Gas phase electronic spectrum of T-shaped AlC₂ radical

C. Apetrei, A. E. W. Knight, E. Chasovskikh, E. B. Jochnowitz, H. Ding, and J. P. Maier

Citation: The Journal of Chemical Physics 131, 064305 (2009); doi: 10.1063/1.3186758
View online: http://dx.doi.org/10.1063/1.3186758
View Table of Contents: http://aip.scitation.org/toc/jcp/131/6
Published by the American Institute of Physics
Gas phase electronic spectrum of T-shaped AlC₂ radical

C. Apetrei, A. E. W. Knight, a) E. Chasovskikh, E. B. Jochnowitz, H. Ding, b) and J. P. Maier c)
Department of Chemistry, University of Basel, Klingelbergstr. 80, CH-4056 Basel, Switzerland

(Received 28 May 2009; accepted 2 July 2009; published online 12 August 2009)

Gas phase electronic transitions for the $\tilde{C}^2B_2 \leftarrow \tilde{X}^2A_1$ and $\tilde{D}^2B_1 \leftarrow \tilde{X}^2A_1$ band systems of T-shaped AlC₂ ($C_{2v}$) radical have been measured in the 345–475 nm range. Vibronic analyses of both band systems are reported. Simulation of several rotationally resolved bands confirms previously obtained rotational parameters for the $\tilde{C}^2B_2$ state. The radical is produced by ablating an aluminum rod in the presence of acetylene gas. The resulting supersonic molecular beam is probed using both mass-selective resonant two-color two-photon ionization and laser induced fluorescence. Ab initio calculations and vertical electronic excitation energies help the assignment. Vibronic frequencies for the $\tilde{X}^2A_1$, $\tilde{C}^2B_2$, and $\tilde{D}^2B_1$ states have been determined. Rotational analysis of a number of bands yields spectroscopic constants for one vibronic state in the $\tilde{C}^2B_2$ manifold and the origin band of the $\tilde{D}^2B_1 \leftarrow \tilde{X}^2A_1$ system. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3186758]

I. INTRODUCTION

The relationship between the structure of organometallic species and the nature of the carbon-metal chemical bonding remains a topic of considerable interest. Such clusters provide an opportunity to understand these interactions and to gain insight into the growth mechanisms of metal-carbon nanomaterials. Of these, metal carbides and dicarbides represent an important chemical class with application in a wide range of processes and materials. However, spectroscopic information that could reveal aspects of metal-carbon bonding at the triatomic level is relatively sparse.

Metal-containing carbon compounds are also of interest in astrochemistry, where a few such molecules have been detected in carbon rich astrophysical environments through their microwave and submillimeter/millimeter transitions. 1,3 Because many elements such as magnesium, iron, and sodium are depleted in molecular clouds, 4 the central question concerns the form in which these metal-containing species exist in the interstellar medium (ISM). It is generally believed that the most refractory elements are condensed out onto the surface of dust grains. Unfortunately, knowledge about the gas-phase abundances and the surface absorption of such species in the ISM is limited. Accordingly, the spectroscopic identification of metal-containing molecular carriers has implications for both gas phase and grain chemistry. 5

To date, 11 main group dicarbides have been investigated spectroscopically (XC₂, X = H, B, C, N, O, Al, Si, P, S, Cl, As), 5 HC₂, NC₂, 6 OC₂, 7 PC₂, 5 SC₂, 8 and AsC₂ (Ref. 5) all possess linear (Cᵥ) structures. ClC₂ has been shown to have bent shaped $\tilde{X}^2A'$ ground state, 9 while AlC₂ and SiC₂ are T-shaped (C₂v). 10,11 Matrix infrared and electronic spectra of BC₂, which is isovalent with AlC₂, have been obtained with features assigned to a cyclic structure. 12,13 As far as heavier systems are concerned, the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2A_1$ transition of the T-shaped YC₂ radical has been studied extensively in vibrational, rotational, and hyperfine detail. 14–16

At high temperatures, vaporous metal dicarbides are the predominant species in thermodynamic equilibrium with metal-carbon condensed systems. 17–19 Aluminum dicarbide was first detected in a high temperature Knudsen cell using mass spectrometry. 18 The study indicated that the atomization energy of AlC₂ is 1104 ± 21 kJ mol⁻¹ and the dissociation energy of Al–C₂ is 514.2 ± 21 kJ mol⁻¹. The latter is slightly higher than the dissociation energy of AlO and thus an apparent exception to the empirical rule that the dissociation energy of a M–C₂ bond is usually 40–130 kJ mol⁻¹ less than the corresponding M–O bond. 18

Photoelectron spectroscopy of AlC₂− revealed a vibrational progression of 590 cm⁻¹, which was assigned as the stretching mode of the neutral Al–C₂. 20 Theoretical calculations provided estimates for all three vibrational frequencies for AlC₂; none of these have been observed in the infrared. 20,21,22

Ablation of an aluminum rod in the presence of a C₃H₅/He gas mixture together with photoionization mass spectrometry with 7.9 eV photons yielded ions at m/z 51 consistent with the mass of AlC₂. The implication that AlC₂ possesses a stable structure in the gas phase was established using laser induced fluorescence (LIF). Confirmation of its T-shaped (C₂v) structure emerged from the measurement of the $\tilde{C}^2B_2 \leftarrow \tilde{X}^2A_1$ transition of AlC₂. Rotational analysis for the origin band provided estimates for the $\tilde{C}^2B_2$ state molecular parameters. 10

In this paper the gas-phase electronic spectrum of AlC₂ is investigated over a broad spectral range using both a mass-
selective resonant two-color two-photon ionization (R2C2PI) technique and LIF. The \( ^{2}B_{2} \rightarrow ^{2}A_{1} \) origin band has been confirmed and new vibronic bands are observed. \textit{Ab initio} calculations on T-shaped AlC\(_{2}\) (C\(_{2v}\)) have been carried out to guide the assignments.

II. EXPERIMENTAL

Jet cooled AlC\(_{2}\) was produced using laser vaporization of an aluminum rod (30 mJ/5 ns pulse from a 532 nm Nd:Yttrium aluminium garnet focused to 0.3 mm) in the presence of a 1\%–5\% acetylene gas mixture seeded in either helium or argon provided by a 0.3 mm orifice pulsed valve. The rod was rotated and translated so that a fresh surface was continuously exposed to the laser, which was fired to coincide with the gas flow over the target area. The ablation plume flows through a channel (3 mm diameter, 5–15 mm long) before entering vacuum. The resulting free-jet expansion is probed using the mass-selective R2C2PI technique\(^{23}\) or LIF.

R2C2PI spectra were collected by probing the skimmed beam of the jet expansion. Ions were removed by applying a perpendicular electric field before entering the ionization region of a Wiley–McLaren time-of-flight mass spectrometer.\(^{24}\) Neutral molecules were irradiated with a pulse of tunable ultraviolet-visible (UV-Vis) radiation, followed by 7.9 eV photons from an F\(_{2}\) excimer laser. Ions were then extracted into a time-of-flight tube where the signal from a microchannel plate ion detector was sent to a fast oscilloscope and data acquisition card. The combination of the UV-Vis and the 157 nm photons was sufficient to ionize AlC\(_{2}\). Low resolution spectra for the vibronic survey scans were collected over the 345–500 nm range using an OPO system (\(\sim 5\) cm\(^{-1}\) bandwidth). A pulsed dye laser was used (\(\sim 0.15\) cm\(^{-1}\) bandwidth, \(\sim 5\) mJ/pulse) for the rotationally resolved work, with calibration through the use of an optogalvanic spectrum obtained from a Fe/Ne hollow cathode lamp.

LIF spectra were measured using an excimer pumped dye laser (bandwidth of 0.15 cm\(^{-1}\)). Fluorescence signal was collected by an f/1 lens and detected using a photomultiplier and digital oscilloscope.

III. THEORETICAL CALCULATIONS

The electronic ground state structures of AlC\(_{2}\) were investigated using both coupled cluster RCCSD(T) theory,\(^{25}\) and the hybrid density B3LYP functional\(^{26}\) with Dunning’s correlation-consistent basis sets.\(^{27}\) The calculations indicate that T-shaped AlC\(_{2}\) (C\(_{2v}\)) is a global minimum. Linear AlC\(_{2}\) (C\(_{2v}\)) and CAIC (D\(_{2h}\)) are local minima lying approximately 0.4 and 7 eV higher in energy, respectively.

Equilibrium geometries for the ground state were optimized using the B3LYP/aug-cc-pVQZ theory and RCCSD(T)/cc-pVTZ approach. Previously\(^{10}\) theoretical calculations of excited electronic states of AlC\(_{2}\) (C\(_{2v}\)) were carried out using the complete active space self-consistent field method (CASSCF) (Ref. 28) and multireference configuration interaction (MRCI) theory.\(^{29}\) Vertical excitation energies were calculated for states up to 3.8 eV above the ground state. In order to predict the spectrum in the UV region, higher lying states for AlC\(_{2}\) (C\(_{2v}\)) have been investigated with CASSCF and MRCI approaches using the GAUSSIAN 98 suite of programs\(^{30}\) and MOLPRO package.\(^{31}\) The resulting vertical transition energies and oscillator strengths are summarized in Table I.

<table>
<thead>
<tr>
<th>Transition</th>
<th>(T_{v}) (eV)</th>
<th>CAS</th>
<th>MRCI</th>
<th>MRCI+Q</th>
<th>CAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A^{2}A_{1} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>1.19</td>
<td>1.27</td>
<td>1.49</td>
<td>2.8 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>(B^{2}B_{1} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>2.21</td>
<td>2.37</td>
<td>2.46</td>
<td>7.5 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>(C^{2}B_{2} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>2.76</td>
<td>2.83</td>
<td>2.73</td>
<td>1.5 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>(D^{2}B_{1} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>2.97</td>
<td>3.31</td>
<td>3.31</td>
<td>7.8 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>(E^{2}B_{2} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>3.59</td>
<td>3.89</td>
<td>3.83</td>
<td>1.5 \times 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>(F^{2}A_{1} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>4.21</td>
<td></td>
<td></td>
<td>1.8 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>(G^{2}A_{2} \rightarrow \tilde{X} ^{2}A_{1})</td>
<td>4.70</td>
<td></td>
<td></td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

IV. RESULTS AND DISCUSSIONS

The R2C2PI low resolution (\(\sim 5\) cm\(^{-1}\) bandwidth) electronic spectra of the \(^{2}B_{2} \rightarrow \tilde{X} ^{2}A_{1}\) and \(^{2}B_{1} \rightarrow \tilde{X} ^{2}A_{1}\) systems of AlC\(_{2}\) for the 345–475 nm range are shown in Figs. 1 and 2, respectively. The wavelengths of the vibronic bands (maxima) and suggested assignments are listed in Table II.

FIG. 1. Low resolution (5 cm\(^{-1}\) bandwidth) spectrum of the \(^{2}B_{2} \rightarrow \tilde{X} ^{2}A_{1}\) electronic system and high resolution (0.15 cm\(^{-1}\) bandwidth) spectrum of the +1398 cm\(^{-1}\) band (inset) for the T-shaped AlC\(_{2}\) radical, recorded in the range of 21 000–26 000 cm\(^{-1}\) using a resonant two-color two-photon ionization technique in a supersonic molecular beam.
frequencies were thus used as a starting point in assigning 22 678 and 22 713 cm$^{-1}$.

A. $\tilde{C} \tilde{B} \tilde{A}$

Previous coupled cluster calculations [CCSD(T)] estimate the harmonic frequencies of ground state $\tilde{X} \tilde{A}$ AlC$_2$ as $\nu_1 = 1735 \ (a_1)$, $\nu_2 = 645 \ (a_1)$, and $\nu_3 = 421 \ (b_2)$ cm$^{-1}$. These frequencies were thus used as a starting point in assigning $\tilde{X} \tilde{A}$ and $\tilde{B}$ band systems of AlC$_2$.

TABLE II. Vibrational band maxima (cm$^{-1}$) in the $\tilde{C} \tilde{B}$ and $\tilde{D} \tilde{B}$ band systems of AlC$_2$.

<table>
<thead>
<tr>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\delta$ (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 098</td>
<td>0.0</td>
<td>$0^0_0$</td>
</tr>
<tr>
<td>22 305</td>
<td>207</td>
<td>$2^1_0$</td>
</tr>
<tr>
<td>22 498</td>
<td>400</td>
<td>$2^2_0$</td>
</tr>
<tr>
<td>22 682</td>
<td>584</td>
<td>$3^1_0$, $2^3_0$</td>
</tr>
<tr>
<td>(22 678, 22 713)</td>
<td>(580, 613)</td>
<td></td>
</tr>
<tr>
<td>22 879</td>
<td>781</td>
<td>$3^2_1$, $2^3_1$</td>
</tr>
<tr>
<td>23 309</td>
<td>1211</td>
<td>$3^2_0$</td>
</tr>
<tr>
<td>23 496</td>
<td>1398</td>
<td>$1^1_0$</td>
</tr>
<tr>
<td>23 710</td>
<td>1612</td>
<td>$2^1_1$, $3^1_1$</td>
</tr>
<tr>
<td>24 733</td>
<td>2635</td>
<td>$3^2_1$</td>
</tr>
<tr>
<td>24 880</td>
<td>2782</td>
<td>$1^1_0$</td>
</tr>
<tr>
<td>26 073</td>
<td>0.0</td>
<td>$0^0_0$</td>
</tr>
<tr>
<td>26 475</td>
<td>402</td>
<td>$3^3_0$</td>
</tr>
<tr>
<td>26 616</td>
<td>543</td>
<td>$2^3_0$</td>
</tr>
<tr>
<td>27 055</td>
<td>982</td>
<td>$3^2_2$</td>
</tr>
<tr>
<td>27 186</td>
<td>1113</td>
<td>$2^2_0$</td>
</tr>
<tr>
<td>27 563</td>
<td>1490</td>
<td>$1^1_0$, $2^3_0$, $3^2_0$</td>
</tr>
</tbody>
</table>

The low resolution $\tilde{C} \tilde{B}=\tilde{X} \tilde{A}$ spectrum depicted in Fig. 1. Higher resolution rotationally resolved spectra were obtained to assist in confirming the most probable identities of the vibrational bands.

The observed rotational structure of the $\tilde{C} \tilde{B}=\tilde{X} \tilde{A}$ origin band of AlC$_2$ is consistent with that expected for an electric dipole allowed perpendicular $b$-type transition in a C$_2$ molecule. Accordingly, transitions involving $a_1$ modes are also electric dipole allowed and will be observed as $a$-type perpendicular. However, those involving nontotally symmetric $b_2$ vibrations in the absence of vibronic coupling are only allowed as even quantum changes (i.e., Franck-Condon allowed). These $\Delta \nu = \pm 2$ transitions will also display rotational contours with $b$-type perpendicular band structure. Using these guidelines, assignments may be made, starting with the dominant 22 108 cm$^{-1}$ band in Fig. 1, which has been already confirmed as the origin.

The partially rotational resolved R2C2PI spectrum of the +1398 cm$^{-1}$ band in the $\tilde{C} \tilde{B}=\tilde{X} \tilde{A}$ transition is shown in the inset of Fig. 1, accompanied by a spectral simulation, assuming a $b$-type perpendicular band for a near-prolate symmetric top, performed using the WANG program. The band is assigned as the $1^1_0$ transition, where $\nu_1$ is the C=C stretching mode. The measured excited state (C) frequency of $\nu'_1 = 1398 \text{ cm}^{-1}$ compares with the calculated ground state frequency for $\nu''_1$ of 1735 cm$^{-1}$. The reduction in the C=C stretching frequency relative to the ground state is consistent with the lengthening of the C=C bond in the C state (both calculation and estimated rotational constants are in support of this). The significant Franck-Condon activity in $\nu_1$ is also consistent with the appreciable lengthening of the C=C bond in the C state relative to the ground state. Spectroscopic constants for $\nu'_1$ vibronic level have been estimated from the spectral simulation with constants reported in Table III. However it must be recognized that difficulties can arise in fitting the finer features of the observed spectrum due to the potential perturbations in the $\tilde{C} \tilde{B}$ manifold arising as a result of interactions with rovibronic levels of the underlying $\tilde{B}$ state. Nevertheless the simulation is quite acceptable.
The second progression member in ν₂, i.e., the 1₂ transition, is observed at +2782 cm⁻¹ (Fig. 1) and displays a b-type perpendicular band contour with shape quite similar to those shown in Fig. 3, thus being associated with transition involving progressions in a₁ modes or even-quantum-change overtones.

Figure 3 displays the LIF detection (0.15 cm⁻¹ resolution) of three vibronic bands observed at +207, +400, and +1211 cm⁻¹ with respect to the origin. The extended K-rotational structure observed for all three bands is consistent with its interpretation as a b-type perpendicular bands for a near-prolate symmetric top. The intensity of the +207 cm⁻¹ band is approximately one-third that of the origin band, while that for +400 cm⁻¹ is less again by a factor of approximately 4. The pattern of relative intensities, as well as the contour being the same as that of the origin band, is consistent with a progression in a totally symmetric mode. Accordingly, the +207 and +400 cm⁻¹ bands are assigned as first two progression members involving the ν₁ (Al–C₂ stretch), with an approximate value of ν₂ = 207 cm⁻¹. The appreciable anharmonicity observed is consistent with a large frequency change occurring for ν₂ between the X and C̃ states (the calculated value for ν₂ = 645 cm⁻¹), indicating a much shallower ν₂ potential function in the C̃ state. The 2₁-zero transition, middle plot, overlaps with the 0-0 and 1-1 bands of the B̃ X̃⁻–X̃ A₁ AIC transition, therefore the trace shown has been obtained using a normalized spectral subtraction to remove the contamination from the AIC diatomic fluorescence. This was possible due to the fact that the above mentioned transition in AIC has a longer fluorescence lifetime than that of AIC₂, thus allowing the collection of a decongested spectrum of the diatomic through gating the tail end of the LIF decay and later subtracting it from the total signal containing fluorescence from both species.

The band observed at +1211 cm⁻¹ from the origin (Fig. 1) shown in high resolution detail as the bottom trace in Fig. 3 is due to the Franck–Condon allowed Δν = 2 transition involving excitation in ν₃, i.e., 3₂-zero. This yields an approximate frequency of 605 cm⁻¹ for ν₃ in the C̃ state.

Based on the assignment ν₂ = 207 cm⁻¹ for the C̃ state, the two bands observed toward lower energy from the C̃ 2B₂−–X̃ A₁ origin (Fig. 1, −218 and −326 cm⁻¹) are both candidates for the 2₁ transition. Our preferred assignment for the −326 cm⁻¹ band is 2₁-zero, which yields ν₂ = 533 cm⁻¹ compared to ν₂ = 645 cm⁻¹ from calculation. Despite the supersonic free jet environment, vibrational cooling may not be that efficient in the helium carrier gas, hence it is not unexpected that there is thermal population in the ν₂, v = 1 level.

The band observed at +1612 cm⁻¹ was also partially rotationally resolved using LIF detection and exhibits a b-type perpendicular K-structure. The frequency is close to the combination of the observed frequencies for ν₁ and ν₂, i.e., 1398 + 207 = 1605 cm⁻¹. Accordingly, this transition is assigned as the 2₁-zero 1₁-zero combination band.

Finally, the LIF spectrum (0.15 cm⁻¹ resolution) recorded in the region near 440 nm (Fig. 1, +584 cm⁻¹) is presented in Fig. 4. Measurement at higher resolution provides clear indication that this does not conform to a b-type perpendicular transition. Figure 4 includes rotational band contour simulations for an a-type parallel band centered at ~22 678 cm⁻¹ and a b-type perpendicular band (intensity ~30% that of the parallel band) at ~22 713 cm⁻¹. The third member of the ν₂ progression, i.e., 3₂-zero excitation, is expected to lie in this region and would be responsible for the b-type perpendicular band. Added together, this combined simulation matches the overall spectral structure in the region 22 640–22 740 cm⁻¹ quite well.

An a-type parallel band derives intensity from the dipole-allowed T₂ transition moment, implying that the vibronic symmetry associated with the +584 cm⁻¹ band is A₁. The conclusion advanced is that the +584 cm⁻¹ band corre-
sponds to the transition $3_1^b$, where the $\nu_3$ vibrational mode ($b_3$ symmetry; $\tilde{C}$ state vibronic symmetry) $= b_2 \otimes B_1 = A_1$ derives intensity through vibronic coupling with the strong, $T_x$ dipole-allowed $\tilde{A}^2 A_1 \rightarrow \tilde{X}^2 A_1$ transition. The $\tilde{A}$ state is calculated to lie approximately 12 000 cm$^{-1}$ below the $\tilde{C}$ state. The fact that the $\nu_3$, $v=1$ vibrational frequency increased in the $\tilde{C}$ state relative to the $\tilde{X}$ state ($\nu_3$ ground state frequency calculated as 421 cm$^{-1}$) is consistent with the $\tilde{A}^2 A_1 \rightarrow \tilde{X}^2 A_1$ electronic state, from which intensity is borrowed, lying lower in energy than the $\tilde{C}$ state. Hence we conclude that the +584 cm$^{-1}$ band is composed of a stronger constituent due the vibronically allowed $3_0^b$ transition together with a lesser contribution from the Franck–Condon allowed $2_0^b$ progression member (Table II).

The attribution of the +781 cm$^{-1}$ band in Fig. 1 as $3_{2}^{\pm 1}$ follows from the observed displacement of +400 cm$^{-1}$ relative to the $3_0^b$ vibronically induced progression origin. Assignment of the +1211 cm$^{-1}$ band as $3_2^b$ is based on the anticipated Franck–Condon intensity for this transition.

Finally, we consider the band at −218 cm$^{-1}$ (toward lower energy) from the $\tilde{C}^2 B_2 \rightarrow \tilde{X}^2 A_1$ origin. A candidate for its assignment might be the $3_{1}^{1}$ sequence band. However, based on the estimate, $\nu'_{2} = 580$ cm$^{-1}$ from the measured position of the $3_{1}^{1}$ transition, this assignment would imply that $\nu'_{2} = 580 + 218 = 798$ cm$^{-1}$. This appears to be too high given the values for $\nu'_{2}$ derived from theory ($\sim 400–450$ cm$^{-1}$). An alternative assignment is the hot band $3_{12}^{1}$, which would yield $\nu''_{2} = 207 + 218 = 425$ cm$^{-1}$.

### B. $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$

The two strongest UV bands found in the $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ band system (Fig. 2, bands at 26 073 and $+543$ cm$^{-1}$) were investigated further at higher resolution (0.15 cm$^{-1}$) with R2C2PI and are shown in Fig. 5. The bands could also be recorded using LIF but due to other overlapping features in this UV region the spectra are congested and more complicated to analyze.

The rotational band profiles are matched successfully with a simulation assuming a conventional Hamiltonian for an asymmetric top considering a $c$-type perpendicular transition in a $C_{2v}$ molecule (dipole allowed $T_x$ transition moment). The simulation compares favorably with the experimental trace for the 26 073 cm$^{-1}$ band. Despite poorer signal to noise for the 26 616 cm$^{-1}$ band, the simulation is acceptable. Attempts to match the measured rotational profile for the 26 073 cm$^{-1}$ band with either a $b$-type perpendicular or $a$-type parallel simulation proved unsuccessful. Accordingly, these are assigned as belonging to another electronic band system, presumably the $T_x$ electric dipole allowed $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ transition. Recent calculations (SA-CASSCF geometry optimization, Table III) estimate that the $\tilde{D}^2 B_1$ state energy is in vicinity of 3.1 eV ($\approx 25000$ cm$^{-1}$), lending further support to the assignment of the AIC$_2$ vibronic structure in the 24 000–28 000 cm$^{-1}$ region as being due to the $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ transition. Assignments for the vibrational structure observed are discussed below and presented in Table II.

The dominant progression forming mode in the $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ transition appears to be $\nu_2$, in contrast with the activity observed in $\nu_1$ for the $\tilde{C} \rightarrow \tilde{X}$ excitation. The $\nu_2$ vibrational mode is principally the Al–C$_2$ symmetric stretch. As may be deduced from the inertial parameters emerging from the $c$-type band contour simulation shown in Fig. 5, the Al–C bond length, hence the Al–C$_2$ perpendicular distance, changes appreciably in the $\tilde{D}$ state relative to the ground state ($\tilde{D}$:1.996 Å; $\tilde{X}$:1.819 Å; $\Delta$=0.165 Å), and considerably more than between the $\tilde{C}$ and $\tilde{X}$ states ($\Delta$=0.016 Å). This large geometric change along the $\nu_2$ normal coordinate associated with $\tilde{D} \rightarrow \tilde{X}$ excitation confirms the assignment of $\nu_2$ as the dominant progression forming mode in the $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ transition. The displacements for the transitions $2_0^b$ and $2_2^b$ are +543 and 1113 cm$^{-1}$, respectively. It is clear that the interval (570 cm$^{-1}$) between $\nu_3$, $v=1$ and $v=2$ suggests a significant positive anharmonicity.

Figure 2 shows a relatively strong transition at +402 cm$^{-1}$ displacement from the origin. The assignment offered is the Franck–Condon allowed $\Delta v=2$ transition in $\nu_3$, i.e., $3_2^b$. No band is observed at twice this displacement from the $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ origin, hence the +402 cm$^{-1}$ band cannot be the first member of a progression in an $a_i$ mode (the only possibility would be $\nu_1$, but in any case the observed frequency is far too low for $\nu_1$ to be a valid candidate). The observed transition cannot be $3_0^b$ because the vibronic symmetry for the $3_1$ level, assuming that this is the $\tilde{D}^2 B_1 \rightarrow \tilde{X}^2 A_1$ transition, is $b_2 \otimes B_1 = A_2$ and the $A_2\rightarrow A_1$ transition moment is zero for a $C_{2v}$ molecule.

Assignments follow for the bands at +982 and 1113 cm$^{-1}$ as $3_{0}^{2}$ and $2_{0}^{2}$. However, it is necessary to address two questions regarding this, as well as the relatively large anharmonicity in the $\nu_2$ progression. First, the $3_{0}^{2}$ assigned band is quite strong for a $\nu'_3$, $v=2$ Franck–Condon...
allowed transition. Second, the positions for $3^2 \sigma_0$ and $2^2 \sigma_0$ appear a little abnormal. The most likely cause of these anomalies is a Fermi resonance between $v_2$, $v=2$, and $v'_{2}, v=1$. This would be a classic case of $3^2 \sigma_0 \cdots 2^2 \sigma_1$ coupling via cubic anharmonicity (the well known ground state stretch-bend coupling in CO$_2$ being the pedagogical example). 34 This explanation is supported by the appearance of the structure in the $+982$, 1113 cm$^{-1}$ region, which is relatively broad and indicative of the expected Fermi triad arising from the coupling between $3^2 \cdots 3^2 \sigma_1 \cdots 2^2 \sigma_1$. Likewise, the broad structure in the $+1490$ cm$^{-1}$ region would be due to the corresponding Fermi quartet. Modeling of these possible Fermi resonances is outside the scope of this paper. It is likely that the first progression member of the $v_1$ mode, i.e., $1^0_1$, may also lie among this structure.

C. Vibronic coupling

The estimates for the AIC$_2$ vibrational frequencies derived for both the $\tilde{C}$ and $\tilde{D}$ states are summarized in Table IV. In the $\tilde{C}$ state, $v_2$ is reduced considerably from its ground state value ($v_2=207$ cm$^{-1}$ versus $v'_2=533$ cm$^{-1}$). The $2^1 \Pi$ level is of $B_2$ vibronic symmetry. The drop in frequency is consistent with the proposal that the $\tilde{E}$ ($2^1 \Pi$) state, calculated $-7500$ cm$^{-1}$ above the $\tilde{C}$ state, perturbs levels of $B_2$ symmetry in the $\tilde{C}$ state.

Vibrionic coupling between states in two interacting manifolds does involve all vibrational levels of appropriate symmetry. However, the dominant interactions are between like states with $\Delta v=\pm 1$ differences in vibrational quantum numbers. 35,36 Hence, the $v=0$ level of the $\tilde{C}$ state will interact with the $v_2, v=1$ level in the higher $\tilde{E}$ ($2^1 \Pi$) state. In contrast, the $v_2, v=1$ level of the $\tilde{C}$ state will be coupled with both the $v_2, v=0$ and $v=2$, levels of the $\tilde{E}$ ($2^1 \Pi$) state.

From simple perturbation theory [energy shift $=|H_{22}^\uparrow (E_{22}^\uparrow - E_{22}^\downarrow)|$, where $H_{22}^\uparrow$ is the vibronic coupling interaction matrix element and $\Delta E=E_{22}^\uparrow - E_{22}^\downarrow$ is the energy difference between the coupled states. Furthermore, the coupling matrix elements (for harmonic oscillator wave functions) are related by the relationship $(v+1)|H_{ij}|v=\sqrt{v}|H_{ij}|0)$. Accordingly, a simple coupling scheme is used to obtain estimates for the shifts in vibrational energy levels due to vibronic coupling.

The coupling matrix elements in the range $-1000$–$3000$ cm$^{-1}$ are typical for coupling between electronically excited states. 35,36

A modest vibronic coupling matrix element of $-1050$ cm$^{-1}$ (with $\Delta E=7500$ cm$^{-1}$ taken as energy gap between the $\tilde{C}$ and $\tilde{E}$ states) is sufficient to “push down” the $v_2, v=1$ level in the $\tilde{C}$ state by $-300$ cm$^{-1}$ relative to what might be an unperturbed frequency for $v'_2$ of $-500$ cm$^{-1}$ (based on $v'_2=533$ cm$^{-1}$). This could explain the considerably reduced frequency for $v_2$ observed for the $\tilde{C}$ state.

The estimates for $v'_2$ and $v'_3$ are 425 and 580 cm$^{-1}$. The question arises as to why $v_1$ is increased in the $\tilde{C}$ state relative to the $\tilde{X}$ state. Observe that $v_1$ is of symmetry species $b_2$, hence the vibronic symmetry of the $3^1 \Pi$ level is $b_2 \otimes b_2=A_1$. As established above from rotational contour simulations, the $3^1 \Pi$ transition arises as a result of vibronic coupling. The $A_1$ electronic state (with significant oscillator strength) that is most likely to be responsible for the intensity borrowing is the lower lying $\tilde{X}^2A_1$ state, calculated as lying $\sim 12000$ cm$^{-1}$ below the $\tilde{C}$ state. From calculations analogous to those discussed above for $v_2$, a coupling matrix element of $-900$ cm$^{-1}$ is sufficient to “push up” the $3^1 \Pi$ level by $\sim 160$ cm$^{-1}$ in the $\tilde{C}$ state relative to its (calculated) frequency $-420$ cm$^{-1}$ in the $\tilde{X}$.

Analogous arguments may be applied to rationalize the frequencies for $v_2$ and $v_3$ observed in the $\tilde{D}$ state. The $2^1 \Pi$ level is observed at $+543$ cm$^{-1}$. This in fact is little different from it’s ground state frequency of $533$ cm$^{-1}$. The vibronic symmetry of $2^1 \Pi$ in the $\tilde{D}$ state is $B_1$. Moreover, the nearest $B_1$ electronic state with which the $\tilde{D}$ state can couple is the lower $\tilde{B}^2B_1$ state, $-6700$ cm$^{-1}$ below. Thus one would anticipate that, if anything, $v_2$ might increase in frequency in the $\tilde{D}$ state. The observed frequency of $543$ cm$^{-1}$ is consistent with the proposal that it has been pushed up, relative to its unperturbed frequency, as a result of vibronic coupling with the lower lying $\tilde{B}^2B_1$ state.

The $v_3$ vibronic frequency in the $\tilde{D}$ state, derived from the observation of the $3^1 \sigma_0$ band at $+402$ cm$^{-1}$ is approximately 200 cm$^{-1}$. This contrasts with $v_3$ in the $\tilde{X}$ state, derived from the spectrum of $\sim 425$ cm$^{-1}$. The vibronic symmetry of $3^1 \Pi$ in the $\tilde{D}$ ($2^1 \Pi$) state is $A_2$. The only $A_2$ state nearby in AIC$_2$ is $\tilde{G}(^2A_2)$, calculated $\sim 12500$ cm$^{-1}$ above the $\tilde{D}$ state. A vibronic coupling matrix element of $-1150$–$1200$ cm$^{-1}$ would be sufficient to depress the $3^1 \Pi$ level in the $\tilde{D}$ state by the requisite amount of $-220$–$250$ cm$^{-1}$. While the above arguments are indicative rather than quantitative, they serve to rationalize the observed frequencies for $v_2$ and $v_3$ observed in the $\tilde{C}$ and $\tilde{D}$ electronic states of AIC$_2$.

V. CONCLUSION

Vibrational structure in the electric dipole allowed $\tilde{C}^2B_2 \leftarrow \tilde{X}^2A_1$ and $\tilde{D}^2B_1 \leftarrow \tilde{X}^2A_1$ transitions has been mea-

\begin{table}[ht]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & $\tilde{X}^2A_1$ & $\tilde{C}^2B_2$ & $\tilde{D}^2B_1$ \\
\hline
$\omega$ & $\nu$ & $\nu$ & $\nu$ \\
\hline
$v_1$ & 1735$^b$ & $\cdots$ & 1398(5)$^b$ & 1490(5)$^b$ \\
v_2 & 645$^a$ & 533(5)$^c$ & 207(5)$^b$ & 543(5)$^b$ \\
v_3 & 421$^d$ & 425(5)$^d$ & 580(5)$^b$ & 201(5)$^d$ \\
\hline
\end{tabular}
\caption{Experimentally determined vibrational frequencies (cm$^{-1}$) for the two electronic systems.}
\end{table}

$^a$Calculated, Ref. 10.

$^b$This work.

$^c$This work (based on the assigned hot bands).

$^d$By dividing double quanta excitations.
Condon activity is dominated by an intense progression in the $\tilde{C}^2B_2 \rightarrow \tilde{X}^2A_1$ transition, as well as vibronic activity in $\nu_3$ due to coupling with the strong dipole allowed $\tilde{A}^2A_1 \rightarrow \tilde{X}^2A_1$ excitation. The strong Franck–Condon activity involving $\nu_1$ and $\nu_2$ in the $\tilde{C}^2B_2 \rightarrow \tilde{X}^2A_1$ transition is consistent with the observed $\tilde{C}^2B_2 \rightarrow \tilde{X}^2A_1$ geometry change, deduced from rotational band contour simulations, which involved appreciable lengthening of the $C=\equiv$C bond. In the higher lying $\tilde{D}^2B_1 \rightarrow \tilde{X}^2A_1$ transition, the Franck–Condon activity is dominated by an intense progression involving $\nu_2$ ($\tilde{Al} \cdot \tilde{C}_2$ stretch). This assignment is supported by an appreciable change in the $\tilde{Al} \cdot \tilde{C}_2$ bond length and hence $\tilde{Al} \cdot \tilde{C}_2$ perpendicular distance, estimated from rotational band contour simulation assuming a $c$-type perpendicular transition. The simulations confirm the attribution of the excitation as $\tilde{D}^2B_1 \rightarrow \tilde{X}^2A_1$. No vibronic activity in $\nu_3$ is possible for this transition because of symmetry constraints. However, there is evidence of $3^2 \cdots 2^1$ coupling via cubic anharmonicity in the $\tilde{D}$ vibrational manifold. New estimates for vibrational frequencies and rotational parameters are thereby provided for the $\tilde{C}$ and $\tilde{D}$ states of AlC$_2$ (Table IV).

**ACKNOWLEDGMENTS**

This work is supported by the Swiss National Science Foundation (Project No. 200020-124349/1). A.K. thanks the Maier group for their friendship and hospitality during his stay in Basel.

31. MOLPRO, a package of ab initio programs designed by H.-J. Werner and P. J. Knowles, version 2006.1.
34. G. Herzberg, Molecular Spectra and Molecular Structure (van Nostrand, New York, 1945).