A CI INVESTIGATION OF THE CORE IONIZED STATES DERIVED FROM
$^1A_1$ AND $^3B_1$ METHYLENE

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Ab initio LCAO MO SCF and extensive CI calculations with different basis sets of double zeta quality (and beyond) have been performed to compute the potential energy surfaces of the $X^2B_1$, $^1A_1$, and $^1B_1$ neutral states and of the $^3B_1$, $1,2^2A_1$ and $1,2^2B_1$ core ionized states of methylene. A discussion of the changes in binding energies for the core-ionized species and of shake up and multiplet splitting effects is presented. The calculation of the potential energy surfaces allows an analysis of the angular characteristic and optimised geometries of the states involved, in terms of basis set and correlation effects.

1. Introduction

Methylene represents one of the simplest species for which detailed experimental studies have been made of reactions involving both the ground and lowest excited states [1]. The relative ease with which methylene may be generated from appropriate precursors either thermally or photochemically [1, 2] to produce either the $^3B_1$ or $^1A_1$ states, has allowed detailed investigations of both the rates and stereoselectivities of, for example, addition and insertion reactions [1-5].

The experimental studies have been complemented by theoretical studies ranging from qualitative discussions of differences in reactivities for the two states based on orbital symmetry [6a] or orbital phase continuity [6b] lines to detailed HF and CI studies [7-9] of the potential energy surfaces including the delineation of the important question of the energy separation between the $^3B_1$ and $^1A_1$ states. The relatively small size of the system has also allowed detailed investigations of potential energy surfaces for certain reactions and recent examples of this genre are provided by studies of the insertion of methylene into the hydrogen molecule and addition to ethylene [3-5].

Whilst there is a considerable body of theoretical and experimental data on both $^1A_1$ and $^3B_1$ methylene, the situation with regard to the ionized states is much less complete. Theoretical studies of a very high quality [8, 10] have recently been reported on CH$_2$ and CH$_2^+$ in an attempt to interpret experimental electron attachment data. Schweig and co-workers [11] have reported a CI perturbation treatment of some of the ionized states of both singlet and triplet methylene; an interesting feature of which was the rather large computed shift for the core ionized states although no discussion
was given of the potential energy surfaces for these states.

In recent years there has been considerable interest in the high resolution ESCA investigation of small molecules to investigate inter alia: vibrational effects accompanying core ionization [12, 13], electronic relaxation phenomena [14] and shake up, configuration interaction [15–17] and multiplet effects [18]. The relative ease with which singlet and triplet methylene may be prepared presents the intriguing prospect of for the first time measuring core level spectra for both the ground and excited state of a simple system. A detailed theoretical investigation of methylene and its core ionized states is therefore particularly apposite at this time for a number of reasons:

(i) We have recently shown [14] that the substantial shift in CIls core binding energy in going from methane to hexane largely arises from intermolecular valence electron relaxation effects and a study of the methylene system therefore allows an investigation of the changes in relaxation energy in going from methane to methylene.

(ii) The potential energy surfaces for 'A1 and 'B1 methylene are significantly different [19] and we might therefore anticipate substantial changes for the derived core ionized states.

(iii) Such changes in potential energy surface should be manifest in vibrational fine structure for the CIls levels and a detailed theoretical investigation will therefore provide a basis for a prediction against which the experimental data can be compared.

(iv) For core ionization of the 'B1 methylene the 'B1 and 'B1 states may be directly derived in a one electron approximation and it is of interest to compare the differences in potential energy surfaces for these states and to compute the magnitude of the multiplet splitting.

(v) A number of low lying shake up states are principle available from both 'A1 and 'B1 methylene and there has been no previous investigation of such states.

In our previous paper [19] we have investigated some of these aspects of the structure and bonding of 'A1 and 'B1 methylenes and their derived core ionized states at the ΔSCF level. The main conclusions from this study may be summarised as follows:

(a) There is a substantial computed shift in binding energy for the 'B1 state derived from 'B1 methylene and the 'A1 state derived from 'A1 methylene, of 2.2 eV.

(b) The computed shift between the CIls levels of 'A1 methylene and methane is substantial: ≈3.4 eV of which the relaxation energy difference contributes 1.2 eV.

(c) Substantial changes in potential energy surfaces are computed in going from the neutral to core ionized states for both states of methylene; the CH bond length decreasing and HCH bond angle increasing on going to the core ionized species.

(d) It is known that exact details of potential energy surfaces for even simple systems require extended basis sets and an inclusion of correlation effects.

It is clear that the computations reported to date indicate that the study of the core ionized states of the 'A1 and 'B1 states of methylene is likely to be a very fruitful field and the ΔSCF computations provide a qualitative indication of some of the phenomena of interest.

In this paper we report a detailed CI investigation of 'A1 and 'B1 methylenes and the derived 'A1, 'B1 and 'B1 core ionized states which provides a more quantitative data base for comparison with experimental data when these become available.

2. Theoretical considerations

Previous calculations on the energetics of simple carbenes [7–9] have concentrated in the main on the question of the disposition of the low lying states of the molecule, and have demonstrated that a consistent picture of singlet–triplet separation may be obtained from rather simple wavefunctions, requiring the use of a two-configuration singlet and one-configuration triplet wavefunction. Thus for CH2 the ground triplet state (X 'B1) is approximately described by the one-configuration (SCF)
function:

\[ 1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1 \]  \hspace{1cm} (1)

while the first excited state \( (1^1A_1) \) requires a two-configuration MCSCF description, involving the terms:

\[ 1a_1^2 2a_1^2 1b_2^2 3a_1^2 \]  \hspace{1cm} (2)

and

\[ 1a_1^2 2a_1^2 1b_2^2 1b_1^2 \]  \hspace{1cm} (3)

Note that in linear (\( D_{nh} \)) symmetry, configuration (1) correlates with:

\[ 1\sigma_g^2 2\sigma_u^2 1\pi_u^2 \]  \hspace{1cm} (4)

The \( 1^1A_1 \) state correlates with one component of the resulting \( 1^1\Delta_b \) state, while the second component of this state correlates with the \( 1^1B_1 \) state in \( C_{2v} \) symmetry, characterised by the term:

\[ 1a_1^2 2a_1^2 1b_2^2 (1b_1 3a_1) \]  \hspace{1cm} (5)

where the parentheses denote singlet coupling of the enclosed orbitals.

The creation of a core hole in methylene leads in the linear symmetric case to the term:

\[ 1\sigma_g 2\sigma_u 1\pi_u \]  \hspace{1cm} (4)

giving rise to a solitary quartet state \( (4\Sigma_u^+ \) and three doublet states \( (2\Sigma_u^-, 2\Delta_g \) and \( 2\Sigma_u^- \) ). The \( C_{2v} \) geometry the correspondence for these states is as follows:

\[ 4\Sigma_u^- \to 2B_1, \quad 2\Sigma_u^- \to 2B_1 \]

\[ 2\Delta_g \to 2B_1, \quad 2\Delta_g \to 2A_1 \]

\[ 2\Sigma_u^- \to 2A_1 \]

In the present paper we report a theoretical investigation of the changes in geometry and force constants accompanying CI \( \Lambda \) core ionization in methylene. Ab initio SCF and CI studies of the angular potential curves for the \( \chi^3B_1, 1^1A_1 \) and \( 1^1B_1 \) states were compared with those of the associated \( 1^3B_1, 1, 2^3B_1 \) and \( 1, 2^2A_1 \) core hole states. An investigation of the effects of basis set size on the form of the angular curves has been undertaken.

### 3. Computational details

SCF and configuration interaction (CI) calculations of the \( \chi^3B_1, 1^1A_1 \) and \( 1^1B_1 \) states of methylene and the associated core hole states were performed in a number of bases of gaussian functions.

Basis I [20] contained a \( (9s5p) \) gaussian basis contracted to \( (4s2p) \) on the carbon atom and a \( (4s) \) set contracted to \( (2s) \) on the hydrogen, with the orbital exponents multiplied by a scaling factor of 1.2.

A more extensive \( s,p \) basis, basis II, employed a \( (10s6p) \) basis for carbon and a \( (5s) \) set for hydrogen, contracted to \( (5s3p) \) and \( (3s) \) respectively [21].

Finally, the influence of polarisation functions was determined by incrementing this basis with a \( d \) function on carbon (basis III). Previous studies on the low lying carbene states suggest the optimum value of this exponent to be sensitive to the state under investigation.

Accordingly single cycle optimizations of this value were performed in SCF calculations on the \( \chi^3B_1 \) state and on the \( 1^4B_1 \) core hole state and in MCSCF calculations on the \( 1^1A_1 \) state of \( \chi_2 \) leading to values of 0.72, 0.76 and 0.56 respectively. Note that throughout the present work spherical harmonic combinations of the six gaussian \( d \) functions were taken, the \( (x^2+y^2+z^2) \) component being eliminated.

The configuration interaction treatment is of the multi-reference double excitation type, with the configuration space comprising in a given case of all single and double excitations relative to a pre-determined reference set. A summary of the pertinent features of the present CI treatment is given in table 1.

Considering the low lying states of \( \chi_2 \), we have utilised a single term Hartree-Fock reference set for the \( \chi^3B_1 \) and \( 1^1B_1 \) and two reference species for the \( 1^1A_1 \) state (cf. table 1). The orbital sets employed for the \( \chi^3B_1 \) states were derived from SCF calculations on the appropriate reference configuration, while the orbitals from two-configuration SCF calculations were used for the \( 1^1A_1 \) state. In each case the MO corresponding to the carbon 1s inner shell
Table 1: Details of the CI treatment for the various states under discussion

<table>
<thead>
<tr>
<th>State</th>
<th>MO basis</th>
<th>Reference configurations</th>
<th>Dimension</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>1a1 2a1 1b2 3a1 1b1</td>
<td>basis I</td>
</tr>
<tr>
<td></td>
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</tr>
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<td>(X^3\text{B}_1)</td>
<td>X SCF-MO</td>
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<tr>
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<td>1023</td>
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<tr>
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<td>(1^2\text{B}_1) (1^1\text{B}_1) SCF-MO</td>
<td>1 2 2 1 1</td>
<td>777 3424</td>
</tr>
</tbody>
</table>

was kept doubly occupied in all configurations, whilst the orbital with highest energy, corresponding to the inner shell complement was excluded: all other MO's were allowed variable occupation.

The orbitals from a Hartree–Fock calculation on the \(4\text{B}_1\) state
\[1a_1 1b_2 2a_1^2 3a_1 1b_1, \tag{6}\]
were used as a starting point for all hole state CI calculations, in which the highest energy virtual orbital was not used as a replacement orbital. The reference set for the \(4\text{B}_1\) state comprised just the SCF configuration (6), while two reference species were employed in the treatment of the \(1, 2^2\text{A}_1\) hole states, namely:
\[1a_1 1b_2^2 2a_1^2 3a_1^2 \tag{7}\]
and
\[1a_1 1b_2^2 2a_1^2 1b_1^2. \tag{8}\]

Calculations on the \(1, 2^2\text{B}_1\) hole states used a reference set comprising the single orbital product
\[1b_2^2 2a_1^2 (1a_1 3a_1) 1b_1, \tag{9}\]
where again the parentheses denote singlet coupling of the enclosed orbitals. Note that this product results in the following two-membered canonical set
\[1b_2^2 2a_1^2 [1a_1 3a_1] 1b_1\]
corresponding to triplet coupling of the valence orbitals (cf. the \(X^3\text{B}_1\) state of methylene), and
\[1b_2^2 2a_1^2 [3a_1 1b_1] 1a_1, \]
where the valence orbitals are singlet coupled (cf. the \(1^1\text{B}_1\) state of CH₂).

Two series of preliminary CI calculations were performed on the hole state species using basis I. First, the configuration space comprised all single+double excitations relative to the specified reference set. A second study was carried out in which all configurations arising from internal orbital replacements, through which the CI's orbital becomes doubly occupied, were omitted from the configuration space. Such an omission corresponds to the use of approximate Feshbach projections operators, and has been suggested as a necessary restriction to avoid collapse onto lower lying continuum states of the ion in the final secular problem [22]. In practice both treatments gave virtually identical angular potential curves for the methylene core hole states under investigation. While the basis I studies reported here utilised the entire MRD-CI space, the internal configurations were omitted in the basis III calculations purely as a matter of computational convenience in solving the eigenvalue problem.

4. Results and discussion

4.1. Energies of core ionized states

We have previously commented [19] on the at first rather surprising fact that the ∆SCF computed binding energy for the \(^1\text{A}_1\) state of methylene (\(^2\text{A}_1\) core ionized state) is substantially higher (by ∼2.2 eV) than for the \(^3\text{B}_1\) state (\(^3\text{B}_1\) core ionized state). A further feature of interest is that the computed shift in binding energy between CH₄ and CH₂ (\(^3\text{B}_1\)) is 1.1 eV and this arises largely from the lowering of the relaxation energy by ∼0.8 eV in going to the smaller system. The energies for the various
states studied in this work (at the equilibrium geometry for the neutral \( ^3\text{B}_1 \) state) are given in table 2.

The first point to note is that the difference in binding energy for the core hole states of \( ^3\text{B}_1 \) (\( ^3\text{B}_1 \)) and \( ^1\text{A}_1 \) (\( ^1\text{A}_1 \)) methylene of 2.2 eV at the SCF level is in excellent agreement with the CI computations, both basis sets (I and III) giving a shift of 2.4 eV. The computed multiplet splitting is 2.9 eV (basis set I) and 3.2 eV (basis set III). It is clear therefore that the core hole state spectra of \( ^1\text{A}_1 \) and \( ^3\text{B}_1 \) methylene should be highly distinctive and that the magnitude of the shifts and multiplet splittings are such that the salient features should be observable even with ESCA instrumentation of modest resolution.Whilst the shifts and energy separations are well reproduced by the smaller basis set computations it is clear that the role of polarization functions and correlation effects is important in determining absolute energies and this will become clearer when a discussion is presented of the potential energy surfaces.

For a linear system (\( \text{D}_{\text{eh}} \)) the \( ^2\text{A}_1 \) core ionized state correlates with the \( ^2\text{A}_1 \) state and the \( ^2\text{B}_1 \) state and it is therefore of interest to investigate this state.

The energy separation between the \( ^3\text{B}_1 \) and \( ^1\text{A}_1 \) states is 0.57 eV (13.1 kcal) for the largest basis set computation and this compares favourably with other recent CI studies [9]. The \( ^1\text{B}_1 \) state has been investigated in some detail by Goddard and Wadt [23] and the GVB CI computed \( ^3\text{B}_1\)\( ^1\text{B}_1 \) energy separation of 1.7 eV computed in this work is in good agreement with their reported value of 1.90 eV. The computed barriers to inversion for the states studied in this work are reported in table 3 and are somewhat smaller than those reported by Goddard and Wadt, viz. 0.29 eV, 1.19 eV and 0.15 eV (this work) versus 0.40 eV, 1.69 eV and 0.28 eV (ref. [23]) for the \( ^3\text{B}_1 \), \( ^1\text{A}_1 \) and \( ^1\text{B}_1 \) states respectively. The relative energies of the states are in good agreement for the computations employing basis sets I and III, however, the absolute energies are obviously much better described by the latter. Considering firstly the \( ^3\text{B}_1 \) state, core ionization gives rise to the \( ^2\text{B}_1 \) and \( ^1\text{B}_1 \) states, the computed energy separations being 2.9 eV (basis I) and 3.2 eV (basis III). The magnitude of this splitting is entirely reasonable on the basis of the multiplet splitting for the doublet states of simple radicals of \( \approx 1.5 \) eV (viz. the splitting should be proportional to the number of unpaired spins) [18]. The \( ^2\text{B}_1 \) state which lies very close in energy is dominated by the configuration \( 1a_1 \) \( 2a_1^2 \) \( 1b_2 \) (\( 3a_1 \) \( 1b_1 \)) which may be regarded as the singlet parentage component of the “triplet parentage” \( ^1\text{B}_1 \) state. This implies that the transition probability \( ^3\text{B}_1 \rightarrow ^2\text{B}_1 \) will be much lower than

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**Table 2**

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<tr>
<th>B(_1) symmetry</th>
<th>A(_1) symmetry</th>
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<table>
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<th>energy(^b) (eV)</th>
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<td>( ^1\text{A}_1 )</td>
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<td>I</td>
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<td>I</td>
<td>( ^1\text{A}_1 )</td>
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<td>I</td>
<td>( ^2\text{A}_1 )</td>
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<td>III</td>
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</table>

\(^a\) With respect to the \( ^3\text{B}_1 \) energy \(-38.982 \) au (I); \(-39.035 \) au (III).

\(^b\) With respect to the \( ^1\text{A}_1 \) energy \(-38.944 \) au (I); \(-39.014 \) au (III).

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**Table 3**

<table>
<thead>
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</table>
for $^3\text{B}_1 \to 1^3\text{B}_1$. As expected the energy separation between these $^2\text{B}_1$ states is very small [$\Delta E = 0.7$ eV (basis I), 0.2 eV (basis III)]. It seems likely that the larger basis set computation will provide an upper limit to the energy separation so that experimentally we might anticipate that the direct photoionization spectrum should consist of two components separated by $\approx 3$ eV with the intensity ratios being close to that appropriate to the statistical weights.

For the $^1\text{A}_1$ state core ionization leads to a $^2\text{A}_1$ state and the CI computations with basis set III place this at a binding energy of 2.4 eV above the $^4\text{B}_1$ state derived from the $X^3\text{B}_1$ state. This confirms the overall picture derived from the ASCF computations previously reported [19]. The $^2\text{B}_1$ state may be regarded as a one-electron shake up state of the $^2\text{A}_1$ state ($\Delta E = 1.4$ eV) involving the 3a$_1$ and 1b$_1$ orbitals. Since the hole state has the same symmetry as the neutral molecule the transition probability should be zero. The $^2\text{A}_1$ state corresponds to a doubly excited state (configuration interaction satellite) of the $^1\text{A}_1$ state also involving excitations of the 3a$_1$ and 1b$_1$ orbitals. It is interesting to note that the computed energy separation for these states of 4.4 eV corresponds to an excitation energy of $\approx 3.5$ eV for the neutral $^1\text{A}_1$ methylene.

### 4.2. Angular characteristics of the states

The angular potential curves for the low lying states of methylene and the associated core hole states as a function of treatment and basis set are given in figs. 1-4. The C-H bond length is thereby held fixed at 1.08 Å i.e. at the experimental minimum for the $X^3\text{B}_1$ state. Curves derived at the SCF level are depicted in fig. 1 ($X^3\text{B}_1$, 1$^1\text{A}_1$ and 1$^1\text{B}_1$) and fig. 2 (1$^4\text{B}_1$ core hole state). The corresponding CI curves for methylene are presented in fig. 3, while those for the core hole states are given in fig. 4 (a and b). The angular minima are given in table 4.

Considering initially the SCF curves of figs. 1 and 2 it is seen that extending the sp basis (basis I to II) has a far greater effect energetically for the $^4\text{B}_1$ hole state than for the states of methylene itself. The energy lowering of 0.003-0.005 au typically found in the latter case are increased to 0.05-0.06 au for the hole state, suggesting that a quantitative description of the valence shell relaxation accompanying core ionization may require a significantly more flexible basis than is required in the description of the neutral species. The additional energy lowering afforded by the introduction of polarisation species (bases II to III) is, however, seen to be approximately equal being typically 0.01 au for both the $X^3\text{B}_1$ and associated core hole. A comparison with the energy lowering derived in the $^1\text{A}_1$ calculation is not strictly valid, since this two-configuration calculation already involves some correlation energy, with the role of the d functions not strictly limited to that of polarisation.
The angular minimum derived from the SCF curves (table 4) for the $X^3\Sigma^+_1$ and associated core hole suggest that the creation of an inner shell vacancy leads to a significant increase in bond angle and decrease in the stabilization which arises from bending away from the linear geometry, a conclusion which we have discussed in detail elsewhere [19]. The basis III studies suggest this stabilization for the ground state (0.53 eV) is approximately halved on core ionization (0.26 eV for the $1^4\Sigma^+_1$ state), with the bond angle increasing from 129° to 136°. Extending the sp basis is seen to have only a minor effect for the $X^3\Sigma^+_1$ and $1^4\Sigma^+_1$ states, leading to a slight reduction in bond angle. The addition of carbon d functions reduces the bond angle still further. Both effects are more pronounced in the $^3\Pi^1$ hole state, the angular minimum of 144.4° derived from the basis I study being reduced to 139.4° (basis II) and 136.3° (basis III) with successive improvements in basis.

Prior to discussing the form of the CI curves in detail, we outline the conclusions arrived at by Bell [24] on the effects of all-valence single and double excitation CI on the predicted geometries of a series of AH$_2$ molecular species. Classifying the species as either rigidly bent (equilibrium angle <115° or barrier to linearity 1 eV or greater) or slightly bent (and, of course, linear), he found:

(a) a considerable increase in predicted bond length with CI occurred for all levels of basis set, and

(b) the effect of CI on predicted bond angle depended on the classification of the molecule. The angle decreased for rigidly bent molecules, but increased for slightly bent molecules on
allowing for correlation effects. The $X^2\Sigma^+$ and $1^1\Pi_1$ states of methylene were included in this study, with the $3^3\Sigma^+$ classified as slightly bent and the $1^1\Pi_1$ as a rigidly bent species. The angular curves of fig. 3 are, not surprisingly, in accord with the results of Bell, bearing in mind the fixed bond length approximation used in deriving the present curves. For the "slightly-bent" $X^2\Sigma^+$ state CI is seen to result in a $3-4^\circ$ increase in predicted bond angle, while the angle for the rigid $1^1\Pi_1$ state remains close to the two-configuration SCF value. The barrier to linearity is correspondingly reduced for the $X^2\Sigma^+$ state (cf. table 2), with the basis III SCF
Table 4
Angular minima for the neutral and core hole states of CH2

<table>
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<th>CI</th>
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</thead>
<tbody>
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estimate of 0.53 eV decreasing to 0.29 eV. The change in barrier for the 1A1 state is more critically dependent on basis, although we note that the basis III CI estimate of 1.19 eV is in excellent agreement with experiment (1.20 eV, ref. [24]).

Turning now to consider the core hole states, we note that both basis I and basis III CI studies predict the state ordering

$4\Sigma_g^- < 2\Sigma_g^- < 2\Delta_g < 2\Sigma_u^+$

for the constrained linear geometries (D∞h), although basis III gives the $3\Sigma_g^-$ and $2\Delta_g$ almost degenerate. The angular characteristics for the hole states are, however, found to be quite different between the two basis sets. Basis I predicts all hole states, with the exception of $1^2A_1 (\tilde{\Delta}_g)$ to be linear (fig. 4). Even this state has such a shallow barrier to linearity that the bending curve exhibits a double minimum, an effect due to use of a fixed C–H bond length at all points. On extending the basis however only the $2^2B_1 (\tilde{\Delta}_g)$ and $2^2A_1 (\tilde{\Sigma}_g)$ are found to be linear, although the barriers to linearity for the other hole states are predicted to be less than 0.1 eV (table 2). These results clearly arise from the balancing of two effects, namely (i) extending the basis at the SCF level acts to increase the barrier to linearity, and (ii) inclusion of correlation effects acts to reduce the barrier, leading to an increase in bond angle. Note that the “improved sp” basis calculations (basis II)

on the $1^2B_1$ core hole state predict an angular minimum (155°) in close agreement with the basis III estimates, (153°) suggesting again the importance of an extended s, p basis in representing core hole species.

Based on the most extensive basis set studies, we may summarise the disposition and angular characteristics of the core hole states as follows:

(i) The $1^4B_1 (\tilde{\Sigma}_g)$ is the most stable 1s hole state, corresponding to ionization of the $X^3B_1$ state of CH2. Core ionization is predicted to result in an increase in bond angle of 17°, and a decrease in barrier from 0.29 to 0.04 eV.

(ii) The $1^2B_1 (\tilde{\Sigma}_g)$ state corresponds to Cls ionization of the $X^3B_1$ state, with triplet coupling of the valence orbitals. The angular minimum of 152.6 and barrier to linearity is similar to that found in the quartet state.

(iii) The $1^2B_1 (\tilde{\Delta}_g)$ state arises from ionization of the $1^1B_1$ state with singlet coupling of the valence orbitals. Ionization is predicted to result in a linear ion, compared to the bond angle of 142° in the $1^1B_1$ state of methylene.

(iv) The $1^2A_1 (\tilde{\Delta}_g)$ state corresponds to C1s ionization of the $1^1A_1$ state: ionization results in an increase in bond angle of $\sim 10^\circ$ and a decrease in the barrier of 0.83 eV relative to that of the methylene radical.

(v) The $2^2A_1 (\tilde{\Sigma}_g)$ state corresponds to Cls ionization of the $2^2A_1$ state of methylene, resulting in a linear ion.

4.3. CI computations of geometries and vibrational fine structure accompanying core ionization

The angular characteristics have been derived from CI computations at a fixed bond distance. Further computations have been carried out over a range of bond lengths and from the two-dimensional grid spanning the regions around the local minima in normal coordinates energy minimized geometries for each state have been derived. These computations, typically involving a grid of 25 points, were carried out with basis III. The results are presented in table 5.

The results are in excellent agreement with experimental data where these are available.
Table 5
Computed CI geometries for neutral and core hole states of CH₂ (basis III). Experimental values (refs. [25, 26]) are in parentheses. (Also shown are the computed stretching force constants)

<table>
<thead>
<tr>
<th>State</th>
<th>(R_e(\text{Å}))</th>
<th>(\theta) (deg)</th>
<th>(k_{\text{symm}}) (m dyne Å⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X ( \text{^2}B_1)</td>
<td>1.081 (1.08)</td>
<td>133.1 (136±8)</td>
<td>5.73</td>
</tr>
<tr>
<td>(1\text{^1}A_1)</td>
<td>1.116 (1.11)</td>
<td>102.4 (102.4)</td>
<td>4.78</td>
</tr>
<tr>
<td>(1\text{^4}B_1)</td>
<td>1.051</td>
<td>150.1</td>
<td>6.38</td>
</tr>
<tr>
<td>(1\text{^2}A_1)</td>
<td>1.057</td>
<td>114.6</td>
<td>6.44</td>
</tr>
<tr>
<td>(1\text{^3}B_1)</td>
<td>1.05</td>
<td>152.0</td>
<td>6.43</td>
</tr>
</tbody>
</table>

In a previous paper [19], we have described the computed changes (ΔSCF) in force constant for the \(v_4\) symmetric stretching mode which may be excited on going from the ground to core hole state. The main conclusion from this previously published study is that the force constants for the stretching mode increase on core ionization and that the increase is substantially larger in the case of the \(1\text{^1}A_1\) \(\rightarrow\) \(2\text{^1}A_1\) as compared to the \(3\text{^1}B_1\) \(\rightarrow\) \(4\text{^1}B_1\) process. The CI computations confirm this; however the difference between the two states is larger than for the ASCF computations. Thus whereas at the CI level the increase in force constant is \(\approx 35\%\) and \(11\%\) on going from the \(1\text{^1}A_1\) and \(3\text{^1}B_1\) to their respective core ionized states at the ΔSCF level the corresponding values are \(23\%\) and \(16\%\). It is interesting to note that the potential energy surfaces in terms of optimized geometries, force constants and barriers to linearity are closely similar for the \(4\text{^1}B_1\) and \(2\text{^1}B_1\) core ionized states. Comparison of the equilibrium computed geometries shows that the previously reported ΔSCF computations underestimate somewhat the changes in CH bond length on going from the neutral to core ionized systems. The net result is that the CI computations indicate a somewhat greater vibrational line profile for the direct core ionization of \(1\text{^1}A_1\) methylene than for the \(3\text{^1}B_1\) state. The computed Franck–Condon factors are given in table 6.

With vibrational energy spacing for the symmetric stretching mode of \(\approx 0.44\) eV and the typical resolution that has been attained in high resolution studies the small degree of asymmetry in the line profile for the Cls levels of the \(1\text{^1}A_1\) state might just be observable. The overall conclusion therefore accords with that derived from the ΔSCF investigation, namely, that vibrational fine structure effects in core ionization of both \(1\text{^1}A_1\) and \(3\text{^1}B_1\) methylene are likely to be small and difficult to detect. This situation contrasts markedly with that for methane.

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References

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