Rotational structure of the origin band in the $1A' \leftarrow X \, 1\Sigma^+$ electronic transition of $C_4H^-$ and $C_4D^-$

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The rotational structure of the origin band for the $1A' \leftarrow X \, 1\Sigma^+$ electronic transition, lying just below the electron affinity of $C_4H$, was recorded by means of a two-colour resonant photo-detachment technique. This allowed a determination of the rotational constants in the $X \, 1\Sigma^+$ ground and $1A'$ dipole bound excited state. The low lying $A \, 2\Sigma^+$ excited state of $C_4H$ is inferred to be the parent of the dipole bound state. The excited electronic state is deduced to have a nonlinear planar structure whereas the ground is linear according to the spectral analysis. The rotational constants have been obtained: $B'' = 0.1552(2)$ cm$^{-1}$ for the $X \, 1\Sigma^+$ state, and $A' = 30.73(1)$, $B' = 0.1587(2)$, $C' = 0.1581(2)$ cm$^{-1}$ for the $1A'$ state.

1. Introduction

The discovery of carbon radicals in space indicates a rich hydrocarbon chemistry and raises questions about their production and evolution in the interstellar medium (ISM) [1, 2]. About 80% of the interstellar molecules contain carbon. Reaction models are mainly based on cation chemistry, but the role of neutral–neutral collisions has been pointed out [3]. Recent studies have investigated the role that anions might play in the formation of the carbon species [4–8]. Rates of radiative attachment reactions between neutral species and electrons to produce negative ions were derived from statistical theory [9]. These rates were found to exceed that of electron detachment in chains containing six or more carbon atoms. Thus it was concluded that for such molecules formation of the stable anion occurs on every collision [7]. Recent studies predict that sufficient population of these carbon anions may be produced to allow their astronomical detection [6].

The rates of radiative attachment were obtained by considering their formation on the electronic ground state potential energy surface. Such attachment via excited electronic states could be a more rapid mechanism than by vibrational states, chiefly due to the larger Einstein A coefficient for electronic as opposed to vibrational emission [10]. Dipole bound states (DBSs) are electronic excited states near the detachment threshold of polar species [11]. They can act as doorway states in formation of the anions in the ISM. These states were observed for small carbon chains [12–17]. Furthermore, it has been proposed that some of the diffuse interstellar absorption bands may arise from rovibronic transitions between the ground states of negatively charged molecules and the DBSs [18].

The neutral $C_4H$ radical was first identified in the millimetre–wave spectrum of dark interstellar clouds [19, 20] and later it was detected in the laboratory [21–23]. The electron affinity (EA) was measured by photoelectron spectroscopy as $3.558 \pm 0.015$ eV [24]. Vibrational structure in the photoelectron spectrum is consistent with theoretical predictions of a linear $1\Sigma^+$ ground state for the anion [6, 25, 26]. The photodetachment spectrum of $C_4H^-$ has been recorded [12]. The observed spectrum was assigned to the $1A' \leftarrow X \, 1\Sigma^+$ electronic transition. The excited $1A'$ state possesses a dipole bound character indicated by the energetic proximity of the electronic transition and electron affinity. On the basis of the observed vibrational and rotational structure the geometry of $C_4H^-$ was inferred as linear and bent in ground and excited electronic states, respectively.

This paper reports the origin band of the $1A' \leftarrow X \, 1\Sigma^+$ electronic transition of $C_4H^-$ and $C_4D^-$ investigated using a resonant two-colour electron detachment method. The band is rotationally resolved, enabling the anion’s geometrical structure to be inferred.

2. Experiment

The experimental set-up and two-colour resonance electron detachment approach have been described in
a previous publication [27]. The anions were generated in a discharge of 0.5% of a C4H2/Ar mixture followed by a supersonic expansion. Deuterated diacetylene seeded in argon was used for the production of C4D−. The discharge occurred between two steel electrodes with an applied voltage \( \sim 500 \text{V} \). The skinned ion beam entered a linear time-of-flight mass spectrometer. At the end of this the mass selected ions were intersected by laser beams. The neutrals resulting from the photodetachment process were collected by a multichannel plate detector. The anions were perpendicularly reflected to another detector and recorded simultaneously for normalization.

The spectra of the origin band were recorded using a two-colour technique that significantly reduced saturation effects and allowed rotational resolution to be obtained. An excimer pumped dye laser was used as a source of resonant photons and the fundamental of a Nd:YAG laser (1064 nm) for the electron detachment process. The spectra were recorded using \( \sim 0.1 \text{cm}^{-1} \) laser step, which is close to the bandwidth of the dye laser. Every experimental point was averaged over approximately 300 laser shots.

### 3. Results

The whole photodetachment spectrum of C4H− has already been analysed and the vibrational structure discussed [12]. A low frequency vibrational progression indicates a change of geometry upon excitation. The origin band lies \( \sim 70 \text{cm}^{-1} \) below the photodetachment threshold energy and its intensity is enhanced when the two-colour photodetachment technique is applied. Thus this is a bound–bound transition.

The rotationally resolved origin band is shown in figure 1. Features marked by * in the figures are assigned to the \( \gamma^1 \) transition [12]. The origin band was recorded under different experimental conditions, achieved by variation of the distance between the source and the skimmer. Increasing this distance leads to a temperature decrease because of a longer cooling time. The top spectrum shown in the figure was recorded at a source–skimmer separation longer than that of the bottom spectrum. Clearly the intensity of the hot band is reduced and the band head of the \( \text{R} \) branch is observed in the cold spectrum. At higher temperatures the \( \text{R} \) branch is hidden by the intense hot band.

The origin band of the \( ^1\Lambda' \leftarrow X^1\Sigma^+ \) electronic transition of C4D− is shown in figure 2 (top trace). The isotopic shift is 30.7 cm\(^{-1}\) to the red. Both species exhibit the same rotational structure. Due to experimental difficulties a spectrum at a lower rotational temperature could not be obtained. The \( \gamma^1 \) transition is also observed and lies at 28 636 cm\(^{-1}\).

### 4. Rotational analysis

The origin band consists of two components, a \( \Sigma-\Sigma \) and a \( \Pi-\Sigma \)-type rovibronic transition. The presence of one perpendicular and one parallel component indicates a bent–linear electronic transition and a bent upper state. In the latter C4H− is therefore an asymmetric top but remains close to a prolate symmetric top, and
the K quantum number is well defined. The parallel and perpendicular bands correspond to \( \Delta K = 0 \) and \( \Delta K = 1 \) transitions, respectively.

The rotational structures on the origin bands of \( \text{C}_4\text{H}^- \) and \( \text{C}_4\text{D}^- \) were fitted with the program Wang [28], using Watson’s effective rotational Hamiltonian [29]. The parameters were the rotational constants \( B'', A', B' \) and origin position. The centrifugal distortion constants were not included in the fit because the precision of the data is inadequate. Thus the molecule was treated as a rigid rotor. \( C' \) was calculated from the relation between moments of inertia for planar molecules \( I_C = I_B + I_A \).

To describe the linear ground state the rotational constant \( A'' \) was set to a large value, which does not affect the results of the fit. The presented data were obtained for \( A'' = 10,000 \text{ cm}^{-1} \). The transition moments were chosen to reproduce the intensity ratio between the || and \( \perp \) components in the experimental spectra (~0.4).

12 lines of the \( \text{P}_{0-0} \) branch, 34 lines of the \( \text{R}_{0-0} \) branch and 9 lines of the \( \text{R}_{1-0} \) branch were used to infer the rotational constants of \( \text{C}_4\text{H}^- \). The positions were determined by fitting the rotational lines to a Gaussian peak. The full width at half maximum was about 0.15 cm\(^{-1}\), close to the laser bandwidth. The uncertainty of the peak positions is \( \pm 0.04 \text{ cm}^{-1} \). The rotational lines near the gap between the \( P \) and \( R \) branches of the \( \Sigma-\Sigma \) component cannot be assigned uniquely, due to the low signal to noise ratio. This might be due to the presence of the \( P \) branch rotational lines with high \( J \) (non-Boltzmann temperature). In figure 3 two simulations and the experimental spectrum are shown. As is seen, the numbering of the rotational lines differs by one quantum. The bottom trace is referred to as first fit, the middle trace as second fit. The RMS deviation between the experimental and simulated spectra is 0.02 cm\(^{-1}\) for both. The fitted values are given in table 1. The ground state rotational constant of the first fit is found in closer agreement with the calculated values [25, 26].

36 lines of \( \text{R}_{0-0} \) branch were used to determine the rotational constants \( B' \) and \( B'' \) of \( \text{C}_4\text{D}^- \). The constant \( A' \) was evaluated from the simulation of the whole band.

Table 1. Rotational constants, origin positions and RMS deviation inferred from the fits of the observed rotational structure in the \( ^1A' \leftarrow X^1\Sigma^+ \) transition origin band of \( \text{C}_4\text{H}^- \). All values are in cm\(^{-1}\).

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<thead>
<tr>
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<th>( X^1\Sigma^+ )</th>
<th>( ^1A' )</th>
<th>( X^1\Sigma^+ )</th>
<th>( ^1A' )</th>
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<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>B</td>
<td>0.1552(2)</td>
<td>0.1587(2)</td>
<td>0.1582(2)</td>
<td>0.1617(2)</td>
</tr>
<tr>
<td>C</td>
<td>0.1552(2)</td>
<td>0.1581(2)</td>
<td>0.1582(2)</td>
<td>0.1604(2)</td>
</tr>
<tr>
<td>origin</td>
<td>—</td>
<td>28 645.51(5)</td>
<td>—</td>
<td>28 645.83(5)</td>
</tr>
<tr>
<td>RMS deviation</td>
<td>0.023</td>
<td>0.018</td>
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</table>

Although the assignment of the rotational lines is not unique, two numberings were finally chosen in consistency with the fit for \( \text{C}_4\text{H}^- \). The values obtained are given in table 2. The RMS deviation between experimental and simulated spectra is about 0.025 cm\(^{-1}\) for each fit.

The rotational profile in the experimental spectrum differs from the one simulated using a Boltzmann population of the energy levels. The temperature of other anions recorded using this experimental set-up was found to be \( \sim 50 \text{ K} \) [30, 31]. In the recorded spectrum of \( \text{C}_4\text{H}^- \) the intensities of the lines at high \( J \) are larger than predicted with a 50 K Boltzmann temperature. The profile could, however, be reproduced by summation of two spectra: one with the expected and one with a higher temperature, with equal weights. They are shown in figures 4 and 5. It should be noted that saturation effects cannot be ruled out as contributions to the cause of the anomalous rotational envelope. The photodetachment spectra for \( \text{C}_4\text{D}^- \) were obtained only in ‘hot’ conditions,
and attempts to decrease the temperature of the anions failed, most probably due to less efficient production of the deuterated anion. The simulation of the origin band of C$_4$D$^-$ is seen in figure 2 (bottom). One temperature (250 K) was sufficient to simulate the profile of the transition. The sum of colder (200 K) and hotter (300 K) components produce a rotational envelope, which is close to one simulated with the average 250 K.

5. Discussion

5.1. Molecular structure

The data obtained are not sufficient to extract all structural parameters in the two electronic states; however, a general conclusion on the geometry may be made. The recorded spectra of the origin band indicate only a slight change in Σ−Σ and Π−Σ band separation upon deuteration. This is attributed to the fact that the H atom is close to the A axis and the off-axis carbon atoms give the main contribution to $I_A$. The search for the structure was made using the bond lengths found previously experimentally and theoretically for the anion and related species (table 3). The dihedral angles were then fitted to reproduce the $A_{C_4D}/A_{C_4H}$ ratio and constant B.

The terminal carbon atom is found to be about 18° off-axis determined by the three other carbons, and the hydrogen atom by ~7°. No distinction between the cis and trans bent structures can be made. The bond lengths calculated for the ground state of the anion [25] and for the 2Π state of the neutral [32] reproduce best the fitted rotational constant. The structure computed using the bond lengths of the isoelectronic (cumulene) H$_2$C$_4$ [33] is found to be effectively too long. The anion is concluded

| Table 2. Rotational constants, origin positions and RMS deviation inferred from the fits of the observed rotational structure in the $^{1}A'-X^{1}\Sigma^+$ transition origin band of C$_4$D$^-$. All values are in cm$^{-1}$. |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|                                | 1st fit                         | 2nd fit                         |                                |
|                                | $X^{1}\Sigma^+$ | $^{1}A'$ | $X^{1}\Sigma^+$ | $^{1}A'$ |
| A                               | —                              | 30.60                            | —                              | 30.30 |
| B                               | 0.1442(1)                      | 0.1473(1)                        | 0.1469(1)                      | 0.1501(1) |
| C                               | 0.1442(1)                      | 0.1465(1)                        | 0.1469(1)                      | 0.1492(1) |
| origin                          | —                              | 28 614.85(1)                     | —                              | 28 615.15(1) |
| RMS deviation                   | 0.025                          |                                  | 0.025                          |
Table 3. Calculated and experimental bond lengths (in Å) for C₄H, H₂C₄ and C₂H⁺, and their rotational constant B (in cm⁻¹).

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</thead>
<tbody>
<tr>
<td>C–H</td>
<td>1.073</td>
<td>1.0527</td>
<td>1.0534</td>
<td>1.055</td>
<td>1.056</td>
<td>1.06</td>
</tr>
<tr>
<td>C₁–C₂</td>
<td>1.320</td>
<td>1.2046</td>
<td>1.2164</td>
<td>1.215</td>
<td>1.227</td>
<td>1.22</td>
</tr>
<tr>
<td>C₂–C₃</td>
<td>1.289</td>
<td>1.3778</td>
<td>1.3445</td>
<td>1.359</td>
<td>1.381</td>
<td>1.36</td>
</tr>
<tr>
<td>C₃–C₄</td>
<td>1.290</td>
<td>1.2096</td>
<td>1.2854</td>
<td>1.224</td>
<td>1.260</td>
<td>1.25</td>
</tr>
<tr>
<td>B</td>
<td>—</td>
<td>0.1587</td>
<td>0.1557</td>
<td>0.1587</td>
<td>0.1532</td>
<td>0.1564</td>
</tr>
</tbody>
</table>

to possess acetylenic rather than cumulenic character in both states. However, the bond length alternation is not as pronounced as in the X 2Σ⁺ ground state of the neutral.

5.2. Dipole bound states

The observed spectrum of C₄H⁻ is assigned to an electronic transition from the linear ground to a bent dipole bound state [12]. The dipole moment required to bind an electron should be greater than 2 D [11]. However, the calculated dipole moment of the linear radical in its X 2Σ⁺ state is about 0.8 D [22, 32, 34]. The formation of a dipole bound state from the ground state of the neutral thus appears impossible, although geometrical distortion might increase the dipole moment. The dipole moment variation along the bending coordinates was investigated by means of MP4 and CCSD calculations (aug–cc–pvdz basis set [35]) using the Gaussian94 package [36]. The computations were made using the bond lengths of C₂H found by microwave spectroscopy [22], changing the structure from linear to a bent, planar chain. No increase in the dipole moment was found. Therefore it seems improbable that the X 2Σ⁺ state of C₂H is responsible for the observed dipole bound state.

Thus the A 2Π excited electronic state of C₂H is the parent of the dipole bound state. Its dipole moment was found to be about 5 D [22, 32], which is high enough to bind an electron. The energy of the A 2Π state relative to X 2Σ⁺ is in the ~70–500 cm⁻¹ range according to various experiments and calculations [22, 24, 34]. The best estimate is judged to be 169 cm⁻¹, obtained by laser induced fluorescence [37]. As the origin band of the 1A’ ← X 1Σ⁺ transition of C₂H⁻ is ~70 cm⁻¹ below the threshold we may estimate the binding energy of the dipole bound state from the sum of these two values, ~240 ± 100 cm⁻¹. A parent A 2Π state is consistent with the structure of the origin band dominated by the perpendicular component, the weak parallel component arising from the distortion of the carbon skeleton.

The charge–dipole interaction is considered to be a non–perturbative process, where the anion inherits the structure of the parent neutral molecule. However, a few cases where the geometry of a dipole bound anion differs from that of the neutral have been observed [11, 17, 38]. Theoretical studies of the electronic structure of dipole bound anions found that the attachment of an electron can lead to a slight modification of the anionic potential energy surface [39]. In the case of C₂H⁻ in the 1A’ dipole bound state the bond lengths are similar to those of the neutral parent state, but a strong distortion of the carbon skeleton is found. The vibronic coupling is suggested to be the reason for this bent structure, rather than electron correlation effects as proposed for other DBS [39]. The bent geometry is consistent with coupling through the ν₇ bending mode [12, 24]. In the ground state of C₂H this bending mode is observed in one quantum excitation in the photoelectron spectrum of C₂H⁻ [24], although the molecule is linear. In the bent DBS it is observed through a vibrational progression [12]. The excited 1Π DBS splits into two components due to Renner–Teller interaction, and the stabilization of the A’ state is strong enough to form the bound state. A large geometry change also was observed for the C₂H radical (2Π ground state) [17].

6. Conclusions

The rotationally resolved origin band of the 1A’ ← X 1Σ⁺ electronic transition was measured for C₂H⁻ and C₂D⁻. The electronic excited state possesses a dipole bound character and exhibits a large distortion from the linear parent structure. The inferred strong vibronic effects are attributed to the open shell electronic structure of the neutral parent. The rotational constants in the ground and dipole bound excited electronic states were determined from the rotational structure analysis. The value B° = 0.1552(2) cm⁻¹ obtained in the anion ground state may be used for the search of the rotational spectrum of the C₂H⁻ anion.

The electronic spectrum recorded in the vicinity of the electron affinity provides information on the potential energy surface of the excited state. The anion may be formed via this state in electron–neutral collisions at low energy. This process may be referred to as an indirect radiative attachment. Detailed investigations of the surfaces of the neutral and the anion are desirable to
analyse this. Models of anion formation should include this indirect process to predict their abundance in the interstellar medium.

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References