiH_4 wagging mode and optimizing the complex again produce a true minimum with C_1 symmetry. However, the C_1 structure is only slightly non-planar, as shown in Fig. 2a and second column of Table 1 (the four dihedral angles), and more stable than the C_s one by merely 0.0065 kcal/mol (-889.864861835 vs. -889.864851533 a.u.).

The C_1 structure should not be overemphasized because the structure of the singlet $H_2C=TiH_2$ complex is very sensitive to the method employed. All the BPW91, MP2, and CCSD calculations have also found a minimum of the complex with a planar C_s structure [4]. The more rigorous CCSD(T)/6-311++G(3df,3pd) calculation found a planar structure, too [18]. Under such backgrounds, the $H_2C=TiH_2$ complex has been optimized again with the BPW91 functional and the MP2 method, respectively, with the *tight* convergence criteria. Both the optimized minima are a planar C_s structure.

Geometric and infrared spectroscopic parameters of the singlet $H_2C=MH_2$ (M = Ti, Zr, Hf) complexes calculated

Table 1
Theoretically computed geometric and infrared spectroscopic parameters of the $H_2C=MH_2$ (M = Ti, Zr, Hf) molecules in the gas phase (B3LYP) and argon matrix (B3LYP/IEF-PCM), respectively

Parameters[a]	$H_2C=TiH_2$			$H_2C=ZrH_2$			$H_2C=HfH_2$		
	Gas	Ar	Δ_{Ar}^{b}	Gas	Ar	Δ_{Ar}^{b}	Gas	Ar	Δ_{Ar}^{b}
$r(C–H_1)$	1.114	1.118	0.004	1.115	1.120	0.005	1.113	1.114	0.001
$r(C–H_2)$	1.084	1.084	0.000	1.084	1.084	0.000	1.084	1.084	0.000
$r(C=M)$	1.811	1.803	−0.008	1.955	1.956	0.001	1.967	1.972	0.005
$r(M–H_3)$	1.738	1.738	0.000	1.874	1.883	0.009	1.870	1.877	0.007
$r(M–H_4)$	1.748	1.744	−0.004	1.884	1.889	0.005	1.875	1.881	0.006
$r(H_1 \cdots M)$	2.150	2.079	−0.071	2.299	2.243	−0.056	2.352	2.343	−0.009
$\angle H_1CM$	91.5	87.4	−4.1	92.9	89.3	−3.6	95.6	94.7	−0.9
$\angle H_1CH_2$	114.4	114.4	0.0	112.5	112.1	−0.4	112.1	112.0	−0.1
$\angle H_2CM$	153.9	157.1	3.2	153.5	157.6	4.1	150.8	152.2	1.4
$\angle CMH_3$	111.5	107.7	−3.8	105.9	103.8	−2.1	104.9	102.9	−2.0
$\angle CMH_4$	122.2	108.2	−14.0	110.2	104.6	−5.6	110.9	107.4	−3.5
$\angle H_3MH_4$	123.6	119.1	−4.5	116.5	114.7	−1.8	113.7	112.3	−1.4
$\angle H_1CMH_3$	−7.7	−17.6	−9.9	21.2	21.2	0.0	22.8	24.2	1.4
$\angle H_1CMH_4$	−169.5	−147.5	22.0	148.0	141.8	−6.2	146.0	142.9	−3.1
$\angle H_2CMH_3$	165.0	145.3	−19.7	−142.8	−142.8	0.0	−139.1	−139.7	−0.6
$\angle H_2CMH_4$	3.1	15.4	12.3	−16.0	−22.3	−6.3	−16.0	−21.0	−5.0
$C–H_2$ str	3181.4/1[c]	3182.1/4[c]	0.7	3178.1/1[c]	3171.3/2[c]	−6.8	3180.0/1[c]	3170.8/1[c]	−9.2
$C–H_1$ str	2868.5/2	2830.7/2	−37.8	2856.4/5	2814.0/7	−42.4	2880.8/7	2871.0/10	−9.8
H_3MH_4 str(s)	1675.7/364	1652.1/399	−23.6	1631.7/296	1599.5/372	−32.2	1668.3/235	1639.5/317	−28.8
H_3MH_4 str(a)	1633.8/647	1617.2/686	−16.6	1600.7/545	1566.6/701	−34.1	1639.6/449	1608.0/593	−31.6
H_1CH_2 scis	1315.1/16	1320.4/18	5.3	1319.9/16	1328.3/18	8.4	1314.4/18	1310.8/19	−3.6
$C=M$ str	818.5/117	817.1/153	−1.4	766.8/130	765.2/176	−1.6	757.4/107	748.0/155	−9.4
H_3MH_4 scis	688.2/17	667.8/51	−20.4	638.4/84	605.2/134	−33.2	635.6/42	607.0/70	−28.6
H_1CH_2 wag	675.4/201	625.5/211	−49.9	664.5/147	638.8/158	−25.7	669.1/167	638.5/194	−30.6
H_3MH_4 rock	532.4/15	487.9/28	−44.5	511.3/9	496.8/27	−14.5	531.6/2	521.6/6	−10.0
H_1CH_2 twist	479.4/2	352.7/55	−126.7	405.7/23	355.6/129	−50.1	397.6/21	364.1/112	−33.5
H_1CH_2 rock	308.5/9	386.9/30	78.4	308.9/76	377.6/32	68.7	230.3/10	222.9/10	−7.4
H_3MH_4 wag	71.7/339	191.6/206	119.9	236.8/133	267.1/94	30.3	312.2/162	322.9/116	10.7

[a] Units of bond length (r), bond angle and dihedral angle ($\angle$), infrared frequency and intensity are Å, °, cm^{-1}, and km/mol, respectively. Atom numbering is shown in Fig. 1.
[b] Parameter difference between argon matrix and gas phase.
[c] Digits before/are infrared frequencies while those after/are the corresponding infrared intensities.
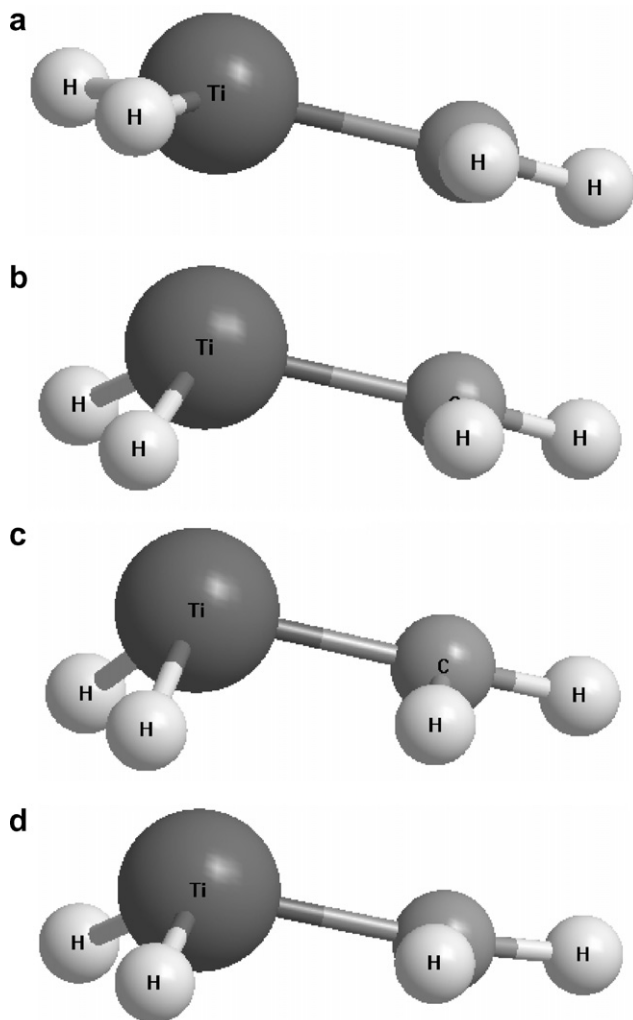
Fig. 2. Molecular structure of the singlet $H_2C=TiH_2$ optimized by the B3LYP (a), B3LYP/IEF-PCM (b), BPW91/IEF-PCM (c), and MP2/IEF-PCM (d) calculations.

PCM simulated matrix effect on the geometry of $H_2C=ZrH_2$ and $H_2C=HfH_2$ is not that evident since the B3LYP optimized structures themselves are fairly pyramidal at the metal atoms. The dipole moment of these two complexes increases ca. 1D upon the matrix effect simulation (4.70 vs. 3.58 D for $H_2C=ZrH_2$ and 4.85 vs. 3.79 D for $H_2C=HfH_2$).

An argon matrix effect on the geometry of the $H_2C=TiH_2$ complex has also been simulated at the BPW91/IEF-PCM and MP2/IEF-PCM levels of theory. At the former level of theory, the planar C_s structure is a transition state and the energy minimum has a pyramidal structure at the Ti atom (Fig. 2c). At the latter level of theory, both the C_s and C_1 structures are energy minima; however, the C_1 structure (Fig. 2d) is more stable than the C_s one by 0.2701 kcal/mol (−888.804431 vs. −888.8040005 a.u.). In summary, all the IEF-PCM simulations indicate that the $H_2C=TiH_2$ complex may have a non-planar pyramidal structure when it is isolated in an argon matrix.

How to understand that the $H_2C=TiH_2$ molecule has a planar structure in the gas phase but may have a pyramidal structure in an argon matrix? The high level CCSD(T) calculation, along with other calculations such as B3LYP, BPW91, MP2, and CCSD, has established that for this molecule the agostic $C–H_1$ bond (1.126 Å [18]) is fairly longer than a common C–H bond (1.085 Å [18]). Meanwhile, the Ti–H bonds are fairly long (1.778 Å [18]) and have significant ionic character (The electronegativity difference between the hydrogen (2.20 [35]) and titanium (1.54 [35]) elements is 0.66 Pauling unit). In other words, this molecule is a transition metal *complex* in nature and should be much softer than the rigid $H_2C=CH_2$ molecule. As a consequence, it may experience a large geometric variation when a small external perturbation such as argon matrix interaction is applied. On the other hand, the present calculations show that for the molecule $H_2C=TiH_2$ the dipole moment of the pyramidal structure is significantly larger than that of the planar structure. For example, according to the BPW91/IEF-PCM calculations, the pyramidal structure (an energy minimum) has a dipole moment of 3.57 D while the planar structure (a transition state) has a dipole moment of only 0.30 D. The pyramidal structure has a much larger dipole moment and thus should be more stabilized by the matrix solvation. Similar instances are the ammonia–hydrogen halide complexes $Cl–H\cdots NH_3$ [9], $Br–H\cdots NH_3$ [10], and $I–H\cdots NH_3$ [11]. According to the observed argon matrix infrared spectrum of the X–H (X = Cl, Br, I) stretching vibrational mode as well as the related matrix effect simulation, the bridging hydrogen atom experiences marked displacement upon the argon matrix solvation. Importantly, for all of these three hydrogen-bonded complexes the matrix-stabilized structure has a much larger dipole moment or ionic character than the gas-phase structure [12,36].

As shown in Table 1, for the molecules $H_2C=TiH_2$ and $H_2C=ZrH_2$, the agostic $C–H_1$ stretching frequency com-

at the B3LYP/IEF-PCM level of theory are also listed in Table 1 (columns labeled as "Ar"). These calculation results correspond to the $H_2C=MH_2$ complexes isolated in an argon matrix. The IEF-PCM simulated argon matrix-induced variations of the parameters are listed in Table 1 (columns labeled as "Δ_{Ar}"), too. As shown in Fig. 2b, the B3LYP/IEF-PCM calculation produced a $H_2C=TiH_2$ minimum that are fairly pyramidal at the Ti atom. In consistency with the remarkable structural variations, the dipole moment of the complex increases from 1.03 D (which corresponds to a gas-phase molecule) to 3.06 D (which corresponds to a molecule isolated in an Ar matrix). On the other hand, the B3LYP/IEF-PCM optimization shows that the $H_2C=TiH_2$ complex has also an energy minimum with a planar C_s structure. This structure is less stable than the C_1 structure (Fig. 2b) by 0.4851 kcal/mol (−889.8734998 vs. −889.8742729 a.u.). Comparing this value with the above 0.0065 kcal/mol indicates that the pyramidal structure may be more stabilized by an argon matrix than the planar structure. The B3LYP/IEF-

puted by the B3LYP/IEF-PCM is red-shifted by 37.8 and 42.4 cm^{-1} compared to that computed by the B3LYP. Meanwhile, the C–H$_2$ stretching frequency of the former molecule is hardly influenced (3182.1 vs. 3181.4 cm^{-1}) and that of the latter molecule is red-shifted by only 6.8 cm^{-1}. These frequency shifts are consistent with the flexible nature of the C–H$_1$ bond and the rigid nature of the C–H$_2$ bond. However, the frequency shift of the C–H$_2$ bond is enlarged slightly (9.2 vs. 6.8 cm^{-1}) while that of the C–H$_1$ bond is reduced significantly (9.8 vs. 42.4 cm^{-1}) when the calculation results of the H$_2$C=HfH$_2$ molecule are compared to those of the H$_2$C=ZrH$_2$ molecule. As a consequence, the IEF-PCM simulated shifts are quite approximate for the two C–H bonds of the H$_2$C=HfH$_2$ molecule (−9.8 vs. −9.2 cm^{-1}).

The C=Ti bond length, H$_1$···Ti distance, and ∠H$_1$CTi of the H$_2$C=TiH$_2$ molecule computed by the B3LYP/IEF-PCM are smaller than those computed by the B3LYP by 0.008 Å (1.803 vs. 1.811 Å), 0.071 Å (2.079 vs. 2.150 Å), and 4.1° (87.4 vs. 91.5°), which indicates that the agostic interaction of the molecule isolated in an argon matrix should be stronger than that of the gaseous molecule. For the H$_2$C=ZrH$_2$ molecule the corresponding parameters computed by the B3LYP/IEF-PCM are smaller than those computed by the B3LYP by −0.001 Å (1.956 vs. 1.955 Å), 0.056 Å (2.243 vs. 2.299 Å), and 3.6° (89.3 vs. 92.9°). For the H$_2$C=HfH$_2$ molecule the deviations are −0.005 Å (1.972 vs. 1.967 Å), 0.009 Å (2.343 vs. 2.352 Å), and 0.9° (94.7 vs. 95.6°). These structural variations are consistent with that the agostic bonding interaction of the H$_2$C=MH$_2$ methylidene complexes decreases on going down the family [6]. In other words, the stronger agostic interaction the complex has the stronger matrix effect the complex will experience.

As shown in Table 1 and Fig. 1, for the H$_2$C=TiH$_2$ complex the ∠H$_1$CTi decreases by 4.1°, the ∠H$_2$CTi increases by 3.2°, and the ∠H$_1$CH$_2$ is kept almost invariant (114.4°) when the B3LYP/IEF-PCM results are compared to the B3LYP ones. This indicates that the ∠H$_1$CH$_2$ angle may be comparatively rigid (like a whole rather than separated C–H$_1$ and C–H$_2$ bonds) when an argon matrix solvation takes place. Consistently, the H$_1$CH$_2$ scissor vibrational frequency has only a slight variation (5.3 cm^{-1}). The same situation is also true for the other two complexes.

H$_1$CH$_2$ wag frequency of the molecules H$_2$C=TiH$_2$, H$_2$C=ZrH$_2$, and H$_2$C=HfH$_2$ was computed as 675.0 [4], 664.7 [5], and 668.3 cm^{-1} [6], respectively, by Andrews et al. Meanwhile, the experimental argon matrix frequencies 635.7 [4] and 630.2 [5] were assigned to the H$_1$CH$_2$ wag mode of the former two molecules while for the hafnium molecule the frequency 665.8 but not 632.6 cm^{-1} [6] was assigned to the wag mode. Perhaps, Andrews et al. have assigned the experimental frequencies 665.8 and 632.6 cm^{-1} to the H$_1$CH$_2$ wag and H$_3$HfH$_4$ scissor (bending) vibrations [6] because these two values are in good agreement with their calculated values (668.3 and 639.5 cm^{-1}) that is based on a gas-phase model (without

modeling of the matrix effect). Apparently, the corresponding relationship between the calculation and the experiment of the hafnium complex (668.3 vs. 665.8 cm^{-1}) is inconsistent with that of the other two complexes (675.0 vs. 635.7 cm^{-1} and 664.7 vs. 630.2 cm^{-1}). And it will become consistent if the experimental value 632.6 rather than 665.8 cm^{-1} corresponds to the wag mode. Under such condition, for all of the three complexes, the B3LYP/IEF-PCM simulated H$_1$CH$_2$ wagging frequencies (625.5, 638.8, and 638.5 cm^{-1}) are in better agreement with the experimental ones (635.7, 630.2, and 632.6 cm^{-1}) than the B3LYP simulated values (675.4, 664.5, and 669.1 cm^{-1}).

As shown in Table 1, the two Zr–H and the two Hf–H bonds computed by the B3LYP/IEF-PCM are lengthened by 0.005–0.009 Å while the computed Ti–H$_4$ bond is shortened by 0.004 Å instead. However, for all of the three complexes both the symmetric and asymmetric H$_3$MH$_4$ stretching frequencies computed by the B3LYP/IEF-PCM are red-shifted by 16.6–34.1 cm^{-1} (1.0–2.1%) compared to those computed by the B3LYP. For the H$_2$C=TiH$_2$ molecule inconsistency between the bond length change and the stretching frequency change (bond length contraction accompanied by the frequency red shift) [37,38] may be caused by the distinct variation of the molecular structure (planar → pyramidal). For the three complexes down to the family the B3LYP/IEF-PCM simulated symmetric and asymmetric H$_3$MH$_4$ stretching frequencies are 1652.1 and 1617.2, 1599.5, and 1566.6 as well as 1639.5 and 1608.0 cm^{-1}, respectively, which are in better agreement with the experimental argon matrix frequencies (1598.1 and 1560.0 [4], 1557.8 and 1524.8 [5] as well as 1641.2 and 1597.1 cm^{-1} [6]) than the B3LYP simulated values (1675.7 and 1633.8, 1631.7 and 1600.7 as well as 1668.3 and 1639.6 cm^{-1}).

For the H$_2$C=ZrH$_2$ complex the experimental Ne and Ar matrix C=Zr stretching frequencies are 757.0 and 747.1 cm^{-1} [5], and for the H$_2$C=HfH$_2$ complex the corresponding C=Hf stretching frequencies are 773.4 and 766.3 cm^{-1} [6]. The Ar to Ne matrix shifts are 9.9 and 7.1 cm^{-1}, respectively. And the experimental Ar matrix to gas-phase shifts should be greater. As shown in Table 1, the B3LYP/IEF-PCM simulated shift (1.6 and 9.4 cm^{-1}) is in qualitative agreement with the experiment for H$_2$C=ZrH$_2$ while is in good agreement with the experiment for H$_2$C=HfH$_2$.

As shown in Table 1, the calculated infrared frequencies of the last four vibrational modes (H$_3$MH$_4$ rock and wag as well as H$_1$CH$_2$ twist and rock) are shifted remarkably, with the largest one as −126.7 cm^{-1} (−26%). In addition, the infrared intensity of the H$_1$CH$_2$ twist vibration increases significantly (for example, 23 → 129 km/mol for the Zr complex) while that of the H$_3$MH$_4$ wag vibration decreases notably (for example, 339 → 206 km/mol for the Ti complex). The distinct variations of the four modes may be due to that the matrix interaction has already altered the mode mixing [5] since each of the vibrations is not a pure mode but a mixture of several modes.
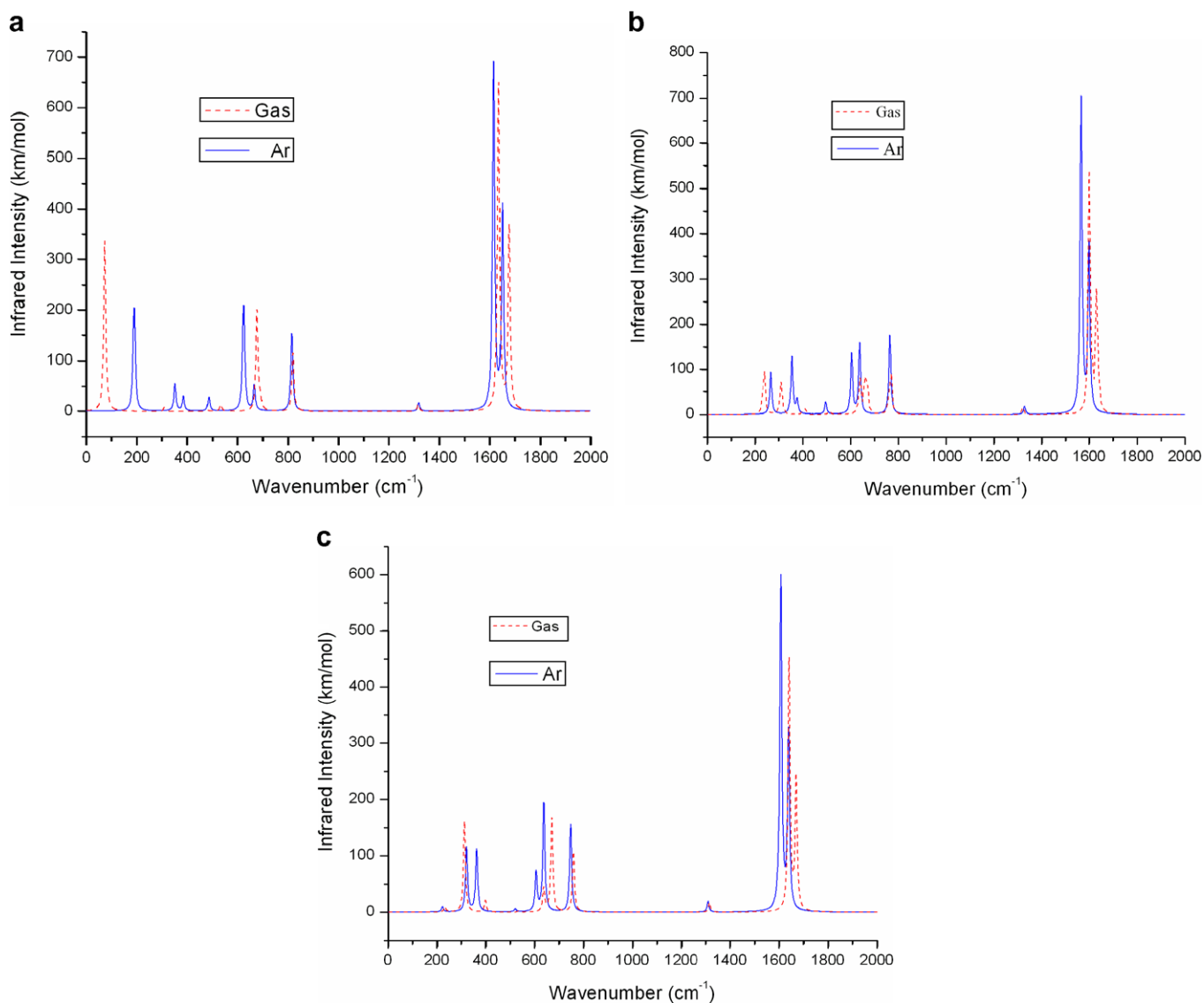
Fig. 3. Comparisons between the B3LYP (corresponding to the gas phase) and B3LYP/IEF-PCM (corresponding to the argon matrix) simulated infrared spectrum of the complexes $H_2C=TiH_2$ (a), $H_2C=ZrH_2$ (b), and $H_2C=HfH_2$ (c).

Finally, the argon matrix effect on the infrared spectrum of the $H_2C=MH_2$ (M = Ti, Zr, Hf) complexes simulated by the B3LYP/IEF-PCM is pictured intuitively in Fig. 3.

4. Conclusions

Using 6-311++G(3df,3pd) basis set for C, H, Ti atoms and Stuttgart/Dresden ECPs MWB28 and MWB60 for Zr and Hf atoms, tight convergence criteria geometry optimizations and harmonic frequency calculations are performed at B3LYP and B3LYP/IEF-PCM levels of theory in order to investigate an argon matrix effect on the geometry and infrared fundamental frequencies of the agostic $H_2C=MH_2$ (M = Ti, Zr, Hf) methylidene complexes. For the $H_2C=TiH_2$ complex similar calculations have also been performed at the BPW91, BPW91/IEF-PCM, MP2, and MP2/IEF-PCM levels of theory for comparing with the

results calculated at the B3LYP and B3LYP/IEF-PCM levels of theory. Based on these calculations and the comparisons with the experiments, the following results are concluded:

(i) All the B3LYP/IEF-PCM, BPW91/IEF-PCM, and MP2/IEF-PCM calculations indicate that the $H_2C=TiH_2$ complex isolated in an argon matrix may have a pyramidal rather than planar structure.

(ii) At the B3LYP level of theory, the dipole moment of the Ti, Zr, and Hf complexes is 1.03, 3.58, and 3.79 D, respectively, and at the B3LYP/IEF-PCM level of theory, the dipole moment of the three complexes is 3.06, 4.70, and 4.85 D.

(iii) The C=Ti bond length, $H_1 \cdots Ti$ distance, and $\angle H_1CTi$ of the $H_2C=TiH_2$ molecule computed by the B3LYP/IEF-PCM are smaller than those com-

puted by the B3LYP by 0.008 Å (1.803 vs. 1.811 Å), 0.071 Å (2.079 vs. 2.150 Å), and 4.1° (87.4 vs. 91.5°). For the $H_2C=ZrH_2$ molecule the deviations are -0.001 Å (1.956 vs. 1.955 Å), 0.056 Å (2.243 vs. 2.299 Å), and 3.6° (89.3 vs. 92.9°). For the $H_2C=HfH_2$ molecule the deviations are -0.005 Å (1.972 vs. 1.967 Å), 0.009 Å (2.343 vs. 2.352 Å), and 0.9° (94.7 vs. 95.6°). The IEF-PCM simulations indicate that the stronger agostic interaction the complex has the stronger matrix effect the complex will experience.

(iv) For the H_3MH_4 symmetric and asymmetric stretching modes as well as the H_1CH_2 wagging mode, the B3LYP/IEF-PCM frequencies (calculated by modeling an argon matrix effect) are in better agreement with the experimental argon matrix frequencies than the B3LYP frequencies (calculated based on a gas-phase model and without the matrix effect modeling). As far as the C=Hf stretching frequency of the $H_2C=HfH_2$ complex is concerned, the IEF-PCM simulated matrix-induced frequency shift (-9.4 cm^{-1}, gas to argon matrix shift) is in good agreement with the experiment (-7.1 cm^{-1}, neon to argon matrix shift).

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