

# Electronic structure of the $\pi$ -bonded Al–C<sub>2</sub>H<sub>4</sub> complex: Characterization of the ground and low-lying excited states

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The equilibrium properties of the  $\pi$ -bonded Al–ethylene complex in its ground state are calculated by coupled-cluster theory. Significant changes in the geometry of the ethylene molecule upon complexation (elongation of the CC bond, pyramidalization of the CH<sub>2</sub> groups) are consistent with the formation of a chemical bond between fragments. The overall interaction is rather weak because bonding is derived from the overlap between: (i) a singly occupied  $p$  orbital of Al and the antibonding  $\pi^*$  orbital of ethylene and (ii) a vacant Al  $sp$  hybrid and  $\pi$  of C<sub>2</sub>H<sub>4</sub>. Electronically excited states are studied by the equation-of-motion coupled-cluster method. The covalent nature of the interaction between fragments is reflected in the excited-state delocalization over both fragments (as opposed to the corresponding van der Waals complex). In the examined energy range (0–5.18 eV) both valence and Rydberg excited states are found. Bonding in the valence states is explained in terms of a simple molecular orbital picture. Two very intense transitions at 3.50 eV and at 3.79 eV can be used as a probe in experimental studies. © 2003 American Institute of Physics.  
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## I. INTRODUCTION

Compounds formed by metals and unsaturated hydrocarbons have long been of interest to researchers in the fields of organometallic chemistry and catalysis.<sup>1</sup> These species can provide insight into the nature of the interaction between chemisorbed molecules and metallic surfaces, thus constituting simple models for catalytic systems.

Since its first isolation by Kasai and McLeod<sup>2</sup> in a rare gas matrix, the molecular complex formed by aluminum and ethylene has been the subject of several experimental<sup>3–5</sup> and theoretical<sup>6–10</sup> studies. Similar species (for instance, complexes formed between Al and acetylene,<sup>4,11,12</sup> Al and various alkenes and arenes,<sup>4</sup> and alkali metals and ethylene<sup>13</sup>) have also been studied.

One of the most interesting fundamental questions addressed in early studies<sup>2–4,7</sup> concerns the type of interaction between the Al and C<sub>2</sub>H<sub>4</sub> fragments. Several bonding schemes of the Al–C<sub>2</sub>H<sub>4</sub> complex<sup>2,3,7</sup> are shown in Fig. 1. The type of bonding in these structures ranges from covalent (i.e., resulting from a bonding overlap of orbitals of the fragments) to van der Waals (i.e., dominated by dispersion). The most significant differences between covalent and van der Waals interactions concern binding energies and equilibrium geometries. While covalently bound molecules have typical binding energies of about 100 kcal mol<sup>–1</sup> and bond lengths smaller than 1.5 Å, van der Waals clusters are only bound by a few kcal mol<sup>–1</sup>, and the distance between fragments is usually larger than 2 Å.<sup>14,15</sup> From a chemical point of view, the defining characteristic of van der Waals complexes is the retention of the properties of the individual entities in the complex.

Recently, considerable attention has been attracted by the so-called weakly bound covalent dimers.<sup>16–19</sup> These species are bound by 2–30 kcal mol<sup>–1</sup>, the bonding having an

intermediate character between chemical and van der Waals. Despite the weakness of the bond, these species can play an important role in low-temperature environments—e.g., in the stratosphere.<sup>16</sup> For example, the interactions of NO<sub>2</sub> dimers with water or ice may differ from those of monomers, which may considerably affect the rate of atmospheric reactions.<sup>20</sup> Likewise, surface reactions of NO at low temperatures (<100 K) are dominated by NO dimers.<sup>21</sup> A particularly relevant class of such molecules are dimers in which bonding is derived from a positive overlap of molecular antibonding orbitals.<sup>18,19</sup>

According to Kasai and McLeod,<sup>2</sup> the Al–C<sub>2</sub>H<sub>4</sub> complex has a  $\pi$ -bonded structure (I-a in Fig. 1). It involves two donor–acceptor bonds: one results from an electron migration from the  $\pi$  orbital of ethylene into the vacant  $sp$  orbital of aluminum and the other results from a backdonation from the singly occupied  $p$  orbital of Al to the  $\pi^*$  orbital of the olefin. This bonding scheme is similar to that proposed by Dewar<sup>22</sup> and Chatt and Duncanson<sup>23</sup> for complexes formed by transition metals and alkenes. In this case, the  $\pi$  orbital of the alkene and a vacant orbital of the metal ( $s$ ,  $dsp^2$ ,  $sp$  or another hybrid of the correct symmetry) are involved in  $\sigma$  bonding, while an occupied  $d$  orbital of the metal and  $\pi^*$  of the olefin form the  $\pi$  bond.

Structures I-c, II-a, and II-b have been ruled out by the features of the electron spin resonance (ESR) spectrum.<sup>2</sup> A subsequent ESR study by Howard *et al.*<sup>3</sup> has also ruled out the tight ion pair [C<sub>2</sub>H<sub>4</sub>]<sup>–</sup>Al<sup>+</sup>, derived by a (complete) transfer of an electron from Al into the  $\pi^*$  orbital of ethylene.

The infrared spectrum of the Al–C<sub>2</sub>H<sub>4</sub> complex in solid argon reported by Manceron and Andrews<sup>5</sup> is consistent with a C<sub>2v</sub> structure which has two equivalent CH<sub>2</sub> groups. Structures I-a, I-b, and I-c all satisfy this condition. Although not

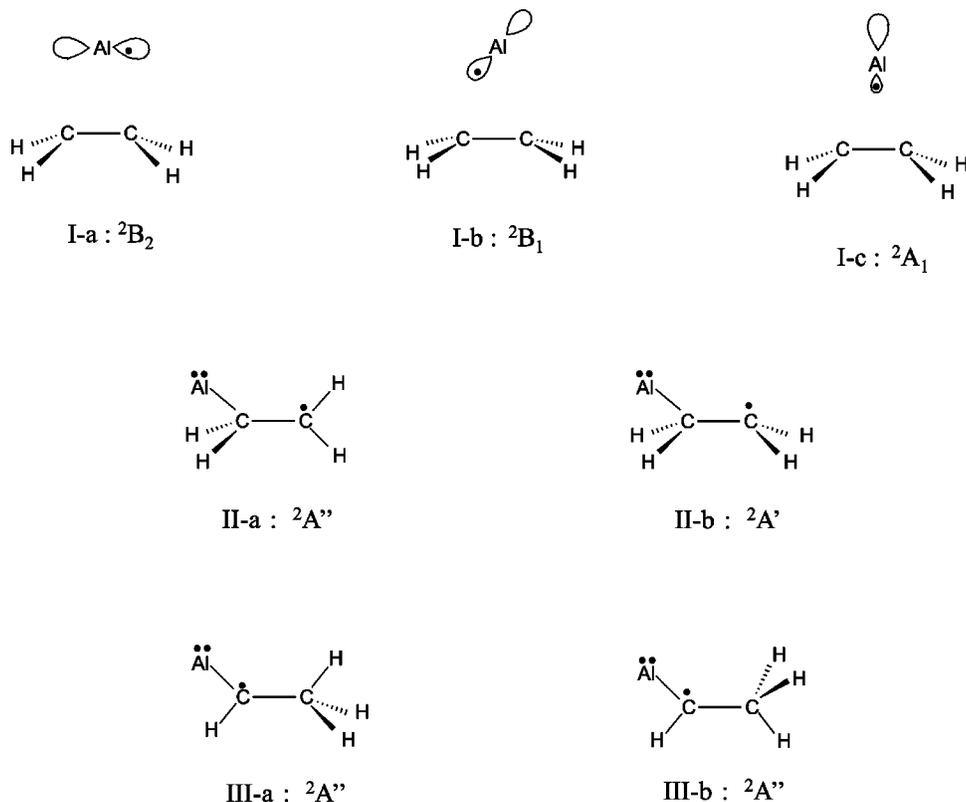


FIG. 1. Possible isomers of the Al-C<sub>2</sub>H<sub>4</sub> complex (Ref. 7). Isomers I-a, I-b, and I-c are of  $C_{2v}$  symmetry. In I-a, the orbital that hosts the unpaired electron results from a positive overlap between a  $p$  orbital of Al and  $\pi^*$  of ethylene. In I-c, the unpaired electron occupies an orbital derived from the  $sp$  hybrid of Al and the  $\pi$  orbital of C<sub>2</sub>H<sub>4</sub>. In I-b, the unpaired electron is on the nonbonding Al  $p$  orbital. The  $\sigma$ -bonded complexes II-a, II-b, III-a, and III-b belong to the  $C_s$  point group. II-a and II-b are ethyl-radical-like structures, while III-a and III-b have an aluminum-methylcarbene structure.

discussed by Manceron and Andrews, the I-b isomer is readily ruled out since its weak van der Waals interaction is inconsistent with the observed decrease of the CC bond force constant (by about 33% relative to free ethylene), which is equivalent to a bond length increase of  $0.12 \pm 0.02$  Å.

From gas phase kinetic studies, the heat of formation of Al-C<sub>2</sub>H<sub>4</sub> at 0 K ( $\Delta E_0^\circ$ ) has been determined to be higher than  $16 \text{ kcal mol}^{-1}$  (Ref. 4). This result is consistent with the formation of a relatively weakly bound  $\pi$  complex. The heat of formation of the van der Waals complex I-b would be smaller [typically, for such complexes  $\Delta E_0^\circ < 2 \text{ kcal mol}^{-1}$  (Ref. 14)], while assuming that a  $\sigma$ -bonded product is obtained (and taking into consideration the energy cost associated with breaking a  $\pi$  bond) leads to an excessively large value of the estimated Al-C bond energy.<sup>4</sup>

In addition to experimental studies, Al-C<sub>2</sub>H<sub>4</sub> has also been characterized theoretically.<sup>6-10</sup> By using the configuration-interaction singles-and-doubles (CISD) model and a double- $\zeta$  basis augmented by polarization functions (DZP), Xie *et al.*<sup>7</sup> have studied both  $C_{2v}$  (I-a,b,c) and  $C_s$   $\sigma$ -bonded structures (II-a,b and III-a,b). They have found that the lowest-energy isomer (i.e., the ground state) is a  $\pi$ -bonded complex of  $B_2$  symmetry (structure I-a in Fig. 1) whose bonding energy equals  $11.6 \text{ kcal mol}^{-1}$ . The  $B_1$  state (I-b) has been found to be very weakly bound, by  $1.4 \text{ kcal mol}^{-1}$ . The weak van der Waals interaction in the  $B_1$  state is consistent with the very small changes in the geometry of ethylene upon complexation. The  $A_1$  state, in which a  $p$  orbital from Al interacts with the  $\pi$  orbital of ethylene, has been found to be  $1.7 \text{ kcal mol}^{-1}$  higher in energy than the separated Al and C<sub>2</sub>H<sub>4</sub> (structure I-c).

Among the  $\sigma$ -bonded isomers, structures II-a, II-b, and

III-b have no local minimum.<sup>7</sup> Structure II-b collapses to the  $C_{2v}$  I-a structure, while II-a and III-b are transition states.<sup>7</sup> A local minimum has been found for the III-a structure, lying  $1.5 \text{ kcal mol}^{-1}$  above the  ${}^2B_2$  ground state.<sup>7</sup>

The  ${}^2B_2$  ground state has been confirmed by subsequent theoretical studies, which have employed perturbation theory<sup>8,9</sup> and multireference configuration-interaction (MRCI) methods<sup>9</sup> with double- $\zeta$  polarized basis sets. In their study of the Al-C<sub>2</sub>H<sub>4</sub> complex using density functional theory (DFT) and a 6-311G(2d,2p) basis set, Alikhani *et al.*<sup>10</sup> have determined a binding energy of  $13.3 \text{ kcal mol}^{-1}$  for the  ${}^2B_2$  ground state (in better agreement with experiment than earlier studies). They have described the bonding as being mostly electrostatic, as a consequence of the charge transfer from Al to the ethylene fragment.<sup>10</sup>

As far as the electronic states of the  $\pi$ -bonded complex are concerned, only the  $\tilde{X} {}^2B_2$  ground state<sup>7-10</sup> and the lowest excited states of the  $B_1$  (Refs. 7 and 9) and  $A_1$  (Refs. 7-9) symmetries (structures I-b and I-c, respectively) have been examined in the previous theoretical studies.

This work presents a systematic study of the electronically excited states in the  $\pi$ -bonded Al-C<sub>2</sub>H<sub>4</sub> complex. We report vertical excitation energies of the 11 lowest excited states and describe these states in terms of a simple molecular orbital picture, as well as their Rydberg and/or valence character. Analysis of the excited-state wave functions offers further insight into the nature of bonding in the Al-C<sub>2</sub>H<sub>4</sub> complex. Indeed, the low-lying excited states of van der Waals complexes at their ground-state equilibrium geometries can be characterized as slightly perturbed states of the fragments.<sup>24</sup> In covalently bonded complexes, however, ex-

cited states are delocalized over both fragments.

The structure of the paper is as follows: Section II outlines computational details, Sec. III A discusses the equilibrium geometry, type of bonding, and stability of the  $\tilde{X}^2B_2$  ground state, and Sec. III B describes electronically excited states. Conclusions are presented in Sec. IV. A discussion of the criteria used in the assignment of valence and Rydberg states is provided in the Appendix.

## II. COMPUTATIONAL DETAILS

As follows from previous studies, the formation of the Al-C<sub>2</sub>H<sub>4</sub>  $\pi$ -bonded complex involves significant chemical interaction between Al and ethylene. However, the experimentally determined bonding energy of 16 kcal mol<sup>-1</sup> (Ref. 4) justifies its classification as a weakly bound complex. For a quantitatively (and, in some cases, even qualitatively) correct description of this type of system high-level correlation treatments and large basis sets are necessary.<sup>18,19</sup> However, basis set requirements can be less stringent than in the case of van der Waals complexes.<sup>25</sup>

The equilibrium structure of the ground state ( $\tilde{X}^2B_2$ ) has been calculated at the coupled cluster singles and doubles<sup>26</sup> with approximate triples correction [CCSD(T)] (Ref. 27) level, with DZP, cc-pVTZ (Refs. 28 and 29) and aug-cc-pVTZ (Ref. 30) bases. The DZP basis is derived from the Dunning double- $\zeta$  basis,<sup>31,32</sup> augmented by one set of polarization functions [with exponents  $\alpha_p(\text{H})=0.700$ ,  $\alpha_d(\text{C})=0.654$ ,  $\alpha_d(\text{Al})=0.325$ ], the contraction schemes being Al(12s8p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s1p/2s1p).

The heat of formation of the  $\tilde{X}^2B_2$  state at 0 K has been calculated as a difference between total energies of the complex and the Al and C<sub>2</sub>H<sub>4</sub> fragments at their CCSD(T)/aug-cc-pVTZ equilibrium geometries. Total energies have been calculated at the CCSD(T) level with several basis sets (aug-cc-pVTZ and d-aug-cc-pVTZ (Ref. 33) with and without frozen core, aug-cc-pVQZ (Refs. 28–30) with frozen core, and aug-cc-pwCVTZ).<sup>29,30,34</sup> Our results indicate that errors up to 5 kcal mol<sup>-1</sup> can arise due to unbalanced core description.

Vertical excitation energies have been calculated at the CCSD(T)/aug-cc-pVTZ geometry, by using the EOM-CCSD method<sup>35,36</sup> and a 6-311(2+,2+)G(3df,3pd) basis set, derived from the 6-311G(d,p) basis set<sup>37,38</sup> by adding additional sets of polarization and diffuse functions.<sup>39,40</sup> Additional calculations have also been performed in the 6-311(2+,2+)G(d,p), 6-311(+,+)G(d,p) and 6-311G(d,p) basis sets. Pure angular momentum functions (5d,7f) have been used throughout this study.

Calculations have been performed using the ACES II (Ref. 41) and Q-CHEM (Ref. 42) *ab initio* packages. Some basis sets have been obtained from the EMSL database.<sup>43</sup>

## III. RESULTS AND DISCUSSION

### A. Characterization of the $\tilde{X}^2B_2$ ground state

The electronic configuration of the  $\tilde{X}^2B_2$  ground state is [core](5a<sub>1</sub>)<sup>2</sup>(3b<sub>2</sub>)<sup>2</sup>(2b<sub>1</sub>)<sup>2</sup>(6a<sub>1</sub>)<sup>2</sup>(1a<sub>2</sub>)<sup>2</sup>

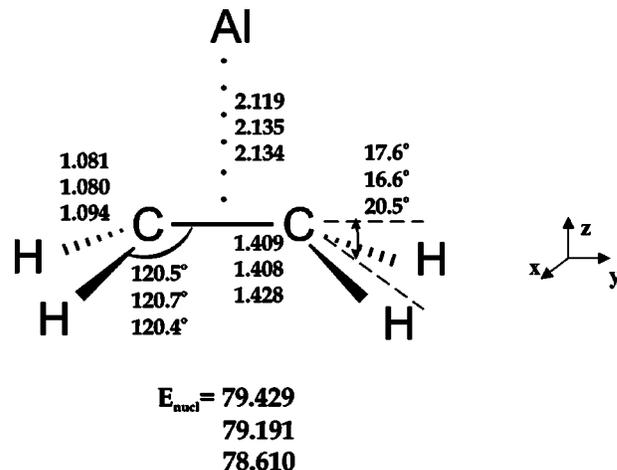


FIG. 2. Equilibrium geometry of the Al-C<sub>2</sub>H<sub>4</sub>  $\pi$  complex in the electronic ground state ( $\tilde{X}^2B_2$ ), optimized at the CCSD(T) level, with aug-cc-pVTZ, cc-pVTZ and DZP bases. The structural parameters and the nuclear repulsion energy calculated in the aug-cc-pVTZ basis are given first, followed by the values computed in the cc-pVTZ and DZP bases, respectively. Bond lengths are in ångströms, angles in degrees, and energies in hartrees. For comparison, the CCSD(T)/aug-cc-pVTZ geometrical parameters for free ethylene at equilibrium are:  $r(\text{CC})=1.333$  Å,  $r(\text{C-H})=1.080$  Å, and  $\theta(\text{HCC})=121.4^\circ$ .

$$\times (7a_1)^2(8a_1)^2(4b_2)^1, \quad (1)$$

where

$$[\text{core}] = (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(2b_2)^2(1b_1)^2(4a_1)^2. \quad (2)$$

The CCSD(T) equilibrium geometries for the ground state calculated in several basis sets are shown in Fig. 2. Bond lengths computed at the CCSD(T)/DZP level are significantly longer than those calculated in the cc-pVTZ and aug-cc-pVTZ basis sets. This observation is in agreement with the tendency of the CCSD(T) model to overestimate bond distances in double- $\zeta$  basis sets.<sup>25,44</sup>

After augmenting the cc-pVTZ basis by one set of diffuse functions, the bond lengths decrease slightly, which suggests that the effect of the basis set superposition error (BSSE) is small in this case.<sup>25</sup> As pointed out by Xie *et al.*,<sup>7</sup> the Al-C bond distance in this complex (2.233 Å in the aug-cc-pVTZ basis set) is considerably larger than the experimentally determined Al-C bond length in trimethylaluminum (1.957 Å).<sup>45</sup> This indicates that the bond in the  $\pi$ -bonded complex is weaker than a conventional Al-C single bond.

On the other hand, the Al-C bond distance in the  $\tilde{X}^2B_2$  ground state is much shorter than the corresponding distance in the  $1^2B_1$  state (characterized as a van der Waals complex), which has been determined to be 3.228 Å (Ref. 46) at the CCSD(T)/aug-cc-pVTZ level.

Moreover, the interaction between the fragments in the  $\tilde{X}^2B_2$  state is strong enough to considerably affect the geometry of ethylene (see Fig. 2). For example, the CC distance in C<sub>2</sub>H<sub>4</sub> increases significantly (by 0.076 Å) upon complexation. This is because the  $\pi_c$  bond in the complex is formed by the  $3p_y$  orbital of Al and the  $\pi^*$  orbital of ethylene, while the  $\sigma_c$  bond is derived from the overlap of the

TABLE I. Excited states of the Al-C<sub>2</sub>H<sub>4</sub> complex.<sup>a</sup> EOM-CCSD/6-311(2+,2+)G(3df,3pd), pure angular momentum.

State	$E_{ex}$ (eV)	$f_{tr}$ <sup>b</sup>	$\mu_{tr}^2$ (a.u.) <sup>c</sup>	Transition <sup>d</sup>
1 <sup>2</sup> A <sub>1</sub> (V)	1.94	0.0017	0.0350 (y)	$\sigma_c \rightarrow \pi_c$
1 <sup>2</sup> B <sub>1</sub> (V)	2.02	0.0000	0.0000	$\pi_c \rightarrow 3p_x$ (Al)
1 <sup>4</sup> A <sub>2</sub> (V)	2.28	0.0002	0.0041 (x)	$\sigma_c \rightarrow 3p_x$ (Al)
2 <sup>2</sup> B <sub>2</sub> (V/R)	3.50	0.0817	0.9515 (z)	$\pi_c \rightarrow \pi_c^*$
2 <sup>2</sup> A <sub>1</sub> (R)	3.77	$2 \times 10^{-6}$	$2 \times 10^{-5}$ (y)	$\pi_c \rightarrow 3s$ (R)
1 <sup>2</sup> A <sub>2</sub> (V)	3.79	0.1162	1.2510 (x)	$\sigma_c \rightarrow 3p_x$ (Al)
1 <sup>4</sup> A <sub>1</sub> (V)	4.03	0.0007	0.0068 (y)	$\sigma_c \rightarrow \pi_c^*$
3 <sup>2</sup> A <sub>1</sub> (R)	4.50	0.0162	0.1466 (y)	$\pi_c \rightarrow 3p_z$ (R)
2 <sup>2</sup> B <sub>1</sub> (R)	4.57	0.0000	0.0000	$\pi_c \rightarrow 3p_x$ (R)
3 <sup>2</sup> B <sub>2</sub> (R)	4.82	0.0053	0.0452 (z)	mixed excitation
4 <sup>2</sup> B <sub>2</sub> (R)	4.93	0.0052	0.0431 (z)	mixed excitation
4 <sup>2</sup> A <sub>1</sub> (R)	4.94	0.0111	0.0916 (y)	$\pi_c \rightarrow$ Rydberg orbital
5 <sup>2</sup> A <sub>1</sub> (R)	5.18	0.0097	0.0768 (y)	$\pi_c \rightarrow$ Rydberg orbital

<sup>a</sup>Geometry of the ground state optimized at the CCSD(T)/aug-cc-pVTZ level.

<sup>b</sup>Oscillator strength.

<sup>c</sup>The direction of the transition dipole moment is shown in parentheses. See Fig. 2 for axes convention. Nonzero values of the transition dipole moment for quartet states are due to the spin contamination.

<sup>d</sup>See Fig. 4 for molecular orbital picture. The excitations described as mixed include the  $\pi_c \rightarrow 3p_y$  (R) and the  $\sigma_c \rightarrow 4s$  (R) transitions with comparable amplitudes.

vacant Al  $sp_z$  hybrid with the  $\pi$  orbital of the olefin. These interactions result in  $3p_y(\text{Al}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$  and  $\pi(\text{C}_2\text{H}_4) \rightarrow sp_z(\text{Al})$  charge transfer, both contributing to the decrease of the CC bond order and, consequently, the bond length increase. Another significant change in the ethylene structure is the bending of the methylene groups by 17.6° (in the aug-cc-pVTZ basis) with respect to the plane of the free molecule. This reflects changes in the hybridization of the C atoms from  $sp^2$  in free ethylene to an intermediate between  $sp^2$  and  $sp^3$  in the complex and is thus in agreement with the reduced bond order. These structural changes reflect a weakening of the CC bond upon complexation. In a context of catalysis, the interaction between aluminum and ethylene in the  $\pi$ -bonded complex results in the CC bond activation.

Another quantity of interest, the heat of formation of the  $\tilde{X}^2B_2$  state at 0 K, corrected for the zero-point vibrational energy (ZPE), is 15.71 kcal mol<sup>-1</sup> (the ZPE correction contributes 0.39 kcal mol<sup>-1</sup> to the total value). This value was computed in the aug-cc-pwCVTZ basis set,<sup>34</sup> which ensures an adequate treatment of the core-core and core-valence correlation. The value calculated in the aug-cc-pVTZ basis with core electrons being frozen is within 0.6 kcal mol<sup>-1</sup> from the aug-cc-pwCVTZ one: however, the aug-cc-pVTZ result obtained with correlated core electrons is lower by 3.88 kcal mol<sup>-1</sup> due to an unbalanced core treatment. Calculations with the d-aug-cc-pVTZ and aug-cc-pVQZ bases and the frozen core are within 0.5 kcal mol<sup>-1</sup> of the aug-cc-pVTZ/frozen core result (and full aug-cc-pwCVTZ calculations). This demonstrates that adding a second set of diffuse functions or improving the  $n-\zeta$  quality beyond triple zeta is not necessary.

The value of  $\Delta E_0^\circ$  characterizes the bonding in this complex as an intermediate between a van der Waals interaction and a conventional covalent bond. The interaction between the fragments in this system is rather weak because it is

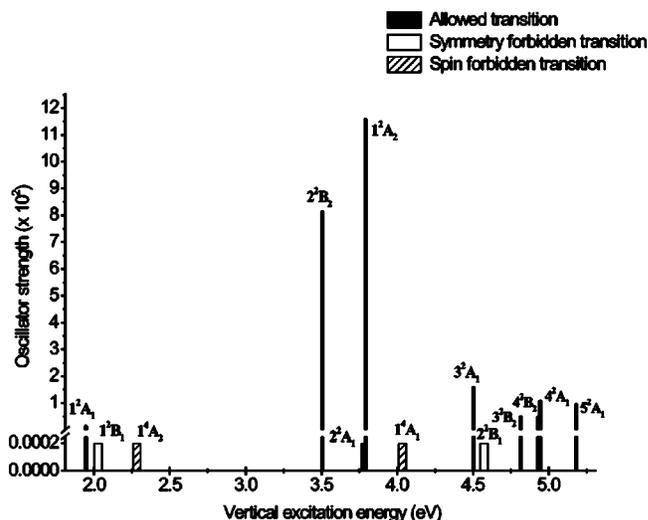


FIG. 3. Vertical excitation energies for the Al-C<sub>2</sub>H<sub>4</sub> complex calculated at the CCSD(T)/aug-cc-pVTZ geometry of the  $\tilde{X}^2B_2$  ground state. The intensity of a transition is proportional to the oscillator strength (no Franck-Condon factors are taken into account).

derived from an overlap between a singly occupied  $p$  orbital of Al and the antibonding ( $\pi^*$ ) orbital of ethylene and also between a vacant  $sp$  Al hybrid and the doubly occupied  $\pi$  orbital of ethylene. A stronger interfragment interaction would require a larger overlap and, consequently, a larger  $p \rightarrow \pi^*$  and  $\pi \rightarrow sp$  charge transfer, thus destabilizing the ethylene fragment. Therefore, energy gain due to stronger interfragment bonding would be exceeded by energy loss due to destabilization of ethylene. This is similar to the (NO)<sub>2</sub> (Ref. 18) and (O<sub>2</sub>)<sub>2</sub> (Ref. 19) dimers, in which antibonding orbitals are also involved in interfragment bonding.

## B. Electronically excited states

Vertical excitation energies and oscillator strengths for all the states studied in this work (with vertical excitation energies up to 5.18 eV) are given in Table I and are illustrated in Fig. 3.

The EOM-CCSD method<sup>35,36</sup> has been used for the characterization of the excited states. This model is known to perform well (accuracy of 0.1–0.3 eV for calculated excitation energies, balanced treatment of valence and Rydberg states) when applied to states dominated by the excitation of a single electron from the ground state.<sup>47</sup> However, excited states which are two-electron promotions are treated much less accurately by the EOM-CCSD method due to an imbalance in the treatment of correlation for the two electrons in the ground and excited states.<sup>48</sup> That is why the weight of doubly excited configurations provides a natural diagnostic for the EOM-CCSD method. We have found that their weight in the wave function is small enough ( $\leq 11\%$  for all the states addressed) to ensure an accurate treatment.

In addition to quantitative characterization of the Al-C<sub>2</sub>H<sub>4</sub> electronically excited states, an important purpose of the present study is to qualitatively analyze the nature of the excited states in terms of molecular orbitals involved in the transition. This analysis necessarily involves the assign-

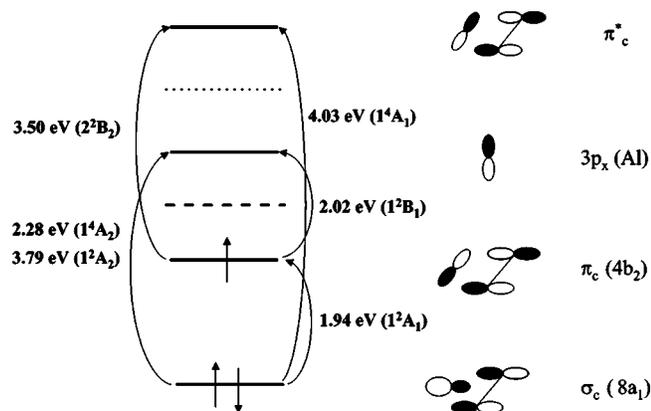


FIG. 4. Molecular orbital diagram for the ground and valence excited states of the Al-C<sub>2</sub>H<sub>4</sub> complex.  $\sigma_c$  (the  $\sigma$  bonding orbital of the complex) results from the interaction of an Al  $sp_z$  hybrid with the  $\pi$  orbital of ethylene. The  $\pi$  bonding orbital of the complex,  $\pi_c$ , results from the positive overlap of  $3p_y$  from Al with the  $\pi^*$  orbital of ethylene. The corresponding antibonding orbital is labeled  $\pi_c^*$ . The aluminum lone pair resides in the  $7a_1$  orbital [see Eq. (1)], an Al  $sp_z$  hybrid. The  $\sigma_c$  and  $\pi_c$  orbitals are the  $8a_1$  and  $4b_2$  orbitals in Eq. (1), respectively.  $3p_x$ (Al) is of  $b_1$ , and  $\pi_c^*$  of  $b_2$  symmetry. The dashed line separates occupied and virtual orbitals. The dotted line indicates a break in the energy level sequence.

ment of a valence or Rydberg character to excited states. As in many radicals, the unpaired electron in the Al-C<sub>2</sub>H<sub>4</sub> complex is relatively weakly bound: i.e., the lowest vertical ionization potential (IP) of the  $\pi$ -bonded complex is estimated to be 6.83 eV.<sup>49</sup> Consequently, these species have low-lying Rydberg states. Indeed, several states with Rydberg character have been found in the energy range examined in this work (0–5.18 eV). Since the complex also has valence states which are low in energy, they can interact strongly with Rydberg states of the same symmetry and multiplicity. Actually, Rydberg states have always contributions of valence excitations and vice versa. Moreover, the Rydberg or valence character of a state may change upon distortion from the ground-state geometry.<sup>50,51</sup> A detailed discussion of the criteria used in the assignment of the excited states as valence, Rydberg, or states with mixed Rydberg–valence character is provided in the Appendix.

The molecular orbitals involved in transitions from the ground state to low-lying excited states with valence character are shown in Fig. 4. The lowest excited state  $1^2A_1$  (structure I-c from Fig. 1) results from the excitation of a  $\beta$  electron from the  $\sigma_c$  to the  $\pi_c$  orbital (which is singly occupied in the ground state). Given the nature of these orbitals—i.e., the contribution of the  $\pi$  orbital of ethylene to  $\sigma_c$  and of the  $\pi^*$  orbital to  $\pi_c$ ,—the  $1^2A_1$  state can be expected to have a CC bond which is longer than in the ground ( $\bar{X}^2B_2$ ) state.

The next in energy is the  $1^2B_1$  state (structure I-b in Fig. 1), at 2.02 eV, which is derived from the promotion of the unpaired electron from the  $\pi_c$  orbital to the (nonbonding)  $3p_x$  orbital of Al. Therefore, one can expect this state to be weakly bound, in agreement with its characterization by Xie *et al.*<sup>7</sup>

The  $1^4A_2$  state at 2.28 eV and its doublet counterpart  $1^2A_2$  at 3.79 eV result from the excitation of an electron from the  $\sigma$  bonding orbital of the complex,  $\sigma_c$ , to  $3p_x$ (Al).

In the final state(s), the  $\sigma_c$ ,  $\pi_c$ , and  $3p_x$  orbitals each host one unpaired electron. Consequently, the two states are expected to be bound, with an even longer CC bond than in the ground state.

The excitation to the  $2^2B_2$  state is dominated by a valence transition—namely,  $\pi_c \rightarrow \pi_c^*$ . Therefore, this state may still be bound (due to the double occupancy of the  $\sigma$  bonding orbital), but the bonding is weaker than in the ground state.

The  $1^4A_1$  state at 4.03 eV is derived from the excitation of an electron from the doubly occupied  $\sigma_c$  orbital to the antibonding  $\pi_c^*$  orbital (the corresponding doublet state lies around 6.49 eV).

In the energy range considered, there are two very intense transitions, which can be used to probe experimentally the Al-C<sub>2</sub>H<sub>4</sub>  $\pi$ -bonded complex. For the  $2^2B_2$  state at 3.50 eV the large intensity of the transition can be explained by its bonding–antibonding ( $\pi_c \rightarrow \pi_c^*$ ) character, as shown by Mulliken.<sup>52</sup> In the case of the  $1^2A_2$  state at 3.79 eV, the nonzero value of the transition dipole moment is due to the  $s$  character of the initial orbital ( $\sigma_c$ ). However, no explanation for the large intensity of the transition has been found.

#### IV. CONCLUSIONS

In the present work, the  $\bar{X}^2B_2$  ground state and 11 lowest vertical excited states of the Al-C<sub>2</sub>H<sub>4</sub>  $\pi$ -bonded complex are characterized at the CCSD(T)/aug-cc-pVTZ and EOM-CCSD/6-311(2+,2+)G(3df,3pd) levels of theory, respectively.

The significant changes in the ethylene fragment upon complexation (elongation of the CC bond by 0.076 Å, back-bending of the CH<sub>2</sub> groups by 17.6°) are structural signatures of a chemical interaction between the Al and C<sub>2</sub>H<sub>4</sub> fragments in the complex. The interaction between the two fragments involves two dative bonds: one results from an overlap of a singly occupied Al  $p$  orbital with the  $\pi^*$  orbital of ethylene ( $p \rightarrow \pi^*$  charge transfer), the other from an overlap of a vacant Al  $sp$  hybrid with the  $\pi$  orbital of C<sub>2</sub>H<sub>4</sub> ( $\pi \rightarrow sp$  charge transfer). The overall Al-C<sub>2</sub>H<sub>4</sub> interaction is rather weak because the interfragment bonding destabilizes ethylene. This is consistent with the calculated value of the heat of formation at 0 K (15.71 kcal mol<sup>-1</sup>), which characterizes bonding in the complex as intermediate between van der Waals and covalent.

Among the 11 lowest vertical excited states (in the 0–5.18 eV energy range), both valence and Rydberg states are found. The delocalized character of the valence states is in agreement with a chemical (weak covalent) interaction between fragments in the complex. Given their large intensity, the two transitions at 3.50 and 3.79 eV can be used to probe experimentally the formation of the Al-C<sub>2</sub>H<sub>4</sub>  $\pi$  complex.

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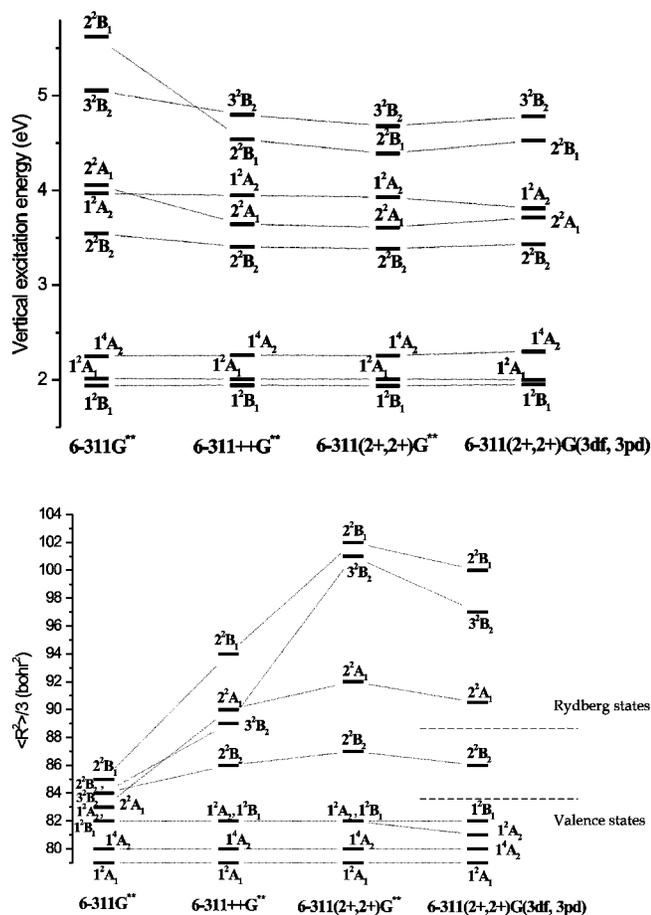


FIG. 5. Basis set dependence of the EOM-CCSD vertical excitation energies (upper panel) and the spherically averaged second moment of the charge distribution (lower panel):  $\frac{1}{3}\langle R^2 \rangle = \frac{1}{3}[\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle]$ . Adding diffuse functions to the basis set causes a significant decrease in the excitation energies of the Rydberg states, while the valence states remain largely unaffected. Likewise, in larger bases,  $\langle R^2 \rangle$  increases considerably for Rydberg states, while it remains virtually unchanged for valence states.

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#### APPENDIX: ASSIGNMENT OF VALENCE AND RYDBERG STATES

In order to characterize the excited states as having valence or Rydberg character, vertical excitation energies and second moments of the charge distribution have been calculated in several basis sets. The dependence of the excitation energies and spherically averaged second moments of the charge distribution ( $\frac{1}{3}\langle R^2 \rangle$  values) on the basis set is shown in Fig. 5. As the basis set is expanded by adding diffuse functions, the excitation energy is expected to decrease and the effective size of the electron distribution ( $\frac{1}{3}\langle R^2 \rangle$ )—to increase significantly for Rydberg states. For valence states, both parameters remain largely unaffected.

Based on these criteria, the  $1^2B_1$ ,  $1^2A_1$ ,  $1^4A_2$ , and  $1^2A_2$  states are valence states, while the  $2^2A_1$ ,  $2^2B_1$ , and

$3^2B_2$  states are of Rydberg character. The  $2^2B_2$  state has a mixed Rydberg–valence character. The  $3^2A_1$ ,  $4^2B_2$ ,  $4^2A_1$ , and  $5^2A_1$  states are assigned as Rydberg and  $1^4A_1$  as a valence state based on a criterion derived from Fig. 5(b):  $\frac{1}{3}\langle R^2 \rangle$  is smaller than or equal to 84 bohr<sup>2</sup> for valence states and larger than or equal to 89 bohr<sup>2</sup> for Rydberg states.

For the assignment of molecular Rydberg states the Rydberg formula is often used:

$$E_{ex} = IP - \frac{13.61}{(n - \delta)^2}, \quad (\text{A1})$$

where  $E_{ex}$  is the excitation energy (in eV), IP is the ionization potential of the ground state,  $n$  is the principal quantum number of the excited electron, and  $\delta$  is the quantum defect, which accounts for the core penetration of the Rydberg orbital and depends on the  $l$  quantum number. The recommended values for  $\delta$  are 0.9–1.2, 0.3–0.5, and  $\leq 0.1$  for  $s$ ,  $p$ , and  $d$  electrons, respectively.<sup>53</sup>

The  $n$  and  $l$  quantum numbers are assigned to the Rydberg excited states based on (i) the excitation energy estimated by means of the Rydberg formula and (ii) the symmetry of the state. Thus, the  $2^2A_1$ ,  $3^2A_1$ , and  $2^2B_1$  states are derived from the excitation of the unpaired electron in the  $\pi_c$  orbital to the  $3s$ ,  $3p_z$ , and  $3p_x$  molecular Rydberg orbitals, respectively. The  $3^2B_2$  and  $4^2B_2$  states have contributions from both the  $\pi_c \rightarrow 3p_y$  and  $\sigma_c \rightarrow 4s$  excitations. Regarding the  $1^2A_1$  and  $5^2A_1$  states, it can only be concluded that they are both derived from the excitation of the unpaired electron to either one of the  $4s$ ,  $3d_{z^2}$ , or  $3d_{x^2-y^2}$  Rydberg orbitals.

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