A density functional study of M–C2H4 complexes (M=Li, Na, K): Singularity of the Li atom

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A density functional study of M−C$_2$H$_4$ complexes (M=Li, Na, K): Singularity of the Li atom

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Quantum chemical calculations on the Li–C$_2$H$_4$ complex have been performed with coupled-cluster and density functional methods. For both methods the electronic ground state of the complex is calculated to be $^2B_2$, with a C_{2v} symmetry equilibrium structure, and the calculated binding energy is quite small (around 2 kcal/mol), and therefore very much basis set dependent. The vibrational spectrum has been calculated at the harmonic approximation, including ^{13}C/^{12}C, ^{7}Li/^{6}Li, and H/D isotopic substitutions. The agreement between experimental and calculated infrared frequencies is correct, except for the low frequency symmetric Li–C stretching mode. These calculations also allow to propose an assignment for the observed C–H/C–D stretching modes. The observed blue-shift of the symmetric CH$_2$ bending mode as well as the red-shift of the antisymmetric CH$_2$ bending, CD$_2$ bending, and C–C stretching modes with respect to the free ethylene have been confirmed by the density functional calculations. The Na$\cdots$C$_2$H$_4$ complex has been found to be unstable in its $^2B_2$ electronic state. The study of the $^2A_1$ electronic state for both Na$\cdots$C$_2$H$_4$ and K$\cdots$C$_2$H$_4$ complexes show that they are at most very weak van der Waals complexes. This result confirms the conclusions of matrix isolation experiments. © *1995 American Institute of Physics.*

I. INTRODUCTION

In the last decade, one notes an increasing interest for studying metal–ligand interactions[1–3] by using the density functional theory (DFT). The main interest for these studies is the relevance of such interactions to the mechanisms of heterogeneous catalysis. The study of M$\cdots$C$_2$H$_4$ (M=Li, Na, K) complexes seems to be interesting for two reasons. First, to our knowledge, these systems have not yet been studied by quantum chemical methods. The second reason is to verify the singularity of the Li atom within the alkali metal series, previously evidenced in the reactivity of these atoms with CO,[4] C$_2$H$_2$,[5] and C$_6$H$_6$ (Ref. 6) molecules.

In the present work the interaction between Li and C$_2$H$_4$ is studied with both DFT and coupled-cluster theories including single and double excitations (CCSD) and triple excitations [CCSD(T)]. With both DFT and CCSD, geometry optimization and vibrational spectra at the harmonic approximation have been computed and the results are compared to available experimental data.[7,8] Vibrational isotopic substitutions have been also computed with the DFT method. This last method has finally been used to calculate the complexation energies of Na$\cdots$C$_2$H$_4$ and K$\cdots$C$_2$H$_4$ systems.

II. METHODS OF CALCULATION

Calculations have been made with the GAUSSIAN 92/DFT and GAUSSIAN 94/DFT quantum chemical packages[9] for calculations with the DFT method. The Becke's three parameters functional[10] with the nonlocal transformed correlation correction functional of Lee–Yang–Parr[11] has been used. The calculations have been carried out with the 6-31G(d,p) and 6-311G($2d,2p$) basis sets of Pople and co-workers[12] for the Li–C$_2$H$_4$ and Na$\cdots$C$_2$H$_4$ systems. For the K$\cdots$C$_2$H$_4$ interaction, calculations have been made using pseudopotential within the LANL2DZ basis set.[13]

Additional coupled cluster calculations have been carried out for the Li–C$_2$H$_4$ complex. Spin-restricted (RHF) and spin-unrestricted (UHF) reference wave function are for closed shell and open shell species, respectively. With the CCSD method,[14] calculations have been developed using the ACESII quantum chemical package[15] and the 6-311G(d,p) basis set of Pople and co-workers.[16] All the electrons and orbitals have been included in the correlated wave function. Single-point calculations at the coupled cluster with single and double excitation augmented by a quasiperturbative estimate of connected triple excitation CCSD(T) (Ref. 17) have been performed using the GAUSSIAN 92 quantum chemical packages[9] with D95($2df,2pd$) basis set.[18] Spin contamination was insignificant for the open shell species studied here with both methods.

III. RESULTS

A. The C$_2$H$_4$ subunit

Table I gathers the results obtained on free ethylene with both DFT and CCSD methods. The geometry has been optimized with a D_{2h} symmetry constraint and it may be seen that DFT and CCSD results are in close agreement with each

TABLE I. Equilibrium geometry and harmonic vibrational frequencies (cm^{-1}) for free ethylene in the electronic state ^1A_g.

Parameters		DFT 6-311G(2d,2p)	CCSD 6-311G(d,p)	Expt.[a]	Mode character[b]
r_{CC}(Å)		1.324	1.337	1.339	
r_{CH}(Å)		1.082	1.087	1.085	
$\angle$HCH (deg)		116.5	116.8	117.8	
E(a.u.)		−78.617 872 6	−78.411 101		
A_g	ω_1	3 142.3	3 180	3 152.2	ν^s_{CH}
	ω_2	1 695.1	1 697	1 654.9	$\nu_{CC}\&\delta^s_{(CH_2)}$
	ω_3	1 383.1	1 384	1 369.9	$\delta^s_{(CH_2)}\&\nu_{CC}$
A_u	ω_4	1 071.5	1 055	1 044.0	twist$_{(CH_2)}$
B_{1g}	ω_5	3 197.5	3 241	3 232.0	ν^{as}_{CH}
	ω_6	1 250.1	1 241	1 245.0	rock$_{(CH_2)}$
B_{1u}	ω_7	975.3	970	969.0	wag$_{(CH_2)}$
B_{2g}	ω_8	976.2	927	958.8	wag$_{(CH_2)}$
B_{2u}	ω_9	3 225.2	3 267	3 234.3	ν^s_{CH}
	ω_{10}	838.2	831	843.0	rock$_{(CH_2)}$
B_{3u}	ω_{11}	3 128.2	3 161	3 146.9	ν^s_{CH}
	ω_{12}	1 482.8	1 487	1 473.0	$\delta^{as}_{(CH_2)}$

[a]Reference 19.
[b]The symbol & indicates strong coupling of the symmetric coordinates in the normal mode.

other and with the experimental values.[19] The experimental vibrational frequencies reported by Duncan[19] are corrected from mechanical anharmonicity and Fermi resonance effects. The examination of Table I shows that the mean relative deviation between calculated and observed frequencies is around 1% with both CCSD/6-311G(d,p) and DFT/6-311G(2d,2p) methods. The vibrational frequencies of ^{13}C$_2$H$_4$, ^{12}C$_2$D$_4$, and ^{12}CH$_2^{12}$CD$_2$ as calculated with the DFT method are reported in Table II. The experimental values collected in Table II come from the infrared spectra recorded by Manceron and Andrews[20] in solid argon.

B. The structure and complexation energy

1. The Li–C$_2$H$_4$ complex

Electronic calculations of the Li–C$_2$H$_4$ complex have been made with the DFT method using the 6-31G(d,p) and 6-311G(2d,2p) basis sets. In both cases, the DFT method predicts a $^2B_2$ electronic ground state for the Li–C$_2$H$_4$ complex with a C_{2v} symmetry equilibrium structure, in agreement with the conclusions of infrared and electron spin resonance studies.[7,8] With the first, smaller basis set the complex has been found to be stable by about 2.2 kcal/mol. Taking into account the basis set superposition error (BSSE), this stability is reduced to 0.14 kcal/mol. With the second, larger basis set, the binding energy is −3.1 kcal/mol, corrected to −2.2 kcal/mol with BSSE. The optimized geometrical parameters of Li–C$_2$H$_4$, with either 6-31G(d,p) or 6-311G(2d,2p) basis sets, are very close to each other and only the equilibrium geometry corresponding to the second basis set is reported in Table III.

The equilibrium structure of the Li–C$_2$H$_4$ complex has been also optimized with the coupled cluster method at the CCSD level using the 6-311G(d,p) basis set and the results are reported in the Table III. It is also found that the elec-

TABLE II. Vibrational frequencies (cm^{-1}) of isotopic free ethylene.

Mode character (D_{2h} symm.)[c]	^{13}C$_2$H$_4$ DFT[a]	^{13}C$_2$H$_4$ Expt.[b]	^{12}C$_2$D$_4$ DFT[a]	^{12}C$_2$D$_4$ Expt.[b]	^{12}C$_2$H$_2$D$_2$ DFT[a]	^{12}C$_2$H$_2$D$_2$ Expt.[b]	Mode character (C_{2v} symm.)
$\nu_{CH/CD}$	3134.5	(3034)	2325.6	2260	3135.4	3023	ν^s_{CH}
$\nu_{CC}\&\delta^s_{(CH_2/CD_2)}$	1647.4	(1577)	1577.7	1518	1645.8	1585	ν_{CC}
$\delta^s_{(CH_2/CD_2)}\&\nu_{CC}$	1370.5	(1334)	1004.7	985	1050.3	1031	$\delta_{(CD_2)}$
twist	1071.4		757.9		928.0		twist
$\nu_{CH/CD}$	3184.6	(3090)	2384.0	2310	2392.4	2340	$\nu^{as}_{(CD)}$
rock$_{(CH_2/CD_2)}$	1231.9	(1204)	1018.7	1010	1161.9	1142	rock$_{(CH_2)}$
wag$_{(CH_2/CD_2)}$	969.8	942	807.4	780	975.8	942	wag$_{(CH_2)}$
wag$_{(CH_2/CD_2)}$	962.2	(926)	737.7	721	773.3	748	wag$_{(CH_2)}$
$\nu_{CH/CD}$	3211.8	3104	2400.9	2346	3211.5	3103	$\nu^{as}_{(CH)}$
rock$_{(CH_2/CD_2)}$	837.0	830	602.5	596	694.7	688	rock$_{(CD_2)}$
$\nu_{CH/CD}$	3123.2	2975	2259.5	2205	2294.0	2234	$\nu^s_{(CD)}$
$\delta^{as}_{(CH_2/CD_2)}$	1476.9	1436	1098.5	1075	1424.0	1390	$\delta_{(CH_2)}$

[a]Harmonic vibrational frequencies calculated by DFT/6-311G(2d,2p).
[b]Vibrational frequencies recorded in solid argon, and the values in parentheses are the fitted values, Ref. 20.
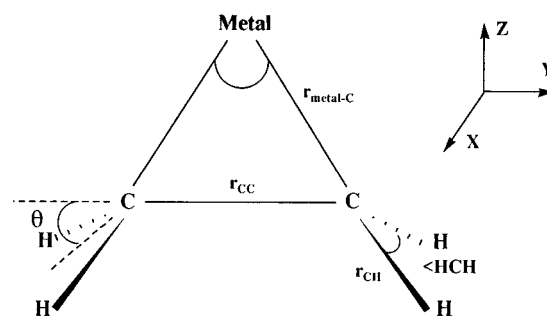[c]The symbol & indicates a coupled mode.

TABLE III. Equilibrium geometry and energy for the ^{7}Li–^{12}C$_2$H$_4$ complex in the ground electronic state $^2B_2$.

Parameters	DFT 6-311G($2d,2p$)	CCSD 6-311G(d,p)	Expt.[a]
in Å			
r_{CC}	1.419	1.431	1.44±0.02
r_{CH}	1.084	1.089	1.09
r_{LiC}	2.054	2.058	1.9
in deg			
$\angle$HCH	115.0	115.1	120.
$\angle$CLiC	40.4	40.8	44.6
$\angle\theta$	20.9	23.1	10.
μ_z (Debye)	+3.766	+4.03	
metal charge (Mulliken)	+0.312		
in a.u.			
E_{Li}	−7.491 296 6	−7.447 241	
$E_{complex}$	−86.114 070 8	−85.853 662	
in kcal/mol			
$E_{binding}^b$	−3.1(−2.16)	+2.9	

[a]Reference 7, the results obtained from HFF calculations.
[b]Value in the parentheses is the BSSE corrected binding energy.

FIG. 1. Geometrical parameters of metal–ethylene complex in the C_{2v}-symmetric equilibrium structure.

tronic state of the complex is of $^2B_2$ symetry. In this calculation, the complex is unstable by about 2.9 kcal/mol. Nevertheless it may be seen from Table III that the equilibrium geometries calculated with CCSD and DFT methods are quite similar. Since CCSD results may also be basis set dependent, another calculation has been performed using the extended D95($2df,2pd$) basis set. Due to the very expensive cost of this method, it has been only possible to make a single-point calculation at the equilibrium geometry determined with the 6-311G(d,p) basis set. With this larger basis set, the complex is calculated to be stable with a small binding energy of −1.22 kcal/mol. A third calculation has been made taking into account triple excitations, CCSD(T)/D95($2df,2pd$). Likewise, it has been only possible to make a single-point calculation at the 6-311G(d,p) equilibrium geometry. At this level the binding energy of the complex is then of −1.78 kcal/mol. To have a good estimation of the BSSE effect, it would be better to perform the full geometry optimization. It may be assumed that the BSSE effect is weak owing to the large size of the basis set used. In any case, one can state that the complex is bound in the $^2B_2$ electronic state with both CC and DFT approaches.

In Table III stands also the equilibrium geometry deduced from approximate harmonic force field (HFF) calculations.[7] There is an overall agreement between HFF and quantum calculations for bond lengths and angles except in the case of the tilt (bending angle of the CH$_2$ groups with respect to the free C$_2$H$_4$ plane, away from the metal) and the HCH angles (see Fig. 1). The experimental interpretation of the infrared spectra[7] had been possible only if the C$_2$H$_4$ subunit did not keep its D_{2h} symmetry upon interaction with Li. Since the variation of the tilt angle does not greatly affect the relative vibrational shifts of the isotopic species, this angle was not accurately determined and, likely, had been underestimated by the HFF method, as shown in CCSD as well as in DFT approaches. In HFF calculations, the HCH angle has been kept equal to its original 120° value as in the free C$_2$H$_4$ molecule, while quantum calculations show a decrease of about 5°, also due to the metal–ligand interaction.

The largest change in the geometry of complexed C$_2$H$_4$ with respect to the free molecule is the increase of the C–C bond length. This increase is calculated to be 0.094 Å (7%) at both CCSD and DFT levels, close to the 0.1±0.02 Å (7.5%) increase deduced from the decrease of the C=C bond force constant.[7]

For the C–H bond length, it is calculated to be nearly invariant upon complexation with an increase of only 0.23% and 0.18% by DFT and CCSD, respectively.

2. The Na···C$_2$H$_4$ and K···C$_2$H$_4$ complexes

It has been previously shown that formation of bound carbonyl complexes of an alkali atom is only observed with lithium, while heavier alkali atoms form at most very weakly bound van der Waals (vdW) pairs.[4,23] It seems interesting to verify if this singularity remains valid for the complexation with ethylene. Experimentally, no binding interaction was found in Na···C$_2$H$_4$ and Cs···C$_2$H$_4$ pairs, while could exist at most as very weak van der Waals (vdW) species.[7] To our knowledge, there is no result on the K···C$_2$H$_4$ complex.

The DFT calculations have been performed with both 6-31G(d,p) and 6-311G($2d,2p$) basis sets on the Na···C$_2$H$_4$ complex. The ground state is found to be $^2A_1$. The binding energy and its BSSE corrected value are −0.3 and +1.9 kcal/mol with the first basis set, while the corresponding values with the second basis set are −0.36 and +0.09 kcal/mol. Extrapolating the above results, one could likely find a very weak vdW complex by increasing the basis set. The equilibrium structure is very slightly basis set dependent, and only the results corresponding to the 6-311G($2d,2p$) basis set are reported in Table IV.

For the K···C$_2$H$_4$ system, the ground stat is also found to be $^2A_1$ at the DFT/LANL2DZ level of theory. It corresponds to a very shallow potential well with −0.4 kcal/mol interaction energy, reduced to −0.08 kcal/mol when BSSE effects are taken into account. For both Na···C$_2$H$_4$ and K···C$_2$H$_4$ systems, the geometrical parameters (reported in Table IV) show very little change in the structure of the ethylene ligand upon complexation and a large metal–ethylene separation

TABLE IV. Equilibrium parameters for the Na and K/C₂H₄ complexes by DFT.

Parameters	Na···C₂H₄ 6-311G($2d,2p$)	Na···C₂H₄ 6-311G($2d,2p$)	K···C₂H₄ Lanl2DZ
in Å			
r_{CC}	1.325	1.426	1.349
r_{CH}	1.088	1.084	1.089
$r_{metal–C}$	4.476	2.419	4.29
in deg			
∠HCH	116.6	115.1	116.6
∠C–metal–C	17.0	34.28	38.3
∠θ	∠1	21.5	∠1
μ_z (Debye)	−0.8014	+5.08	−1.563
metal charge (Mulliken)	−0.02	+0.409	−0.028
in kcal/mol			
$E_{binding}^a$	−0.36(+0.09)	+18.35	−0.4(−0.08)
Electronic state	$^2A_1$	$^2B_2$	$^2A_1$

[a]Values in the parentheses are the BSSE corrected binding energies.

(above 4.2 Å). The direction of the predicted dipole moment and of the net charge transfer between metal and ethylene is reversed with respect to Li–C₂H₄. This means that the nature of the bonding is thus essentially different for heavy alkali metal complexes. The weakness of the interaction and the large metal–ethylene distance suggest that the Na or K/C₂H₄ complexes are best described as weakly bonded vdW pairs. For heavy alkali metals, less favorable metal *p*-ethylene π^* orbital interaction does not compensate the energetic cost of the $nS \rightarrow nP$ valence electron promotion, placing the $^2B_2$ state above the $^2A_1$ electronic state. With sodium, scanning the potential surface cross section along the sodium–ethylene coordinate, using DFT/6-311G($2d,2p$), reveals a

second minimum, some +18 kcal/mol above the ground state corresponding to the first excited state, with $^2B_2$ electronic structure. The geometry of Na···C₂H₄ in the $^2B_2$ state is quite comparable to that of Li–C₂H₄ in the ground state (see Tables III and IV) and the net charge is then in direction of ethylene. This metastable state has not yet, to our knowledge, been observed.

C. Vibrational analysis

1. The $^7Li–^{12}C_2H_4$

The calculated vibrational harmonic frequencies of the main isotopic species are collected in Table V. The vibrational analysis has been carried out with both CCSD and DFT methods at the harmonic approximation for the bound $^2B_2$ state. As it may be seen, the results obtained with the two quantum chemical methods are quite close to each other.

Before comparing calculated frequencies with available experimental data,[7] it must be recalled that the experimental values are not corrected for anharmonicity, thus the comparison between the calculated and experimental values may only be considered as indicative of the main trends. More significative is the comparison of the experimental and calculated vibrational shifts of each mode of free C₂H₄ molecule upon complexation.

In the experimental work, six modes have been observed for each isotopic species. Five of them have been clearly assigned. Let us first consider the C–H stretching modes, for which only one out of four vibrations has been experimentally observed (and left unassigned). There are four ν_{CH} stretching modes of A_1, A_2, B_1, and B_2 symmetry, the A_2 symmetry one being infrared inactive. The three others, of B_1, A_1, and B_2 symmetry are correlated to those of B_{3u}, A_g, and B_{2u} symmetry, respectively, of the free molecule (D_{2h}

TABLE V. Vibrational frequencies (cm⁻¹) and IR intensities (km/mol) for the $^2B_2$ electronic state of the $^7Li–^{12}C_2H_4$ complex.

C_{2v} symmetry		DFT 6-311G($2d,2p$) ω^a	(IR int.)	CCSD 6-311G(d,p) ω^a	(IR int.)	Expt.[b] ν^c	(IR int.)	Mode character[e]
A_1	ν_1	3108.7	(9.0)	3135	(8)			ν_{CH}^s
	ν_2	1501.0	(11.0)	1519	(8)	1453 [d]		$\delta_{(CH_2)}^s$ & ν_{CC}
	ν_3	1181.1	(98.2)	1200	(68)	1176.5	(s)	ν_{CC} & $\delta_{(CH_2)}^s$
	ν_4	737.1	(0.2)	783	(2)	704	(vw)	$wag_{CH_2}^s$
	ν_5	568.3	(4.3)	581	(12)	369	(s)	ν_{LiC}^s
A_2	ν_6	3164.1	(0.0)	3196	(0)			ν_{CH}
	ν_7	1213.0	(0.0)	1232	(0)			rock(CH2)
	ν_8	655.1	(0.0)	629	(0)			twist
B_1	ν_9	3193.7	(36.4)	3224	(43)			ν_{CH}
	ν_{10}	809.3	(1.9)	818	(4)			$rock_{(CH_2)}$
	ν_{11}	395.7	(55.3)	397	(57)			tilt
B_2	ν_{12}	3075.5	(1799.)	3117	(0)	3055	(vw)	ν_{CH}
	ν_{13}	1428.3	(703.5)	1446	(3)	1428	(w)	$\delta_{(CH_2)}^{as}$
	ν_{14}	669.4	(34.4)	667	(141)			$wag_{(CH_2)}$
	ν_{15}	373.1	(518.3)	399	(20)			ν_{LiC}^{as}

[a]Harmonic vibrational frequencies.
[b]Reference 7.
[c]Anharmonic vibrational frequencies.
[d]Fitted value.
[e]The symbol & indicates a coupled mode.

symmetry). If the ν_{CH} observed mode were of B_1 symmetry, it would be red-shifted with respect to the B_{3u} mode of the free C$_2$H$_4$, while both CCSD and DFT calculations predict a blue-shift. Consequently the observed band cannot be assigned to the B_1 mode. The A_1 and B_2 symmetry modes however are calculated to be red-shifted. The red-shift of the A_1 mode is calculated to be 33.6 cm^{-1} with DFT and 45.0 cm^{-1} with CCSD while that of the B_2 mode is 149.7 and 150 cm^{-1} for DFT and CCSD, respectively. If the experimentally observed mode were of A_1 symmetry, the red-shift would be of 97 cm^{-1}. If it is of B_2 symmetry, the red-shift would be 179.3 cm^{-1}. This comparison suggests that the ν_{CH} observed mode is of B_2 symmetry. Note that the calculated relative intensities of these bands are not very helpful here. First, there is a huge discrepancy for the calculated intensity of the B_2 mode between the CCSD and DFT results. Second, the experimental relative intensity with respect to the strongest observed band has not been reported. This example shows that, for some vibrational modes, the comparison between calculated and experimental intensities is difficult. First, infrared intensities calculated by means of quantum chemistry are sometimes basis set dependent.[1,21,22] Second, the calculations are made in the gas phase, and comparisons with data of matrix-isolated species may not be always fair as some distortion in the infrared intensities could be induced, even by solid rare gases.

The Li–C$_2$H$_4$ complex has three intermolecular modes, the symmetric and antisymmetric Li–C stretching motions, and the tilt motion. Only the symmetric Li–C stretching has been assigned experimentally, as a relatively strong band at 369 cm^{-1}. Its relative intensity to the strongest band (ν_3), is about of 0.4. This mode is calculated at 568.3 and 581 cm^{-1} with DFT and CCSD methods, respectively. This discrepancy would suggest to assign the observed band to another intermolecular motion. The antisymmetric Li–C stretching mode has been calculated at 373.1 and 399 cm^{-1} in DFT and CCSD calculations, respectively. The tilt mode is located at 395.7 cm^{-1} in DFT and at 397 cm^{-1} in CCSD calculations. Considering the frequency, the observed mode could be re-assigned to the antisymmetric mode. Caution should be exerted for the following reasons. At first infrared relative intensities are very basis set dependent and not always reliable. The second reason is relevant to the anharmonic character of the intermolecular modes located in the low frequency domain. In systems with such shallow potential wells (800–900 cm^{-1}), the anharmonicity correction to the frequency may be very significant.

Another interesting point, if not the main point, in the discussion about the nature of the complexation between ethylene and metal atoms concerns the ν_2 and ν_3 frequencies. In order to understand the variations of the two C–C stretching and CH$_2$ bending (of A_1 symmetry) modes we must emphasize that these two coordinates are strongly coupled in ν_2 and ν_3 of both C$_2$H$_4$ and Li–C$_2$H$_4$ systems. This important experimental point is verified in the calculated normal modes. Therefore it is not justified to assign the ν_2 and ν_3 frequencies of either ν_{CC} or δ_{CH_2} alone, and the sum of the shifts on ν_2 and ν_3 upon complexation reflects better the perturbations of the two intramolecular modes. The experimental value of

the sum is 395.5 cm^{-1}, in good agreement with quantum chemical predictions (396.1 cm^{-1} and 362.0 cm^{-1}, by DFT and CCSD, respectively).

The A_1 symmetry CH$_2$ wagging mode (ν_4) presents experimentally a large −265 cm^{-1} shift while the calculated values are −238.2 and −187 cm^{-1} with DFT and CCSD methods, respectively. A last significative shift is of −45 cm^{-1} relevant to the observed $\delta^a_{CH_2}$ bending mode. DFT and CCSD values are −54.5 and −41 cm^{-1} for this mode, respectively.

2. The isotopic effects

The results concerning isotopic substitutions, studied only using the DFT method, are gather in Tables VI–VIII. We have not performed the isotopic calculations with the CCSD approach, since this method has provided nearly the same results as DFT for the main Li–C$_2$H$_4$ natural species.

The first comment concerns the ν_{CH} stretching mode. In each isotopic species only one $\nu_{CH/CD}$ stretching mode has been observed. As the Li–^{13}C$_2$H$_4$ and Li–^{12}C$_2$D$_4$ species have the same symmetry as Li–^{12}C$_2$H$_4$, the assignment of the ν_{CH} to the B_2 mode remains valid. In order to confirm this assignment, we now compare the experimental and calculated frequency shifts between Li–^{13}C$_2$H$_4$ and Li–^{12}C$_2$H$_4$ (referred to as Δ_1) on the one hand, and between Li–^{12}C$_2$D$_4$ and Li–^{12}C$_2$H$_4$ (referred to as Δ_2) on the other hand. The −6 cm^{-1} calculated Δ_1 is in agreement with the experimental value (−5 cm^{-1}). The −832 cm^{-1} experimental Δ_2 is also well matched by the calculated one (−853.5 cm^{-1}). For Li–^{12}CH$_2$^{12}CD$_2$ substitution, the symmetry is reduced from C_{2v} to C_s, yet only one frequency located at 2209 cm^{-1} has been experimentally reported. This frequency must be assigned to a ν_{CD} stretching mode, owing to its expected large decrease upon H/D substitution. Among the four $\nu_{CH/CD}$ calculated frequencies, only two of them refer to ν_{CD} modes. One A' symmetry (ν^s_{CD}), and the other one A'' symmetry (ν^a_{CD}). We designate by $\Delta\nu^s_{CD}$ and $\Delta\nu^a_{CD}$, the shifts between the ν_{CD} modes of the free ^{12}C$_2$H$_2$D$_2$ molecule and that of the Li–^{12}C$_2$H$_2$D$_2$ complex. The calculated values of $\Delta\nu^s_{CD}$ and $\Delta\nu^a_{CD}$ are 48.6 and 27.4 cm^{-1}, respectively. The observed value of $\Delta\nu_{CD}$ is of 131 cm^{-1} if the assignment refers to the ν^a_{CD} mode and of 25 cm^{-1} in the case of an assignment of the ν^s_{CD} mode. The conclusion is that the high frequency observed mode is the ν^s_{CD} mode in A' symmetry. Another confirmation of this assignment is given by the observed and calculated difference between the ν_{CD} stretching mode of Li–^{12}C$_2$H$_2$D$_2$ and the ν_{CH} mode of the Li–^{12}C$_2$H$_4$ complex [referred as $\Delta\nu = \nu_{CH}(B_2) - \nu^s_{CD_2}(A')$]. The observed value of $\Delta\nu$ is of 846 cm^{-1}, close to the calculated one (830.1 cm^{-1}).

An important feature in the vibrational analysis of the lithium ethylene complex is the relative positions of the three medium frequencies, i.e., ν_2, ν_3, and ν_{13} modes of the complex, by comparison with the corresponding modes in the free molecule. Upon complexation of ethylene by Li, it has been observed that the CC stretching and $\delta^a_{CH_2}$ bending modes are red-shifted, while there is a blue-shift for the $\delta^s_{CH_2}$ mode. Furthermore, the experiment indicates that the

TABLE VI. Vibrational frequencies (cm^{-1}) and IR Intensities (km/mol) of the two isotopic substitutions ^{12}C/^{13}C and ^{7}Li/^{6}Li.

| | | ^{7}Li–^{13}C₂H₄ | | | | ^{6}Li–^{12}C₂H₄ | | | | |
| | | DFT | | Expt.[b] | | DFT | | Expt.[b] | | |
C_{2v} symm.		ω^a	(IR int.)	ν^c	(IR int.)	ω^a	(IR int.)	ν^c	(IR int.)	Mode character[d]
A_1	ν_1	3102.4	(10.3)			3108.7	(9.0)			ν^s_{CH}
	ν_2	1487.2	(6.0)	1436[e]		1502.0	(11.1)			$\delta^s_{(CH_2)}$&ν_{CC}
	ν_3	1148.6	(95.5)	1150	(s)	1181.3	(98.5)	1179	(s)	ν_{CC}&$\delta^s_{(CH_2)}$
	ν_4	732.5	(0.3)	700	(vw)	737.2	(0.2)	714	(vw)	wag^s
	ν_5	564.7	(4.2)	366	(s)	604.7	(4.8)	387	(s)	ν^s_{LiC}
A_2	ν_6	3151.6	(0.0)			3164.1	(0.0)			ν_{CH}
	ν_7	1206.8	(0.0)			1221.3	(0.0)			rock
	ν_8	654.1	(0.0)			655.1	(0.0)			twist
B_1	ν_9	3180.8	(37.1)			3193.7	(36.4)			ν_{CH}
	ν_{10}	808.4	(2.0)			809.3	(1.9)			rock
	ν_{11}	394.8	(54.5)			399.4	(59.7)			tilt
B_2	ν_{12}	3070.5	(1790.9)			3075.5	(1797.5)			ν_{CH}
	ν_{13}	1422.7	(709.7)	3049	(vw)	1428.3	(701.4)	1428	(w)	$\delta^{as}_{CH_2}$
	ν_{14}	662.6	(28.4)	1421	(w)	670.0	(29.2)			wag
	ν_{15}	364.6	(510.7)			382.6	(585.9)			ν^{as}_{LiC}

[a]Harmonic vibrational frequencies.
[b]Reference 7.
[c]Anharmonic vibrational frequencies.
[d]The symbol & indicates a coupled mode.
[e]Fitted value.

relative positions are CC stretch $> \delta^a_{CH_2} > \delta^s_{CH_2}$ in the ^{12}C₂H₄ molecule while the order is $\delta^s_{CH_2} > \delta^a_{CH_2} >$ CC stretch in the ^{7}Li–^{12}C₂H₄ complex. This feature is well reproduced in both CCSD and DFT calculations. The two isotopic changes, ^{7}Li–^{13}C₂H₄ and ^{6}Li–^{12}C₂H₄ do not change drastically the normal modes in ν_2, ν_3, and ν_{13} modes, and this have been verified by the DFT results. It is interesting to look at these relative positions upon H/D isotopic substitution. Two isotopic species have been investigated: C₂D₄ and CH₂CD₂. Upon partial deuteration, the CC stretch and the δ_{CD_2} observed modes are red-shifted while δ_{CH_2} is blue-shifted. The relative positions are CC stretch $> \delta_{CD_2} > \delta_{CD_2}$ in the free ^{12}C₂H₂D₂ molecule, while the order is $\delta_{CD_2} >$ CC stretch $> \delta_{CD_2}$ in Li–^{12}C₂H₂D₂. This feature is well reproduced in DFT calculations. In the case of the Li–^{12}C₂D₄ compound, the three modes CC stretch, $\delta^a_{CD_2}$ and $\delta^s_{CD_2}$ are experimentally red-shifted through the complexation. The ordering CC stretch $> \delta^a_{CD_2} > \delta^s_{CD_2}$ in the recorded infrared

TABLE VII. Vibrational frequencies (cm^{-1}) and IR Intensities (km/mol) for the ^{7}Li–^{12}C₂D₄ complex.

| | | DFT | | Expt.[b] | | |
$C2v$ symm.		ω^a	(IR int.)	ν^c	(IR int.)	Mode character[d]
A_1	ν_1	2269.0	(0.0)	1312	(s)	ν^s_{CH}
	ν_2	1285.0	(72.3)	931.5	(m)	ν_{CC}&$\delta^s_{(CD_2)}$
	ν_3	947.7	(29.3)	541	(vw)	$\delta^s_{(CD_2)}$&ν_{CC}
	ν_4	595.7	(2.2)	360	(s)	wag^s
	ν_5	524.6	(2.0)			ν^s_{LiC}
A_2	ν_6	2355.7	(0.0)			ν^s_{CD}
	ν_7	973.8	(0.0)			rock
	ν_8	469.3	(0.0)			twist
B_1	ν_9	2374.5	(14.2)			ν_{CD}
	ν_{10}	579.6	(0.4)			rock
	ν_{11}	302.0	(46.5)			tilt
B_2	ν_{12}	2222.0	(949.5)	2223	(vw)	ν_{CD}
	ν_{13}	1058.2	(310.1)	1063[e]		$\delta^{as}_{CD_2}$
	ν_{14}	540.7	(65.7)			wag
	ν_{15}	350.9	(486.6)			ν^{as}_{LiC}

[a]Harmonic vibrational frequencies.
[b]Reference 7.
[c]Anharmonic vibrational frequencies.
[d]The symbol & indicates a coupled mode.
[e]Fitted value.

TABLE VIII. Vibrational frequencies (in cm^{-1}) and IR Intensities (in km/mol) of the ^{7}Li–^{12}CH₂^{12}CD₂ complex.

| | | DFT | | Expt.[b] | | |
C_s symm.		ω^a	(IR int.)	ν^f	(IR int.)	Mode character[d]
A'	ν_1	3092.4	(879.9)			ν^s_{CH}
	ν_2	2245.4	(496.6)	2209	(vw)	ν^s_{CD}
	ν_3	1471.0	(257.4)	1437	(m)	δ_{CH_2}&ν_{CC}&δ_{CD_2}
	ν_4	1233.5	(265.8)	1250	(s)	ν_{CC}&δ_{CD_2}&δ_{CH_2}
	ν_5	996.8	(91.8)	990	(m)	δ_{CD_2}&ν_{CC}&δ_{CH_2}
	ν_6	706.8	(11.2)			wag CH₂
	ν_7	579.8	(13.6)	574	(vw)	wag CD₂
	ν_8	532.5	(33.7)	364.5	(s)	ν^s_{LiC}
	ν_9	361.2	(498.3)			ν^{as}_{LiC}
A''	ν_{10}	3179.1	(18.5)			ν^{as}_{CH}
	ν_{11}	2365.0	(6.7)			ν^{as}_{CD}
	ν_{12}	1127.1	(0.5)	1179	(w)	rock CH₂
	ν_{13}	666.6	(0.6)			rock CD₂
	ν_{14}	583.8	(5.8)			twist
	ν_{15}	328.7	(45.2)			tilt

[a]Harmonic vibrational frequencies.
[b]Reference 7.
[c]Anharmonic vibrational frequencies.
[d]The symbol & indicates a coupled mode.

spectrum of the C$_2$D$_4$ molecule is here again calculated for Li–^{12}C$_2$D$_4$.

Given the strong coupling between CC stretch and $\delta^s_{CH_2/CD_2}$ oscillators in ν_2 and ν_3, we must emphasize that, in the case of such mixing between two oscillators, the best way to appreciate the degree of perturbation of the C=C bond remains the calculation of the force constants. It has been estimated that the force constant of C=C bond decreases about 30% through complexation process, to be compared to 40% calculated here by DFT. It is interesting to recall that the force constant is reduced about 52% from a double-bond (H$_2$C=CH$_2$) to a single-bond (in cyclopropane).[24] This study confirms that the C=C bond of the C$_2$H$_4$ molecule is strongly weakened upon complexation with a lithium.

Of the two wagging modes, only one has been reported for the different isotopic species (located at 541 and 700 cm^{-1} for ^{7}Li–^{12}C$_2$D$_4$ and ^{7}Li–^{13}C$_2$H$_4$, respectively). It had been assigned to the A_1 symmetry wagging mode (ν_4). The observed shift between the symmetric wagging mode of Li–^{12}C$_2$H$_4$ and Li–^{13}C$_2$H$_4$ is -4 cm^{-1}, to be compared to the -4.6 cm^{-1} calculated value. Between Li–^{12}C$_2$H$_4$ and Li–^{12}C$_2$D$_4$, the wagging mode frequency experimentally decreases by -163 cm^{-1}, while the corresponding calculated value is -141.4 cm^{-1}. For the Li–^{12}C$_2$H$_2$D$_2$ complex, only one experimental wagging mode had been located at 574 cm^{-1}, but left unassigned. In order to assign this mode, we again proceed to compare the frequency shifts upon complexation. In the case of a CD$_2$ wagging assignment, the observed and calculated shifts are -174 cm^{-1} and -193.5 cm^{-1}, respectively. While these are -368 and -269 cm^{-1} for a CH$_2$ wagging assignment. The comparison shows that the observed frequency at 574 cm^{-1} for the Li–^{12}C$_2$H$_2$D$_2$ complex, might be assigned to the A' symmetry CD$_2$ wagging mode (ν_7).

IV. DISCUSSION

This study confirms the existence of a stable Li–C$_2$H$_4$ complex with a $^2B_2$ electronic ground state and a largely altered C$_2$H$_4$ subunit, as inferred from vibrational and ESR studies.[7,8] Our results can precise the geometrical change of the C$_2$H$_4$: the C–C distance lengthens to about 1.42 Å and the methylene groups bend some 20° out-of-plane, away from the metal. These geometrical changes are surprisingly similar to those calculated for singlet Ni–C$_2$H$_4$ ($r_{CC} \cong 1.43$ Å and about 19° out-of-plane distortion),[1] a similitude reflected in the relative closeness of the ν_2 and ν_3 vibrational levels in both complexes. For the purpose of understanding why the complexation of ethylene to such different metals as lithium (^2S ground state, devoid of d orbitals) and nickel (a typical late first row transition metal) and setting landmarks for later quantitative comparison, we have performed a natural atomic orbital analysis. It first confirms the global picture proposed in Ref. 8 for the interaction of the $2s$, $2p$ levels of Li with the π and π^* orbitals of ethylene. For lithium, the natural population of the $2p_y$ orbital is the greatest (0.174), while the $2s$ orbital is only weakly populated by back-bonding (0.0174). Comparison of the natural charges in Li–C$_2$H$_4$ and
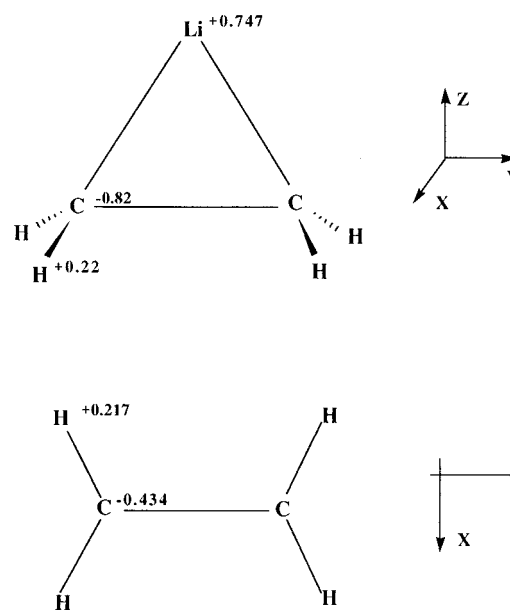

FIG. 2. Atomic natural charges on Li–C$_2$H$_4$ and C$_2$H$_4$.

C$_2$H$_4$ (Fig. 2) reveals the extend of the large charge transfer between lithium and ethylene (about 0.74 e^-, almost completely borne on the $2p$ valence orbitals of C atoms). The bonding between lithium and ethylene is entirely due to interaction between the lithium $2p_y$ and ethylene π^* orbitals, and back-bonding from π ethylene level toward lithium $2s$ and $2p_z$ orbitals is virtually negligible. In addition to weakening and lengthening the C=C bond, this causes the apparition of a large dipole moment (3.77 D calculated with DFT).

We also studied the total dipole moment variation with respect to varying (i) the carbon–carbon bond distance and (ii) the metal–carbon bond distance. The two bond distances were varied independently within 10% of the equilibrium values, keeping all other parameters constant at their equilibrium value, and the total dipole moment was thus calculated. The results are presented in Fig. 3. It shows that a sharp modulation of the total dipole moment is produced upon carbon–carbon distance variation, while a change in the lithium–ethylene distance produces much less effect. Obviously, the amount of charge transfer in the three-centers-one electron bond is sharply depending upon the carbon–carbon distance lengthening. When increasing the lithium–ethylene distance, opposite effects are taking place (decrease of the charge transfer and increase of the charge separation) which evens out the net balance.

V. CONCLUSION

The first point which has been outlined in the present paper is that the results concerning the equilibrium geometry, the binding energy and vibrational frequencies calculated with CCSD, CCSD(T), and DFT methods are quite close to each other.

The predicted vibrational spectra including isotopic substitutions present a good agreement between calculated and
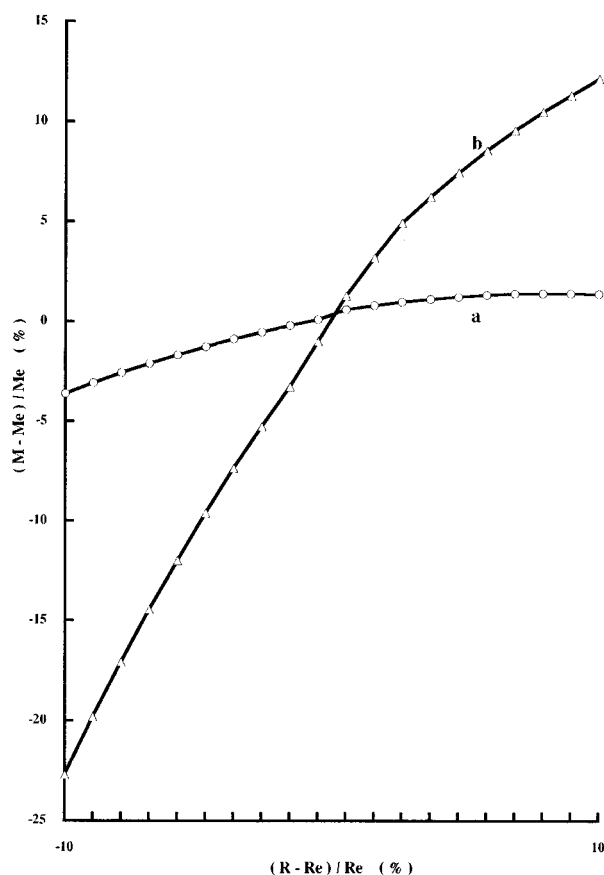
FIG. 3. Plots of the relative variation of the total dipole moment $[(M-M_e)/M_e$ in percent$]$ vs (a) the relative CC bond distance $[(R_{cc}-R^e_{cc})/R^e_{cc}]$, and (b) the relative LiC bond distance $[(R_{LiC}-R^e_{LiC})/R^e_{LiC}]$ in percent.

observed frequencies for five over six observed modes. The only discrepancy occurs for the Li–C stretching mode, where assignment is dubious both experimentally (only one over three low frequency lithium–ethylene modes has been identified) and theoretically because an harmonic model might yield a rather poor description of the corresponding energy surface for weakly bonded species. A more complete experimental study would be helpful, in which both symmetric and antisymmetric Li–C stretching would be observed as it is the case for the Al–C stretching modes in the Al–C$_2$H$_4$ compound.[20]

Calculations have confirmed the strong perturbation of the CC bond upon complexation (-40% decrease in the force constant relative to free ethylene). The CC bond in LiC$_2$H$_4$ is closer to a single bond than to a double bond. The interesting coupling of CC stretch, δ_{CH_2}, δ_{CD_2} coordinates in the ν_2 and ν_3 modes previously discussed on experimental grounds has been confirmed by the quantum chemical calculations. Another point of interest is that a careful study of the frequency shifts upon complexation or isotopic substitutions makes it possible to complete the assignments. In the present case, on the basis of DFT calculations assignments of CH stretching and wagging modes are proposed.

However, one can regret the small number of vibrational modes experimentally identified for each isotopic species

which does not allow us to completely check the validity of the calculated spectra. Considering the noticeable improvements of the spectroscopic technique over these last few years, it is clear that better comparisons between experiments and calculations are needed in the near future. Such is the case of the Ni–C$_2$H$_4$ complex[1,25] presently reinvestigated in this laboratory.

ACKNOWLEDGMENTS

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