

Ab initio spectroscopy of the aluminum methylene (AlCH_2) free radical

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ABSTRACT

Extensive *ab initio* investigations of the ground and electronic excited states of the AlCH_2 free radical have been carried out in order to predict the spectroscopic properties of this, as yet, undetected species. Difficulties with erratic predictions of the ground state vibrational frequencies, both in the literature and in the present work, have been traced to serious broken-symmetry instabilities in the unrestricted Hartree-Fock orbitals at the ground state equilibrium geometry. The use of restricted open-shell Hartree-Fock or complete active space self consistent field orbitals avoids these problems and leads to consistent and realistic sets of vibrational frequencies for the ground state. Using the internally contracted multireference configuration interaction method with aug-cc-pV(T+d)Z basis sets, we have calculated the geometries, energies, dipole moments, and vibrational frequencies of eight electronic states of AlCH_2 and AlCD_2 . In addition, we have generated Franck-Condon simulations of the expected vibronic structure of the $\tilde{A} - \tilde{X}$, $\tilde{B} - \tilde{X}$, $\tilde{C} - \tilde{X}$, and $\tilde{C} - \tilde{A}$ band systems, which will be useful in searches for the electronic spectra of the radical. We have also simulated the expected rotational structure of the 0-0 absorption bands of these transitions at modest resolution under supersonic expansion cooled conditions. Our conclusion is that if AlCH_2 can be generated in sufficient concentrations in the gas phase, it is most likely detectable through the $\tilde{B}^2A_2 - \tilde{X}^2B_1$ or $\tilde{C}^2A_1 - \tilde{X}^2B_1$ electronic transitions at 515 nm and 372 nm, respectively. Both band systems have vibrational and rotational signatures, even at modest resolution, that are diagnostic of the aluminum methylene free radical.

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I. INTRODUCTION

Aluminum is the most abundant metal in the earth's crust, and it has an extensive chemistry in the trivalent state. However, low valent Al(I) and Al(II) species have often been postulated as intermediates in the photochemical and free radical reactions of organoaluminum compounds, and the synthesis and reactions of such species is an active area of current chemistry.¹ In this context, the simple free radical formed by the combination of an aluminum atom and a methylene molecule (AlCH_2) is of fundamental interest. It is a coordinately unsaturated species that is expected to be highly reactive and is a likely intermediate in the organometallic chemistry of aluminum. It has also been suggested on the basis of the abundance of aluminum and methylene in space that this species is a potential interstellar molecule.² The radical has yet to be identified spectroscopically, either in the gas phase or in matrices. The low molecular weight (41 g/mol), large rotational constants ($A \sim 10 \text{ cm}^{-1}$), small

number of electrons (21), and lack of isotopic complications (²⁷Al = 100%) make it a very attractive species for both spectroscopic and quantum chemical studies.

The only available experimental report on AlCH_2 is the 1990 neutralization-reionization mass spectrometry study of Srinivas *et al.*³ They ionized $\text{Al}(\text{CH}_3)_3$ in a mass spectrometer and readily detected the AlCH_2^+ ion. Neutralization and reionization showed that the AlCH_2 radical was stable with a lifetime $>1 \mu\text{s}$ in their apparatus. The fragmentation patterns indicated that isomerization to the hydridoaluminum species HAICH did not occur during the neutralization-reionization process.

The ground state properties of aluminum methylene were explored theoretically by Schaefer and co-workers^{2,4-6} as early as 1980 and most recently in 2013. All of their studies show that the planar C_{2v} AlCH_2 structure is the lowest energy isomer, with linear and trans HAICH some 50 kcal/mol higher in energy and H_2AlC almost 90 kcal/mol above the global minimum. Early

theoretical work^{4,7} showed that, contrary to expectations, AlCH_2 has an aluminum-carbon single bond although BCH_2 (also unknown experimentally) appears to have the expected boron-carbon double bond. These predictions have direct relevance to current issues of single vs multiple bonding in species beyond the first row of the periodic table. In an appendix to their latest paper, Compaan and co-workers² noted that the inclusion of core electron correlation had little effect on the geometric parameters but changed some of the AlCH_2 ground state harmonic vibrational frequencies by as much as 150 cm^{-1} , casting some doubt on all previous predictions of the IR spectrum.

To date, there have not been any published experimental or theoretical studies of the electronic spectra of AlCH_2 . Building on our success in studying the group IV methylenes^{8–15} (SiCH_2 , GeCH_2 , and SnCH_2) and in detecting various reactive aluminum species by electron impact dissociation of trimethyl aluminum^{16–18} (AlC , AlC_2 , and AlCCH), we are engaged in attempts to use laser spectroscopy to detect the aluminum methylene free radical in the gas phase. In the present work, we have used *ab initio* theory to predict the ground and excited state properties of AlCH_2 accurately enough to enable targeted searches for the laser induced fluorescence spectrum. In the process, we have found that this simple species is more of a challenge for theory than hitherto suspected.

II. COMPUTATIONAL METHODS

The geometries and harmonic frequencies of the ground electronic state of AlCH_2 were calculated using the CFOUR¹⁹ and Molpro²⁰ programs. Both single reference and multireference methods were explored, either neglecting or including core correlation. The methods included Møller–Plesset second order perturbation theory (MP2),²¹ coupled cluster singles and doubles with triples added perturbatively (CCSDT(T)),²² complete active space with second-order perturbation theory (CASPT2),^{23,24} and internally contracted multireference configuration interaction (ICMRCI).^{25,26} For all methods, except ICMRCI, we considered both the valence correlation, using the cc-pV(Q+d)Z basis for Al²⁷ and the cc-pVQZ basis for C and H,²⁸ and core correlation, using the cc-pwCVQZ basis for Al²⁹ and C and the cc-pVQZ basis for H.²⁸

Difficulties with obtaining consistent results using single reference methods (*vide infra*) led us to explore multireference methods for calculating the ground and excited states of AlCH_2 . The Molpro suite of quantum chemistry programs was used to this purpose.²⁰ Molecular orbitals were first obtained in a series of state averaged complete active space self consistent field (CASSCF)^{30,31} computations including all electron and valence orbitals (nine electrons in ten orbitals). The lowest two electronic states for each C_{2v} symmetry species were considered for all computations (eight states in total).

The CASSCF results were followed by ICMRCI calculations. To keep all computations at a manageable level and to treat both the ground and excited states in a balanced way, the aug-cc-pV(T+d)Z basis set²⁷ was used throughout and only the valence electrons were correlated. For the ground state only, we also considered core correlation using the aug-cc-pwCVTZ basis²⁹ for Al and C and the aug-cc-pVTZ basis²⁸ for H. Finally, the Davidson correction (denoted as + Q) with relaxed reference^{32,33} was applied to the computed energies.

Once the equilibrium geometries were obtained, harmonic force fields in internal symmetry coordinates were calculated by numerical differentiation using a five point scheme,³⁴ with displacements of 0.01 bohr for stretches and 0.02 rad for angles. In this case, the Davidson correction was not used as for higher excited states, it introduces numerical noise, which affects the numerical differentiation of the out-of-plane bending mode. Harmonic frequencies were finally calculated using the Intder program.³⁵

Our ICMRCI/aug-cc-pV(T+d)Z *ab initio* results were also used to perform Franck–Condon simulations of the absorption and single vibronic level (SVL) emission spectra of the various possible electronic transitions as an aid to their future detection by absorption, laser-induced fluorescence (LIF), and/or emission spectroscopy. The simulation program, originally developed by Yang *et al.*³⁶ and locally modified for the calculation of SVL emission spectra, requires input of the molecular structures, vibrational frequencies, and mass-weighted Cartesian displacement coordinates from the *ab initio* force fields of the two combining electronic states. Franck–Condon factors are then calculated in the harmonic approximation using the exact recursion relationships of Doktorov *et al.*,³⁷ taking into account both normal coordinate displacement and Duschinsky rotation effects.

Finally, the rotational constants, calculated from the *ab initio* molecular structures, have been used to simulate the modest resolution absorption contours of the 0–0 bands of the lowest three electronic transitions under our typical supersonic free jet expansion conditions. The very convenient graphical simulation program PGOPHER³⁸ was employed for this purpose.

III. RESULTS AND DISCUSSION

A. General results

The most striking difficulty met in the first stages of this work was the large fluctuations observed in the calculation of the ω_4 (out-of-plane bending) mode of AlCH_2 using the different methods, as illustrated in Table I. Single reference correlated methods based on unrestricted Hartree–Fock (UHF) orbitals (entries a–d) systematically recover high values of this frequency, compared to the corresponding values obtained starting from restricted open-shell Hartree–Fock (ROHF) orbitals (entries e–j), to multi reference methods (entries l–n), and to density functional theory (entry k). In particular, the UHF/MP2 calculations (entries a and b) generate physically unrealistic values larger than 3600 cm^{-1} .

The problems could not be attributed to a spin contamination of the correlated wavefunctions since the expectation value of S^2 was always very close to the theoretical value of 0.75 [e.g., at the UHF/CCSD(T)/cc-pV(Q+d)Z/FC level, entry d, $\langle S^2 \rangle = 0.7510$]. These disagreements were eventually explained once a stability check of the reference UHF and ROHF wavefunctions was performed. In particular, in the ground state, the UHF orbitals show serious spatial broken-symmetry instabilities,^{39,40} while the ROHF orbitals do not. This anomaly was further confirmed by performing geometry optimizations without symmetry restrictions, both at the UHF and at the ROHF levels. While ROHF recovers a planar structure with C_{2v} symmetry, UHF converges to a C_s pyramidal structure with the Al–C bond $\sim 9^\circ$ out of the HCH plane. These

TABLE I. Equilibrium geometries and harmonic frequencies of the ground state of AlCH_2 calculated at various levels of theory, with the CFOUR (entries A–H) and MOLPRO (entries I–N) quantum chemistry programs. The energy Hessians have been calculated either analytically (entries A–D) or from finite differences of gradients (entries E–H, K and M) or energies (entries i, j, l, and n). The vibrational frequencies are in cm^{-1} . UHF/CCSD(T)/cc-pwCVQZ/AE frequencies were also calculated numerically using finite differences of gradients (G) and finite differences of energies (E). The results, in the same order as in the table, are (G) 3056.1, 1383.2, 637.1, 670.6, 3137.1, 411.7; (E) 3056.1, 1388.6, 653.5, 685.3, 3138.6, and 434.5. ROHF/CCSD(T)/cc-pwCVQZ/AE frequencies were also calculated numerically using finite differences of energies (E). The results, in the same order as in the table, are 3055.0, 1384.7, 637.4, 437.1, 3136.3, and 408.0.

	Method	$r_{\text{AlC}}/\text{\AA}$	$r_{\text{CH}}/\text{\AA}$	$\theta_{\text{HCH}}/^\circ$	$\omega_1 (a_1)$	$\omega_2 (a_1)$	$\omega_3 (a_1)$	$\omega_4 (b_1)$	$\omega_5 (b_2)$	$\omega_6 (b_2)$
A	UHF/MP2/cc-pwCVQZ/AE	1.9586	1.0867	110.2	3115.7	1391.9	642.6	3632.7	3204.9	408.6
B	UHF/MP2/cc-pV(Q+d)Z/FC	1.9684	1.0883	110.1	3109.4	1691.6	640.7	3734.2	3197.5	410.5
C	UHF/CCSD(T)/cc-pwCVQZ/AE	1.9616	1.0912	110.1	3056.1	1383.2	637.1	670.9	3137.1	411.7
D	UHF/CCSD(T)/cc-pV(Q+d)Z/FC	1.9706	1.0929	110.0	3049.0	1382.1	634.9	623.1	3129.2	413.1
E	ROHF/MP2/cc-pwCVQZ/AE	1.9590	1.0869	110.2	3111.6	1390.7	641.0	542.2	3201.1	407.4
F	ROHF/MP2/cc-pV(Q+d)Z/FC	1.9690	1.0886	110.1	3105.4	1390.4	638.9	545.1	3193.8	409.4
G	ROHF/CCSD(T)/cc-pwCVQZ/AE	1.9616	1.0912	110.1	3056.0	1383.1	637.1	463.5	3137.1	411.4
H	ROHF/CCSD(T)/cc-pV(Q+d)Z/FC	1.9706	1.0929	110.0	3048.9	1382.0	634.9	465.3	3129.2	412.8
I	ROHF/CCSD(T)/cc-pwCVQZ/AE	1.9616	1.0912	110.1	3055.9	1383.1	637.1	489.7	3137.0	411.7
J	ROHF/CCSD(T)/cc-pV(Q+d)Z/FC	1.9706	1.0929	110.0	3040.0	1382.0	635.0	489.2	3129.3	412.9
K	DFT/B3LYP/cc-pV(Q+d)Z	1.9734	1.0921	109.8	3034.0	1373.9	618.9	438.4	3107.5	412.4
L	CASPT2/cc-pwCVQZ/AE	1.9612	1.0928	110.1	3036.8	1373.1	636.1	456.5	3121.2	412.3
M	CASPT2/cc-pV(Q+d)Z/FC	1.9716	1.0944	109.9	3029.4	1368.7	631.8	458.5	3111.5	406.5
N	ICMRCI/cc-pV(Q+d)Z/FC	1.9710	1.0932	110.0	3043.2	1388.4	633.9	478.6	3122.9	417.2

instabilities also account for the anomalously large core correlation effects reported by Compaan and co-workers,² which should instead be considered as a side effect of the UHF spatial instability. Indeed, frequencies calculated with single reference methods based on ROHF orbitals correlating all electrons (AE) or with frozen core (FC) (compare entries E,F and G,H in Table I) are rather immune from core correlation effects, with differences less than 20 cm^{-1} . The same is also true for multireference methods (compare entries L and M in Table I). In summary, all previous calculations^{2,4–6} of the ground state vibrational frequencies appear to have suffered from UHF orbital spatial instabilities, as evidenced by ω_4 vibrational frequencies, which are 100 cm^{-1} – 180 cm^{-1} too large. ROHF orbitals do not suffer from the same broken-symmetry instabilities, and the core correlation effects on the resulting vibrational frequencies are small, so the frozen core approximation can be safely

employed in subsequent calculations. Finally, for the ground state, the ROHF/CCSD(T) results (see Table I) are very similar to those obtained with ICMRCI methods, so the latter can be reliably used to extend the calculations to the excited states.

TABLE II. Comparison of T_e excitation energies (cm^{-1}), calculated at the ICMRCI+Q/aug-cc-pV(T+d)Z level of theory, with the available experimental data.

	Expt.	Calc.	Calc.-Expt.
CH			
$A^2\Delta$	23 217.5 ⁴¹	23 512.3	+294.8
$B^2\Sigma^-$	26 050.8 ⁴¹	26 147.6	+96.8
$C^2\Sigma^+$	31 801.5 ⁴¹	31 936.8	+135.3
AlC			
$A^4\Pi$	18 012.2 ⁴²	18 093.7	+81.5
$B^4\Sigma^-$	22 426.2 ⁴³	22 141.3	−284.9
CH₂			
b^1B_1	8351.1 ⁴⁴	8254.0	−97.1

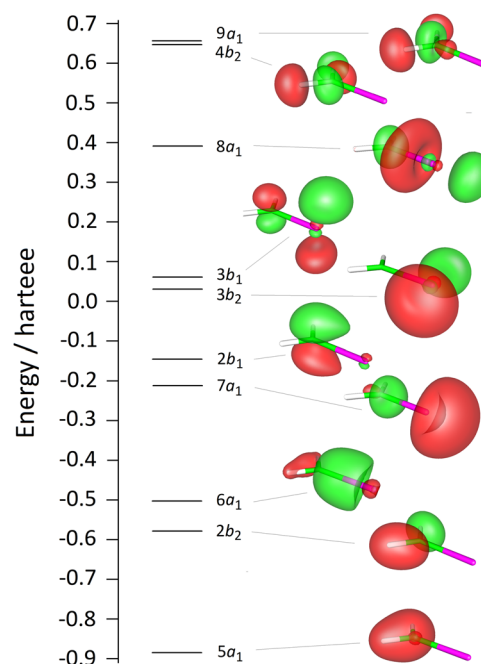


FIG. 1. State-averaged CASSCF aug-cc-pV(T+d)Z molecular orbitals of AlCH_2 . The orbitals are calculated at the ICMRCI+Q/aug-cc-pV(T+d)Z equilibrium geometry of the ground state: $r_{\text{AlC}} = 1.9766 \text{ \AA}$, $r_{\text{CH}} = 1.0953 \text{ \AA}$, and $\theta_{\text{HCH}} = 110.0^\circ$.

One of the key issues in the theoretical study of molecular excited state energies is the accuracy expected by the specific combination of the method and the basis set adopted for the calculation. In the absence of any experimental information on AlCH_2 , the only route is a comparison of the results obtained at the same level of theory for simpler species containing the same atoms. In Table II, we compare the results for CH , AlC , and CH_2 with the available experimental data.^{41–44} In all cases, the calculated excitation energies lie within 300 cm^{-1} of experiment, so similar accuracy can be expected in the calculation of the excited states of AlCH_2 . Of course, these results might be improved by extrapolating to the infinite basis set limit and by considering core correlation. However, these corrections cannot be easily applied to the excited states of AlCH_2 , which were all investigated at the ICMRCI+Q/aug-cc-pV(T+d)Z level.

In Fig. 1, we show the AlCH_2 valence state-averaged molecular orbitals obtained from the CASSCF computations, which give a ground state MO configuration of

$$(\text{core})(5a_1)^2(2b_2)^2(6a_1)^2(7a_1)^2(2b_1)^1.$$

Since there is a large difference in the orbital energies of methylene and aluminum, the lowest two orbitals $5a_1$ and $2b_2$ are essentially unmodified from their parent methylene MOs. The $6a_1$ orbital is also predominantly methylenic with a small out-of-phase aluminum s orbital contribution. The second highest occupied molecular orbital (SHOMO) $7a_1$ is predominantly a lone pair $3s$ orbital on the aluminum atom. The highest occupied molecular orbital (HOMO) $2b_1$ has a single electron and is almost entirely localized as an out-of-plane $2p$ orbital on the carbon atom and does not delocalize to form any sort of minimal π bond. The LUMO ($3b_2$) has the characteristics of an in-plane aluminum $3p$ atomic orbital, and the slightly higher energy $3b_1$ MO is clearly π^* antibonding.

Figure 2 shows the potential energy curves for the first eight electronic states of AlCH_2 calculated at the ICMRCI+Q/aug-cc-pV(T+d)Z level with state-averaged CASSCF orbitals, as a function

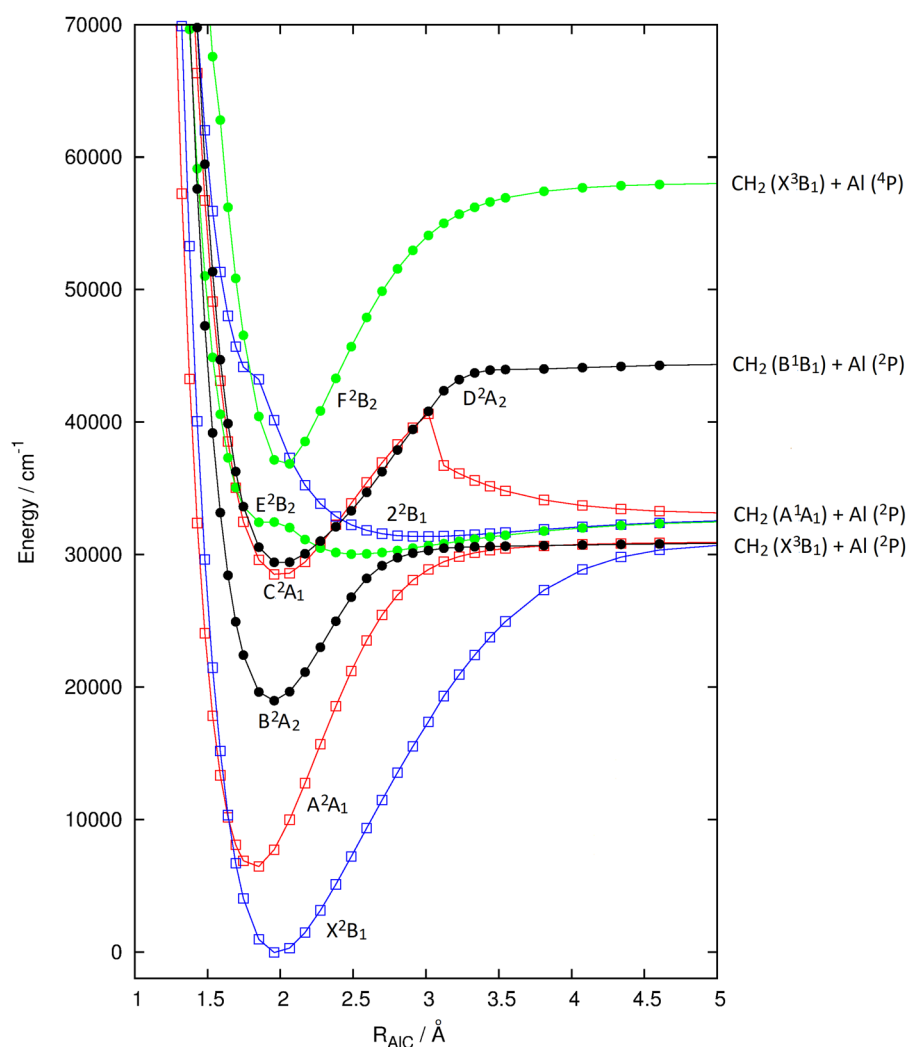


FIG. 2. Potential energy curves for the first eight electronic states of AlCH_2 calculated at the ICMRCI+Q/aug-cc-pV(T+d)Z level with state-averaged CASSCF orbitals as a function of the r_{AlC} stretching coordinate. The remaining geometric parameters were fixed at the equilibrium values of the $\tilde{X}^2B_1$ state: $r_{\text{CH}} = 1.0953\text{ \AA}$, and $\theta_{\text{HCH}} = 110.0^\circ$. Color code (online) blue: 2B_1 states, red 2A_1 states; black: 2A_2 states, and green: 2B_2 states.

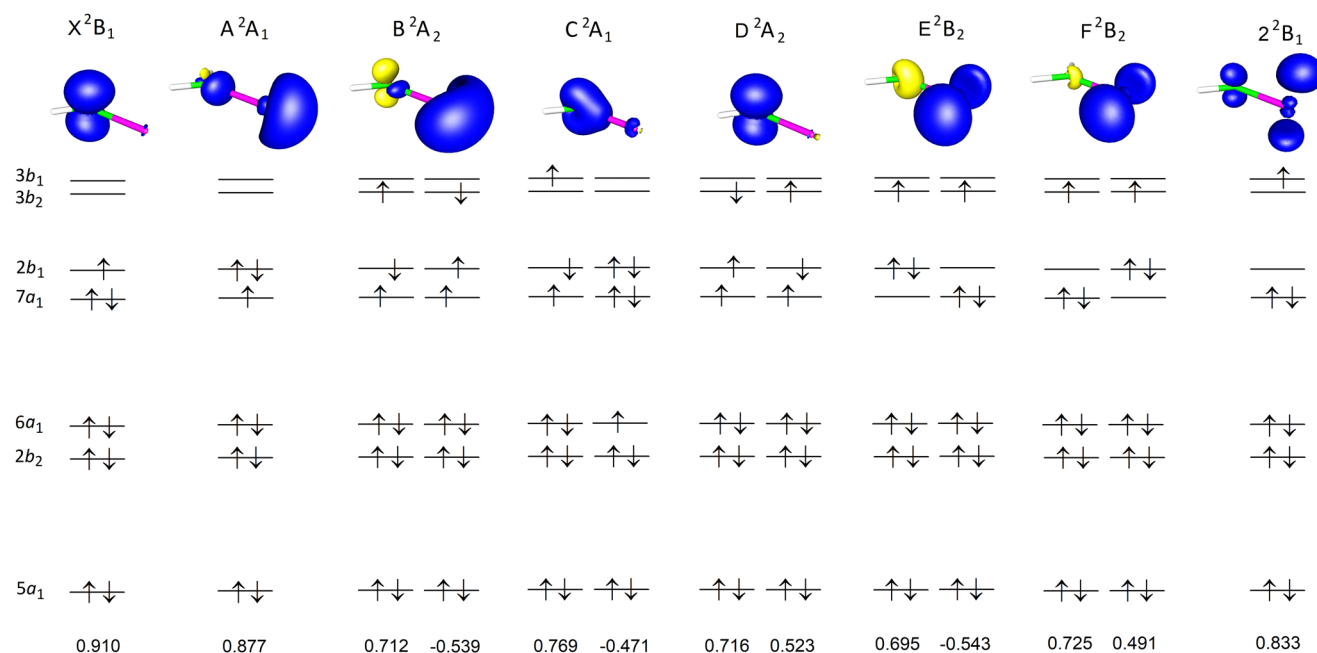


FIG. 3. CASSCF/aug-cc-pV(T+d)Z spin densities and dominant electronic configurations for the electronic states of AlCH_2 , calculated at the ICMRCI+Q/aug-cc-pV(T+d)Z equilibrium geometry of the ground state. The regions where the difference between α and β spin densities is negative/positive are shown in yellow/blue.

of the r_{AlC} stretching coordinate, and their corresponding dissociation products. Figure 3 shows the spin densities, calculated at the CASSCF/aug-cc-pV(T+d)Z level of theory and at the same geometry of the molecular orbitals in Fig. 1, where the difference between the α and β spin densities is shown pictorially together with the dominant electronic configurations.

The optimized geometries, vibrational frequencies, dipole moments, electronic excitation energies, and electronic transition moments calculated at the ICMRCI/aug-cc-pV(T+d)Z/FC level of theory for the ground and seven electronic excited states are summarized in Table III. For the ground state only, we also checked the effects of core correlation at the ICMRCI/aug-cc-pwCVTZ/AE level. As expected, both Al–C and C–H bonds shorten slightly, while the vibrational frequencies are randomly affected by less than 20 cm^{-1} .

The vibrational numbering convention used in Table III is that of Herzberg⁴⁷ in which the vibrations are segregated by symmetry species and numbered starting with the highest frequency within each symmetry species. For ground state AlCH_2 , the vibrations are $\omega_1 (a_1)$ = symmetric C–H stretch, $\omega_2 (a_1)$ = HCH symmetric bend or scissoring, $\omega_3 (a_1)$ = Al–C stretch, $\omega_4 (b_1)$ = out-of-plane bend, $\omega_5 (b_2)$ = C–H antisymmetric stretch, and $\omega_6 (b_2)$ = CH_2 antisymmetric bend or rocking. For consistency, the vibrations of the excited state species are numbered the same as in the ground state. This master table of results will be used throughout the subsequent discussion.

B. The ground $\tilde{X}^2B_1$ electronic excited state

In the ground state, AlCH_2 is predicted to be planar, of C_{2v} symmetry, with an Al–C bond length of $\sim 1.98 \text{ \AA}$, a C–H bond length of

$\sim 1.1 \text{ \AA}$, and a bond angle of 110° . As argued by Cook and Allen,⁷ the metal carbon bond is a single rather than the expected double bond. Comparing the measured Al–C single bond lengths in trimethyl aluminum ($1.957 \text{ \AA}$),⁴⁵ Al–CCH ($1.986 \text{ \AA}$),¹⁸ and the approximate bond length of Al– CH_3 ($1.980 \text{ \AA}$)⁴⁶ derived from microwave data, there can be little doubt that this is the case. The ground state configuration has the single unpaired electron localized on the carbon atom, as shown in Figs. 1 and 3. As discussed elsewhere,⁷ the ground state structure is best represented as $:\text{Al}-\dot{\text{C}}\text{H}_2$, a structure that is compatible with the Al–C bond length and the small dipole moment.

In the ground state, aluminum methylene has a calculated dipole moment of $\sim 0.85 \text{ D}$, so the microwave spectrum should be observable if sufficient concentrations of the radical can be generated in an absorption or emission Fourier transform microwave (FTMW) spectrometer. This could possibly be achieved in a discharge through trimethyl aluminum $[(\text{CH}_3)_3\text{Al}]$ vapor or by laser ablation of aluminum in the presence of a hydrocarbon. The dipole moment is along the Al–C bond with the negative end on the aluminum atom. AlCH_2 is a near prolate asymmetric top, and the microwave spectrum will consist primarily of a -type ($\Delta K_a = 0$, $\Delta K_c = \pm 1$) transitions with a separation of $B + C \sim 24.7 \text{ GHz}$. Nuclear statistical weights favor the $K_a K_c$ = even, even and even, odd levels by a factor of 3. Of course, the microwave spectra will be complicated by the existence of the unpaired electron, which resides primarily on the carbon atom (Mulliken atomic spin density ~ 0.9).

The infrared spectra of $\text{AlCH}_2/\text{AlCD}_2$ (see Table III footnote h) should consist of nearly isotope independent Al–C stretching fundamentals (ν_3) at $625/590 \text{ cm}^{-1}$ and weaker CH symmetric and asymmetric stretches at $3031/2199$ and $3108/2302 \text{ cm}^{-1}$. The other

TABLE III. Optimized geometries, vibrational frequencies, dipole moments, electronic excitation energies, and electronic transition moments calculated at the ICMRCI/aug-cc-pV(T+d)Z level of theory for the ground and seven electronic excited states of AlCH₂ (AlCD₂ in parentheses).

	$\tilde{X}^2B_1^a$	$\tilde{A}^2A_1$	$\tilde{B}^2A_2$	$\tilde{C}^2A_1$	$\tilde{D}^2A_2$	$\tilde{D}'^2A''^b$	$\tilde{E}^2\tilde{B}_2$	$\tilde{F}^2\tilde{B}_2$
r_{AlC} (Å)	1.9766	1.8308	1.9546	2.0072	2.0482	2.0965	1.8984	2.0772
r_{CH} (Å)	1.0953	1.0870	1.0884	1.0864	1.0840	1.0861	1.0795	1.0904
θ_{HCH} (°)	110.0	118.4	114.2	123.6	121.7	120.3	131.2	121.1
ω_1 (a ₁) (cm ⁻¹)	3030.9 (2199.4)	3095.0 (2236.5)	3080.8 (2228.7)	3078.2 (2215.9)	3103.5	^c	3134.7 (2247.3)	3057.3 (2199.1)
ω_2 (a ₁) (cm ⁻¹)	1385.5 (1037.4)	1244.4 (946.4)	1376.7 (1022.6)	1265.6 (964.3)	1258.0	^c	1073.2 (829.5)	1785.2 (1289.0)
ω_3 (a ₁) (cm ⁻¹)	625.9 (590.4)	773.6 (721.4)	662.6 (632.0)	549.0 (513.1)	469.4	^c	598.8 (553.8)	705.4 (696.0)
ω_4 (b ₁) (cm ⁻¹)	445.2 (349.3)	1013.4 (793.8)	807.3 (632.2)	593.4 (462.2)	531.8i	^c	1456.6 (1131.6)	1420.6 (1106.7)
ω_5 (b ₂) (cm ⁻¹)	3108.1 (2302.5)	3209.8 (2387.1)	3176.2 (2361.4)	3235.1 (2412.4)	3248.7	^c	3329.7 (2495.5)	3195.1 (2385.4)
ω_6 (b ₂) (cm ⁻¹)	400.7 (304.3)	457.0 (346.4)	673.9 (509.5)	413.7 (310.5)	724.0	^c	681.2 (508.9)	567.4 (424.9)
T_e^d (cm ⁻¹)	...	6134.7	19 024.0	26 770.3		27 898.6	30 453.3	3 580.9
T_{vd}^e (cm ⁻¹)	...	8057.0	19 132.9	27 308.2		28 445.6	32 140.3	36 288.2
T_0 (cm ⁻¹)	...	6533.1 (6458.8)	19 414.6 (19 325.5)	26 839.6 (26 817.7)		...	31 092.1 (30 944.9)	36 448.2 (36 239.8)
Dipole moment /Debye ^f	0.845	-1.988	0.211	0.266		1.660	-1.322	2.720
Transition moment ^{g,h} /Debye		0.739	0.260	1.297		2.891	0.0	0.0

^aFor the ground state only, the core correlation effects at the ICMRCI level have been checked using the aug-cc-pwCVTZ²⁹ basis. The results are $r_{\text{AlC}} = 1.9644$ Å, $r_{\text{CH}} = 1.0925$ Å, $\theta_{\text{HCH}} = 110.2^\circ$, $\omega_1 = 3044.2$ cm⁻¹, $\omega_2 = 1391.8$ cm⁻¹, $\omega_3 = 630.6$ cm⁻¹, $\omega_4 = 431.2$ cm⁻¹, $\omega_5 = 3125.5$ cm⁻¹, and $\omega_6 = 393.8$ cm⁻¹.

^bNon-planar equilibrium structure with C_s symmetry. Out of plane bending angle: 26.2°. Barrier to planarity: 54 cm⁻¹.

^cVibrational frequencies not calculated.

^dDavidson correction with relaxed reference^{32,33} applied.

^eVertical excitation energies calculated at the geometry of the $\tilde{X}^2B_1$ state. Davidson correction with relaxed reference^{32,33} applied.

^fDipole moment along the Al—C bond. Positive dipole moments correspond to a negative partial charge on Al.

^gAbsolute value of the transition dipole moment from the ground state.

^hIR intensities in km mol⁻¹ for the $\tilde{X}^2B_1$ ground state, in the same order of tabulated ω 's: (AlCH₂) 25.2, 3.3, 92.1, 0.0, 7.0, 1.1; (AlCD₂) 5.2, 14.0, 78.6, 0.0, 3.2, and 0.2.

fundamentals are much weaker in the hydrogen compound, but in the deuterated species, the ν_2 fundamental is more prominent although still 5–6 times weaker than ν_3 .

C. The low-lying $\tilde{A}^2A_1$ electronic excited state

Promotion of an electron from the $7a_1$ orbital to the half-filled $2b_1$ orbital produces the $\tilde{A}^2A_1$ excited state. The dominant electronic configuration is

$$(\text{core})(5a_1)^2(2b_2)^2(6a_1)^2(7a_1)^1(2b_1)^2,$$

and the unpaired electron is located mainly on the aluminum atom. This leads to a substantial shortening (~ 0.15 Å) of the Al—C bond, and the excited state structure can be represented as $\cdot\text{Al}=\text{CH}_2$. The shortening of the Al—C bond is accompanied by a substantial change ($\sim 8^\circ$) in the HCH angle. As argued by Cook and Allen,⁷ this state corresponds to the ground state one would expect based

on simple Lewis dot structures, but it is in fact a low-lying excited state.

The electronic transition from the ground to the $\tilde{A}$ state is calculated to occur in the near-infrared ($T_0 = 6533$ cm⁻¹) with a transition dipole moment of ~ 0.8 Debye. The vertical excitation energy is 8057 cm⁻¹, indicating an extended Franck-Condon profile (*vide infra*). Since the transition occurs in a challenging region where dye lasers do not operate and photomultipliers are blind, it is likely that this electronic transition will be difficult to observe with conventional LIF or other emission techniques.

The calculated cold band $\tilde{A}-\tilde{X}$ absorption spectrum (see Fig. 4) shows a very long progression in ν_3 , consistent with the 0.15 Å decrease in the Al—C bond length on electronic excitation and the corresponding 24% increase in the ν_3 vibrational frequency. The ν_2' frequency shows up in combinations with ν_3' , a consequence of the $\sim 8^\circ$ increase in the HCH bond angle. Although it is not evident in Fig. 4, the 4_0^2 band overlaps the $2_0^13_0^1$ band, and the two features

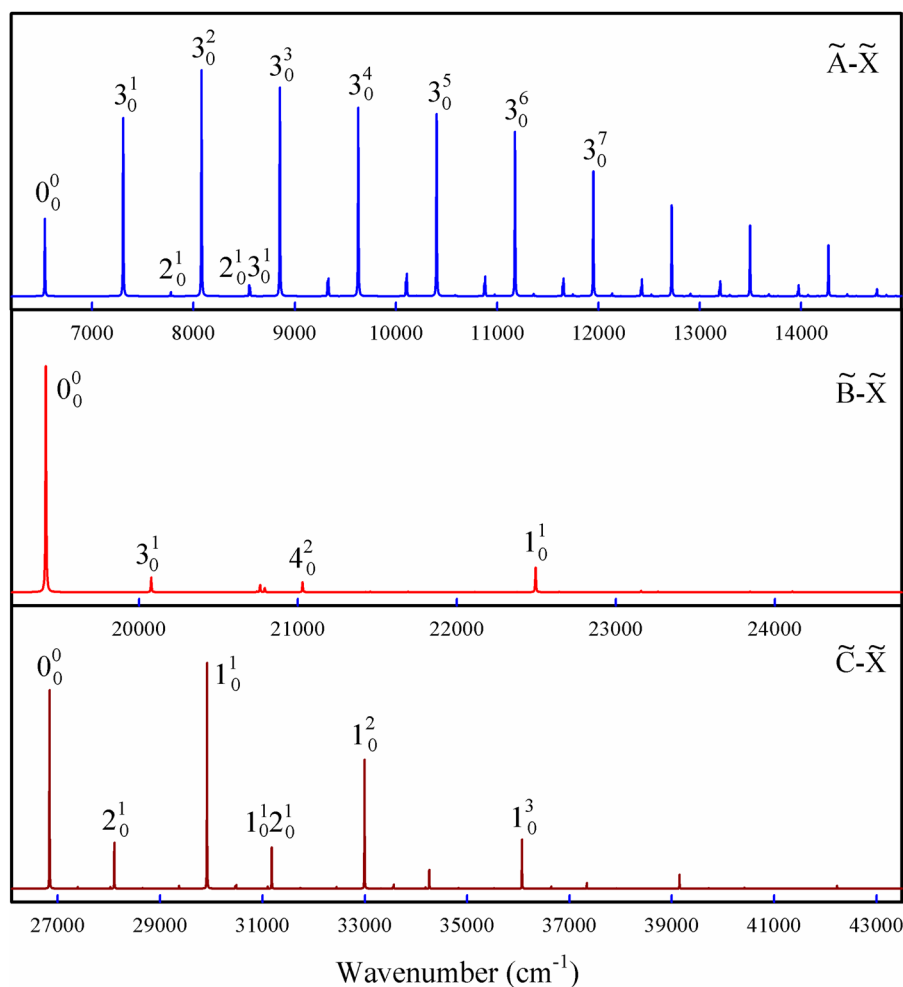


FIG. 4. Calculated Franck-Condon cold band absorption profiles for the three lowest allowed electronic transitions of AlCH_2 . The input to the calculations was taken from the *ab initio* results reported in Table III.

have comparable intensities. This is initially unexpected as double quantum transitions of nontotally symmetric modes, although allowed, are expected to be very weak. An exception, which applies here, is when there is a substantial vibrational frequency change on electronic excitation. In the $\tilde{A}$ state, $\nu_4 = 1013 \text{ cm}^{-1}$, compared to 445 cm^{-1} in the ground state, an increase of 127%.

We have also included in Fig. 5 the calculated rotational structure of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ 0-0 absorption band. The transition moment is oriented out of the molecular plane and follows *c*-type selection rules with $\Delta K_a = \pm 1$, $\Delta K_c = 0, \pm 2$. At 10 K, the calculated spectrum consists of a strong $K'_a = 1 - K''_a = 0$ central subband with weaker features originating in higher K'_a values. Due to the large rotational constants, the spectrum would be readily resolvable at the modest 0.1 cm^{-1} resolution employed in the simulation.

The calculated $\tilde{A} - \tilde{X}$ emission spectrum from the excited state zero-point level is shown in Fig. 6. It is a near mirror image of the absorption spectrum, with a long progression in ν_3' , a weak but significant 4_0^0 band, and a ν_3 progression build upon $2\nu_4$. Observation of the ground state frequencies and their

hydrogen/deuterium isotope effects in emission would provide strong evidence for the identification of AlCH_2 via the $\tilde{A} - \tilde{X}$ electronic transition.

D. The $\tilde{B}^2A_2$ electronic excited state

Promotion of an electron from the doubly occupied $7a_1$ orbital to the empty $3b_2$ orbital produces the $\tilde{B}^2A_2$ excited state. The wavefunction is dominated by electron configurations with three unpaired electrons in three different orbitals, with the main configuration,

$$(\text{core})(5a_1)^2(2b_2)^2(6a_1)^2(7a_1)^1(2b_1)^1(3b_2)^1.$$

Spin density plots (Fig. 3) show that two α electrons are located on the aluminum atom, while one β is located on carbon. Both $7a_1$ and $3b_2$ orbitals have non-bonding character, so the excitation does not change the Al-C bond order significantly, with a slight shortening of approximately $-0.02 \text{ \AA}$.

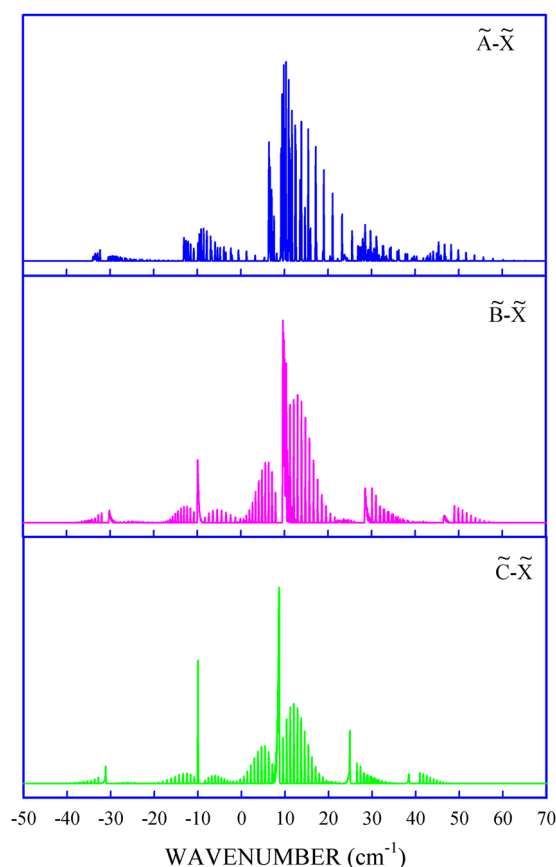


FIG. 5. Calculated rotational structure for the 0–0 absorption bands of AlCH_2 . In each case, the resolution is 0.1 cm^{-1} and the rotational temperature = 10 K. The rotational constants in the combining states were derived from the molecular structures reported in Table III, and the band origins can be obtained from the T_0 values in the Table.

The calculated cold band absorption spectrum (Fig. 4) from the ground state consists of a strong 0–0 band near 19400 cm^{-1} and weak 3_0^2 , 4_0^2 , and 1_0^2 bands and little else. This is as expected since the geometric changes on electronic excitation are minimal with $\Delta r(\text{Al}-\text{C}) = -0.02 \text{ \AA}$, $\Delta r(\text{C}-\text{H}) = -0.007 \text{ \AA}$, and $\Delta\theta(\text{HCH}) = 4^\circ$. Again, the significant intensity of the 4_0^2 band in the spectrum is a direct result of the 81% increase in the ν_4 out-of-plane bending vibrational frequency. The electronic transition moment is small (0.26 Debye) so the transition, although allowed, will be weak with a long fluorescence lifetime. However, this transition is in a favorable region (515 nm–440 nm) for dye laser excitation and may be a reasonable candidate for observing AlCH_2 by LIF spectroscopy. The calculated band contour of the 0–0 band (see Fig. 5) is a very well resolved b-type band with a very prominent $K'_a = 1 - K''_a = 0$ central subband.

In emission (Fig. 6), the $\tilde{\text{B}} - \tilde{\text{X}}$ spectrum is again dominated by a very strong 0–0 band with weak 3_1^0 , 6_1^0 , 4_1^0 , and 1_1^0 features in the 19400 cm^{-1} – 16000 cm^{-1} region. Emission from the $\tilde{\text{B}}$ to the $\tilde{\text{A}}$ state is forbidden by the electric dipole selection rules.

E. The $\tilde{\text{C}}^2\text{A}_1$ electronic excited state

Promotion of an electron from the doubly occupied $7a_1$ orbital to the empty $3b_1$ orbital produces the $\tilde{\text{C}}^2\text{A}_1$ excited state, with the main configuration,

$$(\text{core})(5a_1)^2(2b_2)^2(6a_1)^2(7a_1)^1(2b_1)^1(3b_1)^1.$$

The $3b_1$ orbital has antibonding character, and the excitation produces a slight increase of approximately $+0.03 \text{ \AA}$.

The electronic absorption spectrum to the $\tilde{\text{C}}$ state (Fig. 4) differs substantially from the lower energy band systems. It is dominated by a progression in ν'_1 , the CH stretching vibration, followed by weaker combinations of ν_1 with ν_2 , the symmetric CH bend. These effects are due to the change in the CH bond length [$\Delta r(\text{C}-\text{H}) = -0.009 \text{ \AA}$] and bond angle [$\Delta\theta(\text{HCH}) = 13.6^\circ$], the largest distortions in these geometric parameters among the $\tilde{\text{A}}$, $\tilde{\text{B}}$, and $\tilde{\text{C}}$ states. The very weak 3_0^1 and 4_0^2 bands are the result of only a minor increase in the aluminum-carbon bond length [$\Delta r(\text{Al}-\text{C}) = 0.03 \text{ \AA}$] and only a small increase [33%] in the out-of-plane bending frequency. The transition dipole moment is large (~ 1.3 Debye), and the band system in the 372 nm–270 nm region may be the most likely candidate for LIF spectroscopy as long as nonradiative transitions to the lower $\tilde{\text{B}}$ and $\tilde{\text{A}}$ states do not predominate. The rotationally resolved structure of the 0–0 band (Fig. 5) again follows perpendicular c -type selection rules and would be readily resolvable with typical laser instrumentation.

Allowed emission transitions can occur from the $\tilde{\text{C}}$ state down to both the ground state and to the $\tilde{\text{A}}$ state, as shown in Fig. 6. Mirroring the absorption spectrum, the $\tilde{\text{C}} - \tilde{\text{X}}$ emission system is primarily a long progression in ν''_1 , the CH symmetric stretch, extending from 373 nm–570 nm. This is overlapped by the $\tilde{\text{C}} - \tilde{\text{A}}$ emission spectrum commencing at 492 nm and extending to about 650 nm. This band system consists primarily of a long progression in ν''_3 because the almost $0.18 \text{ \AA}$ diminution is the Al–C bond length in going from the $\tilde{\text{C}}$ to the $\tilde{\text{A}}$ state. The observation of dual emission band systems with Franck–Condon profiles similar to that in Fig. 6 would be strong evidence for the identification of AlCH_2 through the $\tilde{\text{C}} - \tilde{\text{X}}$ absorption system.

F. Higher excited states

For completeness, we have calculated the properties of four higher excited states, as shown in Table III. These excited states are of multiconfigurational character, usually with two predominant electronic configurations. The $\tilde{\text{D}}^2\text{A}_2$ state is very close in energy with the $\tilde{\text{C}}^2\text{A}_1$ state and probably has a non-planar geometry, as indicated by the presence, in C_{2v} symmetry, of a negative ν_4 frequency. However, the out-of-plane bending angle is only 26° , and barrier to linearity is very small (54 cm^{-1}). As these states are fairly high in energy and have three or more electronic excited states below them, it is unlikely that they will fluoresce, so would not be useful for LIF experiments and may well diffuse in absorption. Due to these complications, we have not calculated detailed Franck–Condon profiles or rotationally resolved band contours for transitions to the higher states. However, the results in Table III may be useful for future resonance enhanced multi-photon ionization (REMPI) experiments.

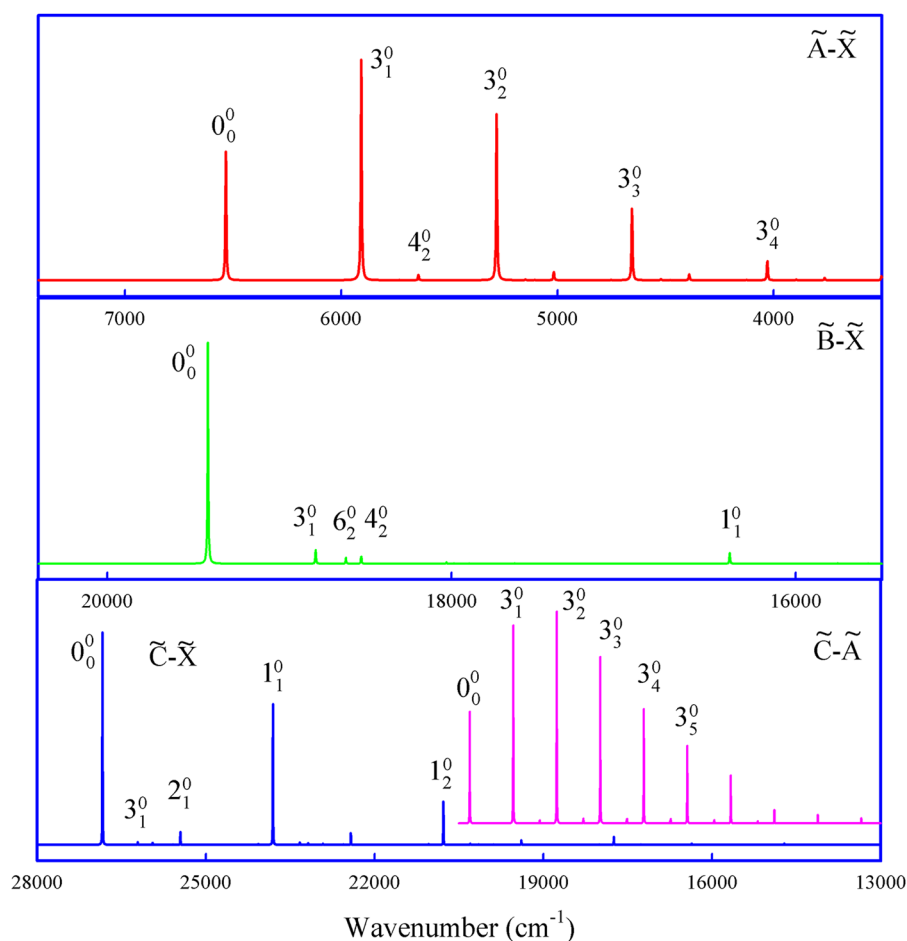


FIG. 6. Calculated single vibronic level emission spectra of AlCH_2 assuming excitation of the 0–0 band in absorption from the ground state in each case, based on the data in Table III. The $\tilde{\text{C}}-\tilde{\text{X}}$ and $\tilde{\text{C}}-\tilde{\text{A}}$ spectra were calculated and normalized separately.

IV. CONCLUSIONS

The ground and excited state properties of the aluminum methylene free radical have been calculated at high levels of *ab initio* theory. Previously reported inconsistencies in the vibrational frequencies of the radical have been traced to serious broken-symmetry instabilities when using UHF orbitals. These difficulties have been overcome by using ROHF orbitals or multireference CI methods, which give consistent and reasonable frequencies for the ground state. Using the ICMRCI method with aug-cc-pV(T+d)Z basis sets, we have predicted the geometries, vibrational frequencies, dipole moments, transition energies, and transition dipole moments for seven excited states of AlCH_2 and AlCD_2 . These results are augmented by Franck–Condon calculations of the expected absorption and emission spectra for the first three excited states and rotational contours of the 0–0 bands of these transitions under typical jet-cooled conditions. The results reported in this work should be of great value in spectroscopic searches for the spectra of this unknown free radical.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to this work.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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