Theoretical Investigation of Spectroscopic Properties of Te₂

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Complete active space MCSCF (CASSCF)/first-order configuration interaction (FOCI) calculations are carried out on the electronic states of Te₂. Spin-orbit interaction is introduced as a correction to CASSCF/FOCI results using a relativistic configuration interaction scheme. The spectroscopic properties of a number of electronic states are calculated. Our calculations enable correct assignment of ambiguous earlier assignments and confirmation of tentative assignments of observed spectra. We also predict the properties of a number of electronic states which are yet to be observed. © 1987 Academic Press, Inc.

1. INTRODUCTION

The electronic spectra of Te₂ have been investigated by a number of workers (1, 17) in the last several years. The electronic spectra of Te₂ are of considerable interest since these serve as possible wavelength standards. Further, the Te₂ molecule has been considered as a candidate for optically pumped lasers. Theoretically, the Te₂ molecule is of great interest as a result of relativistic effects and complexity of electronic states due to large spin–orbit coupling.

The most intense transitions of Te₂ observed to date are B → X and A → X systems. A number of investigators have studied these systems (2, 3, 9–13). These transitions have been observed in standard absorption or emission spectra as well as laser-induced fluorescence and chemiluminescence spectra. Yee and Barrow (3) observed a weak fluorescence series originating from the perturbed B(0ₜ) terminating to a state X which is found by these authors to be <2230 cm⁻¹ above the X ground state. Laser-induced fluorescence investigations by a number of authors (13, 14, 16) later revealed that the X₂ state is 1975–1977 cm⁻¹ above the X ground state.

Bondybey and English (13) have studied laser-induced fluorescence spectra of Te₂ in Ar and Ne matrices. In addition to the observation of well-characterized A–X and X–X systems these authors have observed a fluorescence series in the region of 16 400 cm⁻¹. The lower state involved in this fluorescence is assigned to the X₂(1ₜ) state, since excitation to the emitting state from the ground state X could not be achieved. The emitting state is designated A' by these authors. They argue that the A' state could be 3Π₉(2ₐ). However, Ahmed and Nixon (14) have reassigned the A' state to a 1ₚ state, since they observe another, weaker, fluorescence series in the region of 14 091 cm⁻¹. Ahmed and Nixon believe the upper state in this fluorescence series to be a 2ₐ state. Verges et al. (17) argue that the A' state is most likely 3Σ₉(1ₚ) based on the intensity of the observed bands and a corr

Spectroscopic properties of the observed bands and a corrected 3Σ₉⁻ 3Σ₈ system were well characterized.

There is less information available. Ahmed et al. (12) have characterized a 3Σ₉⁻ 3Σ₈ system using Fourier series of the lower state have been determined. The Aₕ state has been observed to decay to the Xₕ state which is about 6500 cm⁻¹ above the electronic state which is Xₕ state.

In summary, until now X₂ and electronic states have been observed in parentheses have been assigned. The assignment of these electronic states is being made in the present work. Moreover, the only objective of the theoretical investigation of Te₂ is to predict the properties of the electronic states which are yet to be observed.

2. METHOD

We carry out complete active space configuration interaction calculations using a spin–orbit interaction is introduced (RCI) scheme in which different variational schemes are considered.

If one considers only the outer electronic configuration would be

where 1σ₂ and 1πₙ orbitals originate from 1πₙ and 1σ₂ orbitals originate from low-lying configurations and the orbit operator can mix, for example, spin–orbit interaction (SOC) schemes (30).

Balasubramanian and Khanna's work on the correlation relationships for ω–ω and ω–σₙ relationships for the electronic states have been extended to the Te₂ molecule. The th
SPECTROSCOPIC PROPERTIES OF Te₂

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configuration interaction (FOCI) calculation-orbit interaction is introduced as a configuration interaction scheme. The
were calculated. Our calculations enable confirmation of tentative earlier assignments of
a number of electronic states which

The observed bands and a comparison to the analogous O₂ bands for which the
system is well characterized.

There is less information available on electronic states below 10 000 cm⁻¹. Effantin
et al. (12) have characterized a b state which they assign to ¹Σ₂⁺ in the new
(0,1)-b(¹Σ₂⁺) system using Fourier transform spectroscopy. The spectroscopic properties
of the lower state have been characterized. However, no transitions to lower
states have been observed to date although Verges et al. (17) predict that such a
state should be about 6500 cm⁻¹ above the ground state. Verges et al. (17) have also
observed an electronic state which they designate B(1ₜ) which is very close to the
(0,0) state.

In summary, up until now X₁(0₂⁺), X₂(1₂), B(¹Σ₂⁺), A, A', A'(0₂⁺), B'(0₂⁺), and B(1ₜ)
electronic states have been observed. Among these only the states with an Ω value in
parentheses have been assigned. The nature of A' and A states observed by Bondybey
and English (13) and Ahmed and Nixon (14) is not certain. To date, there are no
detailed investigations on Te₂. Relativistic corrections such as mass-velocity, Darwin,
and spin-orbit corrections are known to be significant for molecules containing heavy
atoms (18–29) such as Te₂. The present investigation on Te₂ is undertaken with the
objective of clarifying the confusion in the assignment of some of the observed spectra
of Te₂ as well as in predicting properties of electronic states which are yet to be observed.
Moreover, the other objective of our investigation, as mentioned above, is to study
the effect of spin–orbit coupling on the electronic states of Te₂. Section 2 outlines our
method of investigation while Section 3 contains results and discussions.

2. METHOD OF INVESTIGATION

We carry out complete active space MCSCF (CASSCF) followed by first-order correla-
tion interaction calculations (FOCI) to treat electron correlation properly.
The spin-orbit interaction is introduced through a relativistic configuration interaction
(RCI) scheme in which different λ-s states of the same ω-ω symmetry are mixed in
a variational scheme in the presence of the spin–orbit operator.

If one considers only the outer s²p⁴ shell of the tellurium atom, the lowest possible
electronic configuration would be

1σ₃ᵍ⁻¹σ₄ˢ⁻¹σ₂ₛ⁻¹σ₄ₛ¹π₅ₓ⁻¹

where 1σ₃ and 1σₛ orbitals originate from the s shell of the Te atom, while the 2σₛ,
1πₓ, and 1π₇ orbitals originate from the p orbitals of the Te atom. Table 1 shows a
few low-lying configurations and the λ-s and ω-ω states arising from them. The spin–
orbit operator can mix, for example, ¹Σ₂⁺(0₂⁺) with ¹Σ₂⁻(0₂⁺). The amount of mixing
(spin–orbit contamination) generally increases for the heavier elements in the same
group, since spin–orbit interaction increases as a function of Z. Dissociation relations-
ships for the molecular states of Te₂ would be similar to those of Sn₂ and Pb₂ but in
an inverted order. Balasubramanian and Pitzer (23) have worked out a table of dis-
sociation relationships for ω-ω states of Pb₂ and Sn₂. Table II shows the dissociation
relationships for the electronic states of Te₂. The experimental energies for the separated
atoms are from Ref. (30). The theoretical atomic splittings were obtained using the
TABLE I
Some Low-Lying Electronic Configurations and the Corresponding $\lambda$-$\sigma$ and $\omega$-$\omega$ States for Te$_2$

<table>
<thead>
<tr>
<th>configuration</th>
<th>$\lambda$-$\sigma$ states</th>
<th>$\omega$-$\omega$ states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^2$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^1$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^2$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^1$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^1$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^2$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^1$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6 1s^1 1s^1$</td>
<td>$3^2s$</td>
<td>$^3\Sigma_u^+$</td>
</tr>
</tbody>
</table>

Dissociation

<table>
<thead>
<tr>
<th>Molecular states</th>
<th>$\lambda$-$\sigma$ states</th>
<th>$\omega$-$\omega$ States</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s^2 2s^2 2p^6$</td>
<td>$^3\Sigma_u^+$, $^1\Sigma_u^-$</td>
<td></td>
</tr>
<tr>
<td>$2s^2 2p^6$</td>
<td>$^3\Sigma_u^+$, $^1\Sigma_u^-$</td>
<td></td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6$</td>
<td>$^3\Sigma_u^+$, $^1\Sigma_u^-$</td>
<td></td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6$</td>
<td>$^3\Sigma_u^+$, $^1\Sigma_u^-$</td>
<td></td>
</tr>
<tr>
<td>$1s^2 2s^2 2p^6$</td>
<td>$^3\Sigma_u^+$, $^1\Sigma_u^-$</td>
<td></td>
</tr>
</tbody>
</table>

* Ref. (30)

orbitals spanned by $s$ and $p$ calculations were actually chosen as the molecular axis and $2b_1$ orbitals. The $d$ orbitals

and CASSCF.

separations of the molecular states at long distance. As one can see from Table II, our calculations yield the correct behavior for the molecular states of Te$_2$ in the dissociation limits.

We employ relativistic effective core potentials with the outer $d^{10}s^2p^4$ shell included in the valence space. LaJohn et al. (31) have recently generated analytical Gaussian potentials and a valence Gaussian basis set for the tellurium atom. We employ these potentials in the present calculations. The valence Gaussian basis set optimized by these authors (31) for the $3P$ ground state of the Te atom is shown in Table III together with a Slater-type basis set we employ in our relativistic CI calculations. The Slater-type basis set was optimized by Balasubramanian et al. (32) in their TeH investigation.

The orbitals for first-order CI calculations were generated using the CASSCF method. In this method, the most active electrons of the separated atoms ($s^2p^4$ in the case of Te) are distributed in all possible ways among the strongest occupied orbitals of the separated atoms. The CASSCF calculations included $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $1\pi_u$, and $1\pi_g$. 

(a) Gau

(b) Stat

* Ref. (31)
or corresponding $\lambda-\pi$ and $\omega-\omega$ States for $\text{Te}_2$

<table>
<thead>
<tr>
<th>$\omega$ states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{a}^{<em>}$, $\sigma_{g}^{</em>}$</td>
</tr>
<tr>
<td>$\pi_{g}$</td>
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<tr>
<td>$\delta_{u}$, $\delta_{g}$</td>
</tr>
<tr>
<td>$\epsilon_{u}$</td>
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<td>$\epsilon_{g}$</td>
</tr>
<tr>
<td>$\epsilon_{u}$, $\epsilon_{g}$</td>
</tr>
<tr>
<td>$\delta_{u}$, $\delta_{g}$</td>
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<tr>
<td>$\epsilon_{u}$</td>
</tr>
<tr>
<td>$\epsilon_{g}$</td>
</tr>
<tr>
<td>$\epsilon_{u}$, $\epsilon_{g}$</td>
</tr>
<tr>
<td>$\lambda$</td>
</tr>
<tr>
<td>$\lambda_{g}$</td>
</tr>
<tr>
<td>$\lambda_{u}$</td>
</tr>
<tr>
<td>$\lambda_{u}$, $\lambda_{g}$</td>
</tr>
<tr>
<td>$\lambda_{g}$</td>
</tr>
<tr>
<td>$\lambda_{u}$</td>
</tr>
<tr>
<td>$\lambda_{u}$, $\lambda_{g}$</td>
</tr>
</tbody>
</table>

TABLE II

Dissociation Relationships of Some Low-Lying States of $\text{Te}_2$

<table>
<thead>
<tr>
<th>Molecular states</th>
<th>Atomic states</th>
<th>Energy of separated atoms (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ states</td>
<td>$\pi$ states</td>
<td>Theory</td>
</tr>
<tr>
<td>$\lambda_{g}$, $\lambda_{g}$, $\lambda_{u}$, $\lambda_{u}$, $\lambda_{g}$, $\lambda_{g}$, $\lambda_{u}$, $\lambda_{u}$</td>
<td>$\pi_{g}$</td>
<td>$3\pi_{g}$</td>
</tr>
<tr>
<td>$\lambda_{u}$, $\lambda_{u}$, $\lambda_{g}$, $\lambda_{g}$, $\lambda_{u}$, $\lambda_{u}$, $\lambda_{g}$, $\lambda_{g}$</td>
<td>$\pi_{u}$</td>
<td>$3\pi_{u}$</td>
</tr>
<tr>
<td>$\lambda_{u}$, $\lambda_{u}$, $\lambda_{g}$, $\lambda_{g}$, $\lambda_{u}$, $\lambda_{u}$, $\lambda_{g}$, $\lambda_{g}$</td>
<td>$\pi_{g}$</td>
<td>$3\pi_{g}$</td>
</tr>
</tbody>
</table>

$^a$ Ref. (30)

orbits spanned by $s$ and $p$ orbitals of the Te atom in the $D_{2h}$ group. Our CASSCF calculations were actually carried out in the $C_{2v}$ group with the $C_2$ axis of the group chosen as the molecular axis. In this orientation the active space consisted of $4a_1$, $2b_2$, and $2b_1$ orbitals. The $d$ orbitals on Te were kept inactive but allowed to relax in the CASSCF.

TABLE III

Basis Sets Used in the Present Calculation

(a) Gaussian Basis for CASSCF/FOCI calculation

<table>
<thead>
<tr>
<th>Type</th>
<th>Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>0.6387</td>
</tr>
<tr>
<td>$p$</td>
<td>0.1264</td>
</tr>
<tr>
<td>$d$</td>
<td>0.1094</td>
</tr>
</tbody>
</table>

(b) Slater-type Basis Set for relativistic CI

<table>
<thead>
<tr>
<th>Type</th>
<th>Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5s$</td>
<td>2.7825</td>
</tr>
<tr>
<td>$5p$</td>
<td>1.5871</td>
</tr>
<tr>
<td>$4d$</td>
<td>3.6781</td>
</tr>
</tbody>
</table>

$^a$ Ref. (31) $^b$ Ref. (32)
The FOCI calculations included all configurations in the zeroth-order CASSCF plus
the configurations generated by distributing 11 electrons in the internal space and
electron in the orthogonal MCSCF external space in all possible ways. The configuration
counts in the C2v group for CASSCF and FOCI are shown in Table IV. The CASSCF
FOCI calculations were carried out using the Gaussian basis set from Ref. (31).

The spin–orbit interaction was introduced using the relativistic CI method developed
in Ref. (25). Since the RCI code is interfaced with a STO basis integral generator, we
employ a STO basis to generate MOs for CI calculations. Since the spin–orbit effects
are introduced as corrections to the CASSCF/FOCI energies and properties, a single
configuration SCF treatment was used to carry out RCI calculations. The SCF cal-
culations were carried out for the 3Π_g ground state.

In RCI calculations, in general all λ–s states which give rise to a ω–ω state of the
same symmetry could mix. For example, 3Σ_g(0_e^*) 1Σ_g(0_e^*), 3Π_g(0_e^*), etc., mix and the
mixing, in general, varies as a function of internuclear distances. If one is interested
in the properties of electronic states for all distances, then it is necessary to include
all possible λ–s states which yield a ω–ω state of compatible symmetry with the refer-
enced ω–ω state. For the 0_e^* state, if one distributes in all possible ways the outer p electrons
among the p orbitals one gets 131 cartesian reference configurations. Similarly, the
1_r, 2_r, 1_u, 2_u, and 3_u states generate 112, 109, 112, 98, and 60 reference configurations,
respectively. While all these reference configurations are not equally important, in
order to dissociate the molecule and to describe properly the electronic states at en-
nuclear distance, it is necessary to include them in RCI. However, extensive single
+ double excitations are not possible from all the above mentioned references since
the configuration space becomes too large for our RCI code. Further, correlation is
taken into account properly in the CASSCF/FOCI method. Thus, we allowed single
and double excitations among the valence space of orbitals in RCI which could
be labeled zeroth-order RCI. Then an identical set of CI calculations were carried out
omitting the spin–orbit term. The difference between the calculated spectroscopic
properties with and without spin–orbit correction was then introduced to the calculated
CASSCF/FOCI properties and energies. This procedure was found to be adequate for
most of the electronic states except the A(0_u^*) and B(0_u^*) states for which extensive
MRSDRCI calculations were carried out in the vicinity of near-equilibrium geometries
with only the important λ–s reference configurations for these geometries included.
CASSCF/FOCI calculations were carried out using K.B.'s (33) modified version of
ALCHEMY II codes" to were carried out using

In Table V, we present obtained in the present
potential energy curves the curves are for λ–s state Fig. 2 include spin–ω state. For exam-
Fig. 2. As one state. The 1_r state which is a 0_u^* state. The calculated value of 1975 cm^-1 repres
re in very good agreement with experimental data. For s that deviations, especially the theoretical v
than the experimental v for the excited states it diffuse functions and p
functions. The earlier exeriments 400(X(0_u^*)) and B(0_u^*)
was found to be 759 cm^-1 As noted in the Intra-
states in the w

| TABLE IV |
The Dimensions of the CASSCF and FOCI Calculations in the C2v Group |

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>CASSCF</th>
<th>FOCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^A_1</td>
<td>104</td>
<td>7304</td>
</tr>
<tr>
<td>3_A_1</td>
<td>90</td>
<td>1134</td>
</tr>
<tr>
<td>3_A_2</td>
<td>96</td>
<td>10752</td>
</tr>
<tr>
<td>1_B_1</td>
<td>96</td>
<td>10680</td>
</tr>
<tr>
<td>3_B_1</td>
<td>80</td>
<td>7136</td>
</tr>
</tbody>
</table>

The major authors of AL

Ahmed and Nixon (15) observed the A' state and the 14091 cm^-1 bar
Agers et al. (17) corre

from Table V it can be

As shown in Ref. (25). Further, the cal-

The major authors of AL
the zeroth-order CASSCF functions in the internal space and possible ways. The configuration is shown in Table IV. The CASSCF basis set from Ref. (3J) was the relativistic CI method developed by Pople and co-workers. Since the spin–orbit effects are large, the CI calculations were carried out using a modified code developed based on the one developed earlier (25).

3. RESULTS AND DISCUSSION

In Table V, we present the spectroscopic constants for 22 low-lying states of Te2, obtained in the present calculation, along with available experimental values. The potential energy curves for several of these states are given in Figs. 1 and 2. In Fig. 1, the curves are for λ=π states in the absence of spin–orbit interaction, while the curves in Fig. 2 include spin–orbit corrections. In the case of Te2, of course, this interaction is significant and the curves shown in Fig. 1 will split corresponding to various ω=ω states (Fig. 2). For example, the \( \Sigma^+_\text{o} \) ground state in Fig. 1 splits into the \( \Sigma^+_\text{o} \) and \( \Sigma^+_\pi \) states in Fig. 2. As one can see from Table V, the ground state of Te2 is the \( \Sigma^+_\pi \) state. The \( \Sigma^+_\pi \) state which is the other \( \Sigma^+_\pi \) component of the \( \Sigma^+_\text{o} \) state is above the \( \Sigma^+_\pi \) state. The calculated \( T_e \) value of 2229 cm\(^{-1}\) is in very good agreement with the value of 1975 cm\(^{-1}\) reported in Refs. (13, 14). The calculated \( R_e, T_e, \) and \( \omega_e \) values are in very good agreement for the electronic states below 10 000 cm\(^{-1}\) with available experimental data. For the excited electronic states above this region, it must be noted that deviations, especially in \( R_e, \) values are observed. Calculated \( R_e \) values are larger than the experimental values. This difference is due to mainly our basis set limitations. For the excited states it seems that one needs to extend the basis set further with more diffuse functions and polarization functions.

The earlier experimental assignments of the strongest A–X and B–X transitions to \( \Delta(0^+_\pi) \rightarrow X(0^+_\pi) \) and \( \Delta(0^+_\pi) \rightarrow X(0^+_\sigma) \) are in accord with our theoretical calculations. The \( 0^+_\sigma \) state was found to be \( \Pi(0^+_\sigma) \) while the \( 0^+_\pi \) state is \( \Sigma^+_\pi(0^+_\pi) \).

As noted in the Introduction the nature of the two electronic states attributed to the calculated spectroscopic function introduced to the calculated A–X and B–X transitions is not certain. The \( A^\prime \) state observed by Bondy and English (13) in the weak fluorescence which was assigned to \( \Pi(2^+_\sigma) \) by these authors is most consistent with the \( \Delta(1^+_\pi) \) as seen in Table V. The calculated \( T_e \) value of 17 759 cm\(^{-1}\) is in very good agreement with the \( \Delta(1^+_\pi) \) state. Unfortunately, the \( \Delta(1^+_\pi) \) has also been used for another electronic state with a \( T_e \) value of 14 091 cm\(^{-1}\) by other authors. The state which Bondy and English (13) designate \( A^\prime \) is observed in the \( A \rightarrow X(1^+_\pi) \) fluorescence. The lower state is assigned to \( 1^+_\pi \) since excitation to the \( A^\prime \) state could not be achieved from the \( X(0^+_\pi) \) ground state. We suggest the notation of \( A^\prime \) for the \( \Delta(1^+_\pi) \) state to avoid confusion with the \( A^\prime \) state participating in the 14 091 cm\(^{-1}\) bands.

Ahmed and Nixon (14) have observed another weaker fluorescence series in the region of 14 000 cm\(^{-1}\) which they assign to the forbidden \( 2^+_\sigma \rightarrow X(0^+_\pi) \) transition. However, Verges et al. (17) correctly argue that the \( A^\prime \) state should most probably be \( \Sigma^+_\pi(1^+_\pi) \). From Table V it can be seen that the calculated \( T_e \) value of the \( \Sigma^+_\pi(1^+_\pi) \) state (14 369 cm\(^{-1}\)) is in remarkable agreement with the experimental \( T_e \) value of the \( A^\prime \) state (14 091 cm\(^{-1}\)). Further, the calculated and observed \( \omega_e \) values also agree well if one assigns the \( A^\prime \) state to \( \Sigma^+_\pi(1^+_\pi) \). Thus, we agree with Verges et al. (17) in their tentative assign-

\( ^2 \) The major authors of ALCHEMY II codes are B. Lengsfeld, B. Liu, and M. Yoshimine.
### TABLE V
Spectroscopic Constants for the $\text{T}_{2g}$ Molecule

<table>
<thead>
<tr>
<th>State</th>
<th>$R_e$ (A) Theory</th>
<th>$R_e$ (A) Expt.</th>
<th>$T_e$ (cm$^{-1}$) Theory</th>
<th>$T_e$ (cm$^{-1}$) Expt.</th>
<th>$\tilde{\nu}_e$ (cm$^{-1}$) Theory</th>
<th>$\tilde{\nu}_e$ (cm$^{-1}$) Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Sigma_g^+ (0^+_g)$</td>
<td>2.68</td>
<td>2.56$^a$</td>
<td>0.0</td>
<td>0.0</td>
<td>210</td>
<td>247$^a$</td>
</tr>
<tr>
<td>$^3\Sigma_u^+ (2^+_g)$</td>
<td>2.66</td>
<td>2.55$^a$</td>
<td>2229</td>
<td>1975$^a$</td>
<td>216</td>
<td>250$^a$</td>
</tr>
<tr>
<td>$^1\Sigma_g^+ (1_u)$</td>
<td>2.70</td>
<td>6383</td>
<td>[6050]$^c$</td>
<td>199</td>
<td>[2255]$^e$</td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_u (3_u)$</td>
<td>2.92</td>
<td>9142</td>
<td>158</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_g (3_g)$</td>
<td>2.73</td>
<td>10 444</td>
<td>960$^d$</td>
<td>182</td>
<td>228$^d$</td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_u (2_u)$</td>
<td>2.97</td>
<td>11 193</td>
<td>127</td>
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<tr>
<td>$^5\Pi_g (1_u)$</td>
<td>3.00</td>
<td>14 365</td>
<td>127</td>
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<tr>
<td>$^5\Pi_u (1_u)$</td>
<td>3.00</td>
<td>17 759</td>
<td>17 76$^b$</td>
<td>128</td>
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<tr>
<td>$^5\Sigma_g^+ (0^+_g)$</td>
<td>3.25$^f$</td>
<td>17 052</td>
<td>19 45$^c$</td>
<td>142</td>
<td>146$^c$</td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_u (0^+_g)$</td>
<td>3.25$^f$</td>
<td>3218</td>
<td>222</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^5\Sigma_u^+ (1_u)$</td>
<td>2.68</td>
<td>6900</td>
<td>205</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_g (3_g)$</td>
<td>2.97</td>
<td>9318</td>
<td>187</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_u (2_u)$</td>
<td>2.98</td>
<td>13 900</td>
<td>137</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_g (1_g)$</td>
<td>19 629</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Sigma_g^+ (1_g)$</td>
<td>3.03$^f$</td>
<td>22 414</td>
<td>22 42$^d$</td>
<td>130</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_u (1_u)$</td>
<td>3.59$^f$</td>
<td>25 722</td>
<td>92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_g (1_g)$</td>
<td>3.13$^f$</td>
<td>27 233</td>
<td>53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^5\Pi_u (1_u)$</td>
<td>3.48$^f$</td>
<td>27 647</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^5\Pi_g (1_g)$</td>
<td>3.69$^f$</td>
<td>34 043</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3\Pi_g (1_g)$</td>
<td>3.48$^f$</td>
<td>37 169</td>
<td>84</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

$^a$ Ref. (14)  $^b$ Ref. (14)  $^c$ Predicted value as in Ref. (13). This state is yet to be observed.
$^d$ Ref. (12)  $^e$ Ref. (13)  $^f$ Calculated $R_e$ and $\tilde{\nu}_e$ values for these states may not be accurate due to basis set limitations.

---

**Fig. 1.** Potential energy curve without spin-orbit interaction.

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**Verges et al.** (11) and Effantin et al. (12) have observed a $B(1_u)$ state which is close to the $B(0_u^+)$ state in energy. Since our basis set was rather limited to calculate the properties of this state accurately we have estimated the separation of this state at the $R_e$ of $^3\Sigma_g^-$. This value (22 414 cm$^{-1}$) is close to the experimental $T_e$ of 22 222 cm$^{-1}$. Verges et al. (11) identify a singlet state which they designate $b$ whose $T_e$ value was found to be about 9600 cm$^{-1}$. These authors tentatively assigned the $b$ state to $^1\Sigma_g^-$. As one can see from Table V our calculations are in agreement with this assignment. The calculated $T_e$ value is in reasonable agreement with the experimental value. Verges et al. (17) in a later investigation also calculated separation of $T_e$ values for these states were perturbed by the $0_u^+$, $3_u^+$, and $2_u$ states, observation should be noted that forbidden but we believe the $0_u^+$, $3_u^+$, and $2_u$ states are not be regarded as very important. The calculated dissociation energy with $T_e$ values is 40 01 cm$^{-1}$. The calculated dissociation energy decreases with spin-orbit interaction.
FIG. 1. Potential energy curves of some electronic states of Te$_2$ obtained using the CASSCF/FOCI method without spin–orbit interaction.

et al. (17) in a later investigation have predicted that there should be a $^1\Delta_g$ state with an approximate $T_v$ value of 6500 cm$^{-1}$ although this state is yet to be observed. Our calculated separation of the $^1\Delta_g$ state (6383 cm$^{-1}$) is in remarkable agreement with this prediction.

As one can see from Table V, among the low-lying states $^3\Delta_u(3_u)$, $^3\Delta_u(2_u)$, and $^1\Delta_g(2_g)$ electronic states are yet to be observed. Although at the level of theory described here the $^1\Pi_u(1_u)$ and $^1\Pi_u(1_u)$ states were found to be repulsive, for the isoelectronic Se$_2$ (28), these states were perturbers of the $B(0_u^+)$ state. See Ref. (28) for a detailed discussion of this. We did not calculate the properties of $^3\Pi_u(0_u^+)$ since the $0_u^- \leftrightarrow 0_u^+$ transition is forbidden but we believe that this state should be close to the $A(0_u^+)$ state. Although the $0_u^-$, $3_u$, and $2_u$ states cannot be observed directly from the ground state, an indirect observation should be possible through multiphoton techniques.

In Table V, we list the properties of many electronic states without spin–orbit coupling with $T_v$ values above 25 700 cm$^{-1}$, none of which, so far, have been observed experimentally. The calculated $R_v$, $T_v$, and $\omega_v$ values for these states, however, should not be regarded as very accurate since our basis set and level of theory are not adequate to calculate these properties with reliable accuracy for these states.

The calculated dissociation energy for the $X(0_u^+)$ state of Te$_2$ is 1.69 eV. The spin–orbit interaction decreases the $D_v$ value, since the separated atoms are more stabilized by spin–orbit interaction than the molecule. Huber and Herzberg (34) list a $D_v$ value
of 2.68 eV based on a weighted mean of a number of values obtained from spectroscopic and thermochemical methods. The difference between this value and our calculated value is primarily due to limitations of our calculations arising from basis set and correlation errors.

Table VI shows the leading configurations in the FOCI wavefunctions of the bound electronic states of Te₂. This table should be useful in understanding the nature of electronic states listed in Table V in the absence of the spin–orbit interaction.

Spin–orbit coupling makes significant contributions to the electronic states of Te₂. Besides influencing the spectroscopic properties of Te₂, as seen in Table V, the spin–orbit coupling contaminates different λ–σ states. The X(0′₂) ground state was found to be actually 71% \( \Sigma^+_g(0′₂) \) and 19% \( \Sigma^-_g(0′₂) \) at its equilibrium geometry. The 0′(II) state was similarly 73% \( \Sigma^+_g(0′₂) \) and 18% \( \Sigma^-_g(0′₂) \) at its equilibrium geometry. The spin–orbit contaminations for other states such as \( 1\Delta_g(2s) \), \( 3\Sigma_g^+(1s) \), \( 3\Delta_u(3p) \), \( 3\Sigma_u^+(1s) \), etc., were not particularly significant at their equilibrium geometries. At long distances, the spin–orbit contaminations become important for all electronic states so that these states would dissociate into correct atomic states.

4. CONCLUSION

In this investigation we have carried out CASSCF/FOCI followed by relativistic CI calculations on 22 electronic states of Te₂. Our calculations confirm the earlier assignments of B–X, A–X , observed by Bondybay and state with a \( T_e \) value of 1 agreement with the earlier although the \( 1\Delta_u \) state is yet a number of other electronic

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2. R. F. BARROW AND R. P. DI
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9. K. LIN, L. C. BALLING, A
SPECTROSCOPIC PROPERTIES OF \( \text{Te}_2 \)

TABLE VI

Leading Electron Configurations Contributing to Some Low-Lying \( \lambda-\sigma \) States of \( \text{Te}_2 \) near Equilibrium Geometry

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>Electron Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3\pi_g )</td>
<td>( 2e_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (15) )</td>
</tr>
<tr>
<td>( ^1\pi_u )</td>
<td>( 2e_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (55) )</td>
</tr>
<tr>
<td>( ^1\pi_g )</td>
<td>( 2e_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (142) )</td>
</tr>
<tr>
<td>( ^3\sigma_u )</td>
<td>( 2e_1^2 s_1^e s_0^\sigma (142) )</td>
</tr>
<tr>
<td>( ^3\sigma_g )</td>
<td>( 2e_1^2 s_1^e s_0^\sigma (101) )</td>
</tr>
<tr>
<td>( ^3\pi_u )</td>
<td>( 2e_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (101) )</td>
</tr>
<tr>
<td>( \lambda \epsilon )</td>
<td>( \bar{e}_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (101) )</td>
</tr>
<tr>
<td>( \lambda = 1(11) )</td>
<td>( \bar{e}_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (101) )</td>
</tr>
<tr>
<td>( \lambda = 2(11) )</td>
<td>( \bar{e}_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (101) )</td>
</tr>
<tr>
<td>( \lambda = 3(11) )</td>
<td>( \bar{e}_1^2 s_1^e s_0^\pi (101), \ 2e_1^2 s_1^o s_0^\pi (101) )</td>
</tr>
</tbody>
</table>

\( \lambda \) obtained with spin–orbit interaction.

of values obtained from spectroscopic and calculations arising from basis set.

of the FOCI wavefunctions of the bound states useful in understanding the nature of the spin–orbit interaction.

ations to the electronic states of \( \text{Te}_2 \) as seen in Table V, the spin.

of its equilibrium geometry. The \( \lambda \epsilon \) states at their equilibrium geometries. At important for all electronic states.

SCF/FOCI followed by relativistic calculations confirm the earlier assignments of \( B-X, A-X, B-b \) transitions. We reassign the weak fluorescence series observed by Bondybe and English (13) to the \( ^3\Delta_u(1\omega) \rightarrow ^3\Sigma_g^-(1\omega) \) transition. The electronic state with a \( T_e \) value of 14091 cm\(^{-1}\) is assigned to \( ^3\Sigma_g^+(1\omega) \). Our results are also in agreement with the earlier predictions of the properties of the \( B(1\omega) \) and \( ^1\Delta_g \) states although the \( ^1\Delta_g \) state is yet to be observed. Our calculations predict the properties of a number of other electronic states which are yet to be observed.

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An infrared spectrum with a resolution of (1), 198 cm−1, B12, one-dimensional data of the equilibrium and the diene. Both of these values are reported to be 510 ± 9 cm−1 and 27.8 ± 8 cm−1. Because of the in

Two-Dim Met
TORU EI

Department of Chemist

It is known that always a good approach can be observed as if can be analyzed by analysis is particular. modes such as 2,5-7 butane, the change i