Electronic states of $\text{Ta}_2\text{C}^+$

D. Majumdar, K. Balasubramanian

Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA

Received 28 August 1997

Abstract

Geometries and energy separations of low-lying electronic states of $\text{Ta}_2\text{C}^+$ with isosceles triangular and linear structures have been investigated. Complete active-space multiconfiguration self-consistent field method followed by large-scale multireference singles and doubles configuration interaction (MRSDCI) computations and relativistic configuration interaction that included up to two million configurations were used. The $^4\text{A}_2$ electronic state of an isosceles triangular structure was found to be the ground state at the MRSDCI level of calculation. The electronic states of the linear structures were found to be higher. © 1997 Elsevier Science B.V.

1. Introduction

Gas-phase chemistry of transition metal carbides has been the subject of extensive research for the past 40 years [1–7]. Transition metal carbides are characterized by their high melting points, great hardness and metallic conductivity. These properties allow them to play a vital role in material science and electronics [1–3]. In addition to the Kundsens cell effusion technique [8], which has been used to study gaseous carbides since its discovery, newer techniques such as direct laser vaporization (DLV) in conjunction with Fourier transform mass spectrometry (FTMS) [9] and injected drift tube techniques [10] have yielded useful information on metal carbides.

Tantalum carbide cluster ions have been the subject of experimental studies for several years. They have been observed in direct laser vaporization of metal powder and carbon mixture in a Fourier transform mass spectrometer [5,6] and in the Kundsens effusion mass spectroscopic experiment [11]. Recently the ground-state structures of large cluster cations of these carbides have been studied by Roszak and Balasubramanian [12]. The electronic and structural properties of small diatomic and triatomic carbides of tantalum are also interesting as rigorous analysis of their structures, bonding and dissociation properties are key factors to understand several properties of higher carbides and in the prediction of spectroscopic properties. Among smaller tantalum carbides $\text{Ta}_2\text{C}^+$ is an interesting candidate in that the dissociation property of this ion is different from $\text{TaC}_n$ ($n \geq 2$) [6] and it is very unique. From the fragmentation channels observed in the low-energy collision induced dissociation of $\text{Ta}_2\text{C}_y^+$ ($y = 1–7$), McElvany and Cassady [6] speculated the structure of $\text{Ta}_2\text{C}^+$ to be linear [Ta–Ta–C]$^+$. This is contrasted in the current study in that we find the isosceles triangular and the [Ta–C–Ta]$^+$ structure to be considerably lower in energy compared to the [Ta–Ta–C]$^+$ linear structure. It would be quite interesting to investigate the nature of not only the ground state of $\text{Ta}_2\text{C}^+$ but also its low-lying excited elec-
tronic states and investigate the nature of the dissociation process and its structure.

The present Letter deals with theoretical studies on the ground and low-lying excited electronic states of Ta₂C⁺ using the complete active space multiconfiguration self-consistent field (CASMCCSF) followed by multireference singles and doubles configuration interaction (MRSDCI) calculations. The spin–orbit effects on the low-lying electronic states of Ta₂C⁺ are also addressed through the relativistic configuration interaction (RCI) technique. Prior to the CASMCSCF and MRSDCI calculations, we also carried out density functional technique (DFT) computations.

2. Theoretical methods and computational details

The calculations presented here were carried out using the DFT [13], CASMCSCF and MRSDCI approaches. The DFT technique used Becke’s 3-parameter functional [14] with a local correlation part provided by Vosko et al. [15] and the nonlocal part provided by Lee et al. [16] (short B3LYP). The geometry searches in the DFT calculations were made using the Berny optimization algorithm in redundant internal coordinates [17]. The structures considered for Ta₂C⁺ are shown in Fig. 1. An isosceles triangular structure (Fig. 1a) and two linear structures (Fig. 1b,c) have been considered. Relativistic effective core potentials (RECP) that retained the outer 5s²5p⁶5d³6s² shells of tantalum were taken from Ross et al. [18]. For the carbon atom the RECPs that retained the outer 2s2p shells in the valence space were employed [19]. The (4s4p) optimized Gaussian basis set for carbon was contracted to (3s3p). The basis set for carbon was supplemented with a set of 3d functions adopted from Dunning and Hay [20] (α₃ = 0.75). This resulted in a (4s4p1d/3s3p1d) basis set for carbon atom. The optimized (5s5p4d) valence Gaussian basis set of Ta was contracted to (5s4p3d) valence Gaussian basis set. The first two large exponent of p and d functions were contracted in the present investigation. This basis set was found to be accurate in our previous study on TaCO [21].

To get a more detailed picture of the different electronic states of Ta₂C⁺, the geometries of the isosceles triangular and linear structures were further optimized using the CASMCSCF technique. For the isosceles triangular structure the full active space consisted of eleven a₁, four b₂, six b₁, and three a₂ orbitals in the Cᵥ group. This leads to too large a number of configuration spin functions (CSF) for our codes. Consequently, in order to make the computations tractable, we considered alternative choices of smaller active spaces and used the one yielding the lowest energy. Our final CASMCSCF calculations for the isosceles triangular structure included seven a₁, three b₂, four b₁ and one a₂ orbitals to generate electronic states of different spin multiplicities. The lowest a₁ and b₁ orbitals were kept inactive in that no excitations from these orbitals were allowed, although they were allowed to relax. The active space for the linear structure was chosen in the Cᵥ group in an analogous manner. The final active space for the linear structure included eight a₁, three b₁, three b₂ and one a₂ orbitals. Geometry optimizations of various electronic states arising from the isosceles triangular and linear structures were carried out using a quasi Newton–Raphson technique [22].

The low-energy geometries obtained from the CASMCSCF calculations were considered further for energy calculations at higher levels of theory. MRSDCI calculations were carried out to include higher-order correlation. All configurations in the CASMCSCF calculations with coefficients ≥ 0.07 were included in the reference configurations for the MRSDCI. All possible singles and doubles excita-

![Diagram](https://example.com/diagram.png)

Fig. 1. Isosceles triangular (a) and linear (b,c) structures of Ta₂C⁺. The optimized bond lengths (a and b) and the bond angle (θ) are available in Tables 1–3.
3. Results and discussion

3.1. Structural aspects of Ta₂C⁺

The primary structural analysis of Ta₂C⁺ for its isosceles triangular (Fig. 1a) and linear structures (Fig. 1b,c) were carried out using the DFT calculations. The results of the DFT (B3LYP) optimizations for the different structures are presented in Table 1. The geometries of different electronic states were fully optimized without imposing any geometrical constraints. The results indicate that the 4A₂ electronic state with an isosceles triangular structure (Fig. 1a) is the lowest energy electronic state. As seen from Table 1, we have considered both [Ta–C–Ta]⁺ and [Ta–Ta–C]⁺ linear structures in our computations. We find that the electronic states of the linear [Ta–C–Ta]⁺ structure are within 1.3–1.8 eV higher than the isosceles triangular ground state, whereas the electronic states formed by the [Ta–Ta–C]⁺ linear structure are considerably higher. The

<table>
<thead>
<tr>
<th>Structure</th>
<th>State</th>
<th>Geometrical parameters</th>
<th>Energy separation (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>bent⁺</td>
<td>4A₂</td>
<td>1.833</td>
<td>2.589</td>
</tr>
<tr>
<td></td>
<td>2A₁</td>
<td>1.898</td>
<td>2.406</td>
</tr>
<tr>
<td></td>
<td>6A₁</td>
<td>1.879</td>
<td>2.958</td>
</tr>
<tr>
<td>linear⁺</td>
<td>sextet</td>
<td>1.888</td>
<td></td>
</tr>
<tr>
<td></td>
<td>quartet</td>
<td>1.865</td>
<td></td>
</tr>
<tr>
<td></td>
<td>doublet</td>
<td>1.857</td>
<td></td>
</tr>
<tr>
<td></td>
<td>quartet</td>
<td>2.512</td>
<td>1.768</td>
</tr>
<tr>
<td></td>
<td>doublet</td>
<td>2.278</td>
<td>1.924</td>
</tr>
<tr>
<td></td>
<td>Sextet</td>
<td>2.485</td>
<td>1.815</td>
</tr>
</tbody>
</table>

For the geometrical parameters, refer to Fig. 1a–c for the definition of the geometrical parameters of the respective structures.

CASMSCF calculations on the different electronic states of [Ta–Ta–C]⁺ have also indicated that they are of very high energy. The lowest energy electronic state of this structure (2Π) was found to be 3.21 eV above the isosceles triangular ground state. Consequently, on the basis of these studies, we have discarded the possibility of a [Ta–Ta–C]⁺ structure for Ta₂C⁺ and used the isosceles triangular (Fig. 1a) and the other linear structure [Ta–C–Ta]⁺ (Fig. 1b) for higher-order MRSDCI calculations. The results of the CASMCSCF and MRSDCI calculations for the isosceles triangular and linear [Ta–C–Ta]⁺ structures of Ta₂C⁺ are shown in Tables 2 and 3, respectively. The geometries of the electronic states shown in Tables 2 and 3 were fully optimized at the CASMCSCF level using a quasi Newton–Raphson technique [22]. In contrast to DFT, the CASSCF technique favors the 4Σ⁻ electronic state of the linear structure as the lowest-energy electronic state, although it is almost degenerate with the 2Σ⁻ electronic state of the same structure. The next low-lying electronic state with respect to this state arises from the isosceles triangular structure (4A₂) and it is only 0.26 eV above the ground state (Table 2). However, the more accurate MRSDCI calculations on the isosceles triangular (Table 2) and the linear structures (Table 3) of Ta₂C⁺ indicate a different trend. The results indicate that the low-lying electronic states of the linear structure in the CASM-
Table 2
Geometries and energy separations ($\Delta E$) of the various low-lying electronic states of Ta$_2$C$^+$ in the isosceles triangular structure

<table>
<thead>
<tr>
<th>State $^a$</th>
<th>Geometrical parameters $^b$</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$b$ (Å)</td>
</tr>
<tr>
<td>$^3\Sigma^-$</td>
<td>1.884</td>
<td>2.545</td>
</tr>
<tr>
<td>$^3\Sigma^+$</td>
<td>1.887</td>
<td>2.400</td>
</tr>
<tr>
<td>$^3\Sigma^-$</td>
<td>1.917</td>
<td>2.353</td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>1.885</td>
<td>2.550</td>
</tr>
<tr>
<td>$^2\Pi^-$</td>
<td>1.925</td>
<td>2.564</td>
</tr>
<tr>
<td>$^2\Pi^-$</td>
<td>1.911</td>
<td>2.576</td>
</tr>
<tr>
<td>$^4\Sigma^+$</td>
<td>1.942</td>
<td>2.440</td>
</tr>
<tr>
<td>$^5\Sigma^+$</td>
<td>1.960</td>
<td>2.518</td>
</tr>
<tr>
<td>$^6\Sigma^+$</td>
<td>2.014</td>
<td>2.515</td>
</tr>
<tr>
<td>$^8\Sigma^+$</td>
<td>2.006</td>
<td>2.440</td>
</tr>
<tr>
<td>$^9\Sigma^+$</td>
<td>1.974</td>
<td>2.355</td>
</tr>
<tr>
<td>$^{10}\Sigma^+$</td>
<td>2.009</td>
<td>2.382</td>
</tr>
</tbody>
</table>

$^a$The states are assigned in the C$_2v$ group.
$^b$Refer to Fig. 1a for the definition of the parameters.

CSCF calculations are higher at the MRSDCI level. As seen from Table 2, at the MRSDCI level, the $^4\Sigma^+$ electronic state of the isosceles triangular structure is the ground state, consistent with the outcome of the DFT method. The $^2\Sigma^+$ electronic state of the isosceles triangular structure is the next low-lying excited electronic state and it is 0.23 eV above the ground state. The MRSDCI + Q calculations also follow the same trend (Tables 2 and 3), but stabilizes the $^2\Sigma^+$ isosceles triangular structure relative to $^4\Sigma^+$ thus reducing the energy separation to only 0.02 eV. In order to establish the reliability of our MRSDCI calculations, we have further optimized the geometry of the $^2\Sigma^+$ electronic state of the linear structure. The optimized bond lengths vary by only 0.01 Å for the bond length and the total energy changes by only 0.002 eV which indicates that the MRSDCI results are quite reliable. It further reveals the need for higher-order correlation methods to establish the structures of such molecules unambiguously. The energy differences of the different electronic states of the linear [Ta–C–Ta]$^+$ structure with respect to the ground state in the DFT calculations are higher than the corresponding values in the CASMCSF and MRSDCI calculations. Our results and conclusion thus differ from McElvany and Cassady [6] who assumed a linear [Ta–Ta–C]$^+$ structure for Ta$_2$C$^+$. We not only find the isosceles triangular structure to be lower but the [Ta–Ta–C]$^+$ structure is considerably higher than both [Ta–C–Ta]$^+$ and the isosceles triangular structures.

We have carried out RCI calculations to visualize the spin–orbit effect on the low-lying electronic states of Ta$_2$C$^+$ in its isosceles triangular structure. Reference configurations from the $^4\Sigma^+$, $^2\Pi^-$, $^2\Pi^+$, $^2\Pi^+$, $^4\Pi$, $^4\Pi^+$, $^4\Pi^+$, $^6\Sigma^+$ and $^4\Pi$ electronic states were included in the RCI calculations to generate the first three roots of the spin–orbit coupled E state. The spin–orbit effect was found to stabilize this structure by 0.082 eV.

Table 3
Geometries and energy separations ($\Delta E$) for the low-lying electronic states of Ta$_2$C$^+$ in its [Ta–C–Ta]$^+$ linear structure

<table>
<thead>
<tr>
<th>State $^a$</th>
<th>Ta–C bond length (Å) $^b$</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CASMCSF</td>
<td>MRSDCI</td>
</tr>
<tr>
<td>$^3\Delta$</td>
<td>1.880</td>
<td>0.302</td>
</tr>
<tr>
<td>$^3\Sigma^+$</td>
<td>1.862</td>
<td>0.0</td>
</tr>
<tr>
<td>$^3\Pi$</td>
<td>1.862</td>
<td>0.001</td>
</tr>
<tr>
<td>$^4\Sigma^+$</td>
<td>1.905</td>
<td>1.048</td>
</tr>
<tr>
<td>$^4\Pi$</td>
<td>1.950</td>
<td>1.176</td>
</tr>
<tr>
<td>$^4\Pi$</td>
<td>1.952</td>
<td>1.245</td>
</tr>
<tr>
<td>$^5\Delta$</td>
<td>1.880</td>
<td>1.939</td>
</tr>
<tr>
<td>$^6\Pi$</td>
<td>1.996</td>
<td>2.094</td>
</tr>
<tr>
<td>$^6\Sigma^+$</td>
<td>1.951</td>
<td>4.250</td>
</tr>
</tbody>
</table>

$^a$The states are assigned the in C$_{nv}$ group.
$^b$Refer to Fig. 1b for the definition of the geometrical parameters.
3.2. Dissociation of Ta$_2$C$^+$

The dissociation process of Ta$_2$C$^+$ requires some discussion. McElvany and Cassady [6] have suggested that the dissociation occurs from a linear [Ta-Ta-C]$^+$ structure of Ta$_2$C$^+$ into Ta$^+$ and Ta-C fragments. They concluded this on the basis of lower dissociation energy of the Ta-Ta bond compared to the Ta-C bond [6]. Thus it was assumed that the dissociation process is likely to occur from a linear [Ta-Ta-C]$^+$ structure. Our theoretical calculations indicate that this structure is quite unlikely for Ta$_2$C$^+$, as its energy is considerably higher than both [Ta-C-Ta]$^+$ and the isosceles triangular structures. Moreover very high energy requirement for the fragmentation of this structure and the dissociation of Ta$_2$C$^+$ into [Ta-C-Ta]$^+$ and C$_2$ [6] also suggest the improbability of the [Ta-Ta-C]$^+$ structure for Ta$_2$C$^+$. We have calculated the dissociation energy ($D_e$) of Ta$_2$C$^+$ for the following process:

$$\text{Ta}_2\text{C}^+\left[4\Sigma^-, \text{linear(Fig. 1B)}\right] \rightarrow \text{TaC}\left(3\Sigma^+\right) + \text{Ta}^+(3F).$$

This was done as a supermolecular computation by keeping TaC and Ta$^+$ at 10 Å separation. The dissociation energy is thus computed as 5.453 and 5.696 eV, respectively, at the MRSDCI and MRSDCI+Q levels of calculation. Since the isosceles triangular structure of Ta$_2$C$^+$ would also fragment into TaC and Ta$^+$, we have also computed the dissociation energy of the isosceles triangular structure using the same dissociation limit as 6.715 and 7.335 eV, respectively, at the MRSDCI and MRSDCI+Q levels of theory. Combining this with the computed $D_e$ of 5.2 eV for the diatomic TaC in its $2\Sigma^+$ ground state, we obtain the atomization energy of the Ta$_2$C$^+$ ion to be 11.9 and 12.5 eV without and with Q corrections, respectively.

3.3. Electronic configuration and Mulliken populations

The leading configurations of several low-lying electronic states of Ta$_2$C$^+$ in the isosceles triangular as well as linear geometries are shown in Table 4. Most of the electronic states have leading configurations with coefficients below 0.9, indicating multireference character of these states. The compositions of the singly occupied 6a$_1$, 3b$_1$, and 3b$_1$ natural orbitals of the isosceles triangular $4\tilde{A}_2$ ground state are

$$\Psi(6a_1) = (\text{Ta}_1 + \text{Ta}_2) \times \left[ 6\sigma - 5d_{x^2-y^2} + 5d_{z^2} + 5d_{xz} \right],$$

$$\Psi(3b_1) = (\text{Ta}_1 + \text{Ta}_2) \times \left[ 5p_x - 5d_{x^2} - 5d_{xz} \right],$$

$$\Psi(3b_1) = (\text{Ta}_1 + \text{Ta}_2) \times \left[ -6\sigma + 5p_y + 5d_{x^2-y^2} - 5d_{z^2} \right].$$

The configurations indicate that in the singly occupied orbitals of the ground state ($^4\tilde{A}_2$) of Ta$_2$C$^+$, are composed only of the tantalum orbitals. The sd hybridization is seen in the 6a$_1$ orbital, whereas the 3b$_1$ and 3b$_1$ orbitals involve pd and spd orbitals of Ta$_1$ and Ta$_2$. The principal composition of the singly occupied orbital (1$\delta$) of the lowest energy electronic state of the linear structure of Ta$_2$C$^+ (^2\Delta)$ (Fig. 1b) is $5d_{x^2-y^2}$ of Ta$_2$. In the next low-lying electronic state:

<table>
<thead>
<tr>
<th>Electronic Coefficient Configuration</th>
<th>Bent structure (Fig. 1a)$^a$</th>
<th>Linear structure (Fig. 1b)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6\sigma</td>
<td>0.82</td>
<td>0.89</td>
</tr>
<tr>
<td>18\delta</td>
<td>0.82</td>
<td>0.92</td>
</tr>
</tbody>
</table>

$^a$The 1a$_1^+$ 2a$_1^+ 3a_1^+ 4a_1^+$ portion of the configuration is common to all electronic states of the isosceles triangular structure.

$^b$The 1\sigma$^+$ 2\sigma$^-$ 3\sigma$^+ 4a$_1^+ 5\sigma^+ 1\pi^+ 2\pi^+ 3\pi^+$ portion of the configuration is common to the $^2\Delta$ and $^2\Sigma$ electronic states of the linear structure.
state \(^{4}\Sigma^{−}\) of the linear structure the composition of
the singly occupied \(6\sigma\), \(1\delta\) and \(2\delta\) natural orbitals could be expressed as
\[
\Psi(6\sigma) = C(2s) + Ta_1(\ -6s + 5p_z),
\]
\[
\Psi(1\delta) = Ta_2(5d_{x^2−y^2},)
\]
\[
\Psi(2\delta) = Ta_1(5d_{x^2}) .
\]
These compositions indicate essential bonding difference between the isosceles triangular and linear structures. A comparison of the TaC bond distances between the isosceles triangular and linear structures of \(Ta_2C^+\) (Tables 2 and 3) further indicates that Ta–C bond in the ground electronic state of isosceles triangular structure \(^{4}A_2\) is 0.1 Å larger than that of the lowest electronic state of the linear structure \(^{2}\Delta\). This indicates that the Ta–C bond in the linear structure of \(Ta_2C^+\) in the \(^{2}\Delta\) electronic state is not purely single bond. The longer Ta–C bonds in the \(Ta_2C^+\) in the isosceles triangular structure \(^{4}A_2\) indicate that they could be single bonds but the Ta–Ta distance in this electronic state is quite short (2.35 Å) indicating multiple bonding at the base of the isosceles triangular structure.

The Mulliken population analysis of different low-lying electronic states of \(Ta_2C^+\) in the isosceles triangular (Fig. 1a) and linear structures (Fig. 1b) are shown in Table 5. In the \(^{4}A_2\) electronic state of the isosceles triangular structure, electrons from the \(s\) orbitals of Ta and C are donated to the \(\sigma\) bond. About 0.9 \(s\) electron from Ta and 0.42 electron from C are donated toward \(\sigma\) bond formation. These donated electron densities are then absorbed by the \(p\) orbitals of each atom. This effect makes Ta–C bond polar. In case of Ta–Ta bonding in the \(^{4}A_2\) electronic state, the electron density donated for the \(\sigma\) bond is balanced by the back donation to the \(\pi\) molecular orbitals. The electron distribution on the different atoms of the lowest energy electronic state of the linear structure \(^{2}\Delta\) shows that the extent of \(\sigma\) donation and \(\pi\) back donation is larger than the isosceles triangular structure (Table 5) and this would make Ta–C bonds more polar than the isosceles triangular structure. Similar effects are also observed in the change distribution patterns other electronic states shown in Table 5.

4. Conclusions

The tantalum carbide cluster ions were observed in a direct laser vaporization [5,6] experiment and were also produced from mixtures of metal powder on graphite in high-temperature ovens [5,6]. The \(Ta_2C^+\) ion is quite interesting among them because of its unique nature of fragmentation pattern that led to propose a \([Ta-Ta-C]^+\) linear structure of this ion [6]. We have optimized the geometries of the different electronic states of this ion using the DFT (B3LYP), CASMCSCF and MRSDCI calculations. The ground state of the molecule has been found to be an isosceles triangular structure \(^{4}A_2\) at the highest MRSDCI level. Although the electronic states of the linear structure \([Ta–C–Ta]^+\) were found to be lower at the CASMCSCF level, more accurate MRSDCI calculation place this structure higher than the

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electronic states</th>
<th>(^{4}A_2)</th>
<th>(^{2}B_2)</th>
<th>(^{2}A_1)</th>
<th>(^{2}A_2)</th>
<th>(^{4}B_1)</th>
<th>(^{4}B_1)</th>
<th>(^{2}\Delta)</th>
<th>(^{4}\Sigma^−)</th>
<th>(^{1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s</td>
<td>1.579</td>
<td>1.575</td>
<td>1.649</td>
<td>1.574</td>
<td>1.693</td>
<td>1.519</td>
<td>1.437</td>
<td>1.444</td>
<td>1.445</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>2.831</td>
<td>2.810</td>
<td>2.703</td>
<td>2.830</td>
<td>2.718</td>
<td>2.740</td>
<td>3.439</td>
<td>3.467</td>
<td>3.464</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>0.050</td>
<td>0.050</td>
<td>0.048</td>
<td>0.050</td>
<td>0.050</td>
<td>0.049</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>3.022</td>
<td>3.133</td>
<td>3.218</td>
<td>3.004</td>
<td>2.938</td>
<td>2.809</td>
<td>2.163</td>
<td>2.489</td>
<td>2.491</td>
</tr>
</tbody>
</table>

\(^{a}\) Electronic states refer to the bent structure (Fig. 1a).

\(^{b}\) Electronic states corresponding to the linear structure (Fig. 1b).
isosceles triangular structure. The linear [Ta-Ta-C]**
structure proposed by McElvany and Cassady [6],
was found to be considerably higher than both the
the isosceles triangular and [Ta–C–Ta]** linear struc-
ture. Our calculated dissociation energy of Ta3C**
was found to be quite reasonable in view of the
high-energy requirement for the fragmentation of
this molecule into TaC and Ta** [6]. The nature of
bonding in the low-lying electronic states of this ion
has been explained from the composition of the
orbitals as well as Mulliken population analysis. The
σ donation and π back donation processes have
been found to be operative in bonding and results in
substantial bond polarity. Different electronic states
of the [Ta–C–Ta]** linear structure have been found
to be more polar than the low-lying electronic states
of the isosceles triangular structure.

Acknowledgements

The research was supported by the US Depart-
ment of Energy under Grant DEPG0286ER13558.

References

2393.
(1990) 4788.
2057.
[10] G. Von Helden, M.T. Hsu, P.R. Kemper, M.T. Bowers, J.
(1997) 553.
1200.
2664.
ods of Electronic Structure Theory (Plenum Press, New
(1996) 263.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G.
Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersen,
J.A. Montgomery, K. Raghavachari, M.A. Al-Laham,
V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski,
B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng,
P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Re-
plogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley,
D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C.
Gonzalez, J.A. Pople, GAUSSIAN 94, Revision B.1 (Gaus-
Gordon, J.A. Jensen, S. Kosuki, N. Matsunaga, K-A. Nguyen,
S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Com-
[27] The major authors of ALCHEMY II are B. Liu, B. Lengsfeld
and M. Yoshimine.