

A Pseudopotential SCF-MO Study of Te_4^{2+}

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Received August 13, 1979

A recently developed *ab initio* pseudopotential molecular orbital approach was applied to the Te_4^{2+} ion, a system outside the practical reach of conventional all-electron treatments. Computations were carried out with a minimal STO-4G basis set. Results account reasonably well for the observed optical absorption spectrum and suggest the origin of a hitherto unassigned weak band. Ground-state properties, which included the structure, force field, and vibrational frequencies, were also investigated. Treated as a free, gas-phase ion, tetratellurium (II) yielded a bond length 0.05 Å shorter than the experimental value for the ion in a crystal lattice. Placement of static, point-charge counterions in the Te_4^{2+} coordination sphere increased the bond length to a value 0.005 Å longer than derived by experiment. Calculations on neutral, cyclic Te_4 provided a theoretical single-bond reference length 0.09 Å longer than that obtained for the ion in a counterion environment. Comparisons between observed and calculated frequencies suggest an assignment of the vibrational spectrum different from the provisional assignment in the literature.

The enormous impact of *ab initio* molecular orbital calculations on the field of chemistry during the last decade is well known. Nevertheless, practical considerations have severely limited the region of the periodic table that receives attention. A recent development that promises to reduce this restriction drastically is the successful procedure described elsewhere for incorporating the Phillips-Kleinman pseudopotential operator into polyatomic, molecular orbital calculations.¹⁻³ Calculations based on this procedure, which requires an explicit accounting only of the valence electrons, appear to yield orbital energies, structures, and force fields in close agreement with those of *ab initio* all-electron calculations without introducing empirical parameters. Therefore, calculations are virtually as simple to carry out with systems of heavy atoms as with those of light atoms, although, to be sure, relativistic corrections may become important for the former cases.

One interesting class of compound not amenable to treatment by standard *ab initio* procedures constitutes the heavy-atom homopolyatomic cations principally studied by Gillespie,⁴⁻⁹ Corbett,¹⁰⁻¹² Bjerrum,¹³⁻¹⁵ and Stephens.^{16,17} An at-

tractive candidate for study, whose "beautiful crimson red color," noted two centuries ago,¹⁸ was interpreted only recently, is Te_4^{2+} . Because its structure is known accurately from x-ray analyses,¹² and some information is available about its vibrational spectrum,^{8,9,11,12} it is a useful trial system for the pseudopotential method. As discussed below, the method was found not only to account for established properties of the ion but also to provide an alternative interpretation of the vibrational spectrum and to corroborate the recent assignment of the crimson color.

PROCEDURE

Pseudopotential Method

The method for computing electronic energy closely followed that described in detail in ref. 3. Briefly, it is a valence-only LCAO-MO procedure that incorporates the molecular Phillips-Kleinman pseudopotential operator

$$V^{PP} = \sum_i^{\text{valence}} \sum_j^{\text{core}} \sum_k^{\text{nuclei}} |\phi_{ck}^j\rangle \times (\epsilon_v^i - \epsilon_{ck}^j) \langle \phi_{ck}^j | \left(1 - \sum_{l \neq i}^{\text{valence}} |\chi_v^l\rangle \langle \chi_v^l| \right) \quad (1)$$

into the molecular Fock equations

$$(F + V^{PP})\chi_v^i = \epsilon_v \chi_v^i \quad (2)$$

to prevent the molecular valence pseudowavefunctions χ_v from collapsing into the region of the core atomic orbitals ϕ_c , when the latter are frozen in their free-atom form with no explicit constraint for orthogonality to the valence orbitals. In addition, the full Fock operator F in eq. (2) is replaced by the operator-equivalent quantity $\hat{F} + W^i$, where \hat{F} is the Fock operator for valence electrons only and W^i is a contribution to the effective potential derived as outlined in ref. 3. The method is *ab initio* in its entirety because neither the V^{PP} nor W^i contain adjustable parameters. Our calculations differ from those described in ref. 3 in the adoption of a seven- instead of five-term Gaussian representation of W^i and in the use of individual W^i functions instead of an average \bar{W} for s and p orbitals.

Single-determinant calculations on D_{4h} structures each required approximately 65 sec of CPU time on an Amdahl 470/V7 machine. Distorted structures took up to twice as long.

Basis Set

The basis set was an STO-4G representation¹⁹ of atom-optimized single-zeta STOs.²⁰ The seven-term Gaussian expansion parameters of the $5s$ and $5p$ Te model potentials are recorded in Table I.

Structure and Vibrations

Most calculations were carried out on free gas-phase Te_4^{2+} ions. A few, discussed in a later section, included point-charge counterions. Bond lengths were determined in the usual way for ground and excited states and for neutral Te_4 .

Force constants were found by deforming the ion, successively, along each of its symmetry coordinates. Deformations moved atoms by less than 0.02 Å. Because each distinct normal mode corresponds to a different irreducible representation, normal coordinates are simply proportional to symmetry coordinates. Vibrational frequencies were calculated, neglecting counterions and anharmonicity, via Wilson's F and G matrix formalism.²¹ Symmetry coordinates and G matrix

Table I. Coefficients and exponents for the Gaussian expansion of the $5s$ and $5p$ local potentials (W^s, W^p).^a

5s		5p	
Coefficient	Exponent	Coefficient	Exponent
-0.71581	6.7437	-1.47079	13.0661
0.44677	4.3327	0.35148	3.0238
1.01458	1.7069	0.24685	1.8549
-0.76564	1.5608	0.03419	1.0278
0.11029	1.1110	0.00630	0.4555
0.00409	0.3940	0.00108	0.1638
0.00041	0.0130	0.00051	0.0318

^a The form of the expansion is defined by eq. (23), ref. 3.

Table II. Te_4^{2+} bond lengths.

	Experimental	Calculated ^a	
		Bare	With counterions
$r(\text{Te}-\text{Te})\text{Å}$	2.6633(16)– 2.6738(17) ^b	2.6108	2.6739

^a This work.

^b Reference 12.

elements were those listed by Cyvin.²² The designation of irreducible representations of orbitals and vibrations follows Cyvin's convention (x, y axes through the atoms). In the literature on Te_4^{2+} the convention adopted for vibrations differed from that for orbitals.

RESULTS

According to our pseudopotential calculations, the ground state of the tetratellurium (II) cation is a square planar ring with six π valence electrons as forecast by Brown et al.⁴ and Corbett.¹⁰ Equilibrium bond lengths calculated for the hypothetical gas-phase ion and the ion in an environment of counterions are listed (Table II) with force constants calculated for all symmetry coordinates (Table III), and vibrational frequencies (Table IV). For purposes of comparison, available experimental data for S_4^{2+} , Se_4^{2+} , and Te_4^{2+} are also tabulated.

Several alternative electron configurations were investigated. The most stable closed-shell configuration which filled all four valence π orbitals corresponded to a promotion of the highest a_{1g} electron pair. This state was calculated to lie 0.28

Table III. Te_4^{2+} force constants in $\text{mdyn}/\text{\AA}$.

	S_4^{2+a}	Se_4^{2+a}	Te_4^{2+a}	Te_4^{2+b}
a_{1g}	3.22	2.48	1.80	2.36
b_{2g}	2.65	2.36	1.80(?) ^c	3.90
e_u	0.665 ^d	0.725	0.212(?) ^c	0.897
b_{1g}	0.257	0.214	0.182	0.176
b_{2u}				0.037

^a Force constants were derived from frequencies in Table IV.

^b This work; calculations carried out without counterions.

^c Assignment tentative. See text.

^d Assignment tentative.

Table IV. Te_4^{2+} vibrational frequencies in cm^{-1} .

	S_4^{2+a}	Se_4^{2+b}	Te_4^{2+c}	Te_4^{2+c}
a_{1g}	584	327	219 ^d	251
b_{2g}	530	319	219(?) ^{e,f}	322
e_u	460 ^g	306	130(?) ^{e,h}	268
b_{1g}	330	192	139 ^d	137
b_{2u}				45

^a Reference 7.

^b Reference 6.

^c This work.

^d Reference 8.

^e Assignment tentative. See text.

^f Reference 9.

^g Assignment tentative.

^h References 11 and 12.

Table V. Te_4^{2+} orbital energies for the ground state.^a Orbitals through $e_g(\pi)$ are occupied. Energies in hartrees.

b_{1g}	-0.2484	a_{1g}	-0.8344
a_{2g}	-0.3097	$a_{2u}(\pi)$	-0.8395
e_u	-0.3850	b_{2g}	-0.8881
$b_{2u}(\pi)$	-0.4794	b_{1g}	-1.0407
$e_g(\pi)$	-0.7315	e_u	-1.2412
e_u	-0.7782	a_{1g}	-1.3803

^a $r(\text{Te}-\text{Te}) = 2.6108 \text{ \AA}$, $E_{\text{valence total}} = -30.8119$ hartrees.

hartree above the ground state and to have a longer bond length (2.875 \AA) than the ground state when constrained to a D_{4h} configuration. Other geometric configurations were not examined. Orbital energies for the ground state are shown in Table V.

Other states studied were those with open-shell configurations that corresponded to the promotion of a single $e_g(\pi)$ or e_u (in-plane lone pair) electron

to the $b_{2u}(\pi)$ LUMO. Excitation energies found by open-shell calculations* with the same basis set and structure corresponded to optical transitions at 719 nm ($\pi \rightarrow \pi^*$, fully allowed) and 574 nm ($n \rightarrow \pi^*$, dipole-forbidden for a rigid D_{4h} structure).

DISCUSSION

The geometric and electronic structures deduced from the present calculations are in good accord with inferences drawn from x-ray diffraction and spectroscopy. Hückel MO calculations had suggested the same ground-state electron configuration, though with a rather different ordering of orbitals.¹⁰ The strong absorption band at 510 nm^{5,17} observed in strongly acidic solutions was attributed to $\pi \rightarrow \pi^*$ transition soon after Brown et al.⁴ interpreted the properties of the similar ion Se_4^{2+} . An analysis of the magnetic circular dichroism of Te_4^{2+} by Stevens¹⁷ strengthened the optical assignment but did not provide a conclusive verification. Our own numerical calculation for the hypothetical free ion, which yielded 719 nm for this transition, is in only qualitative agreement. Nevertheless, because the magnitude and direction of this discrepancy are approximately what can be expected for an *ab initio* calculation of this quality, the present result supports the above assignment.

More interesting is the pseudopotential prediction of an $n \rightarrow \pi^*$ transition (${}^1A_{1g} \rightarrow {}^1E_g$) 0.44 eV to the blue of the $\pi \rightarrow \pi^*$ (${}^1A_{1g} \rightarrow {}^1E_u$) band. An unassigned weak band shifted by 0.52 eV is, in fact, observed. Presumably correlation and basis set errors tend to cancel in such a comparison, for they degrade the value of the shift less than that of the transition energy. Other considerations which hint that the observed band may correspond to the calculated $n \rightarrow \pi^*$ transition were provided by the present calculations. As shown in Tables III and IV, the weakest restoring force, lowest frequency, hence the largest amplitudes of vibration of the Te_4^{2+} ion correspond to the b_{2u} ring-puckering deformation. Vibrational motions along this

* Calculations for the excited states were carried out by a method closely related to that described in ref. 3. Details of the method will be described elsewhere.

coordinate destroy the center of symmetry, induce vibronic mixing between the 1E_g and 1E_u states (which, according to the present calculations, lie close enough together to be reasonable candidates for significant Herzberg-Teller mixing²³), and impart intensity to the nominally $g \rightarrow g$ electronic transition.

Structural results offered several comparisons worthy of note. First, calculated bond lengths in the free, isolated Te_4^{2+} were 0.054 Å shorter than the average of reported bond lengths of ions in crystalline environments (which lengths, in turn, tend to be a bit short because motional corrections were not applied). To determine, crudely, whether the influence of counterions, neglected in our initial calculations, can account for this discrepancy, we carried out an alternative calculation by treating the AlCl_4^- counterions present in the crystallographic studies as if each of the chlorides bore a charge of $-1/4$. Then the 18 chlorides closest to the tetratellurium (II) ion* were simulated by placing point charges (of $-1/4$) at the Cl coordinates published by Couch et al.¹² When a D_{4h} Te_4^{2+} ion was centered at the corresponding crystallographic site, its bond lengths expanded by nearly 0.06 Å over those of the isolated ion to a value just 0.005 Å greater than the experimental. Counterions, then, appear to perturb quite appreciably even the structure of an ion as rigid as Te_4^{2+} .

Also of interest are the comparatively short bonds in Te_4^{2+} . X-ray results make them 0.20 Å shorter than the 2.864-Å bonds in elemental tellurium (consisting of spiral chains)²⁴ and 0.07 Å shorter than Pauling's hypothetical Te—Te single-bond length.²⁵ The present pseudopotential results give the ion (in a counterion environment) a bond length 0.094 Å shorter than the 2.763-Å value we calculated for neutral, singly bonded Te_4 . A vapor-phase species, Te_2 , which possibly corresponds to a double bond, is reported to have a length of 2.59 ± 0.02 Å.²⁶ Pauling's empirical relation† makes a double bond 0.18 Å shorter than a single bond and his resonance structures for Te_4^{2+}

would imply a bond order of 1.25. Brown et al.⁴ have called attention to the "aromatic" character of Te_4^{2+} (satisfying the $4n + 2$ rule) and the 1.5 Hückel bond order ($\sigma + \pi$). Despite the differing quantitative assessments of the bond order provided by the various points of view given, the substantial π stabilization of Te_4^{2+} is plainly evident.

Pseudopotential calculations of the force field of the tetratellurium (II) ion suggest a somewhat different distribution of vibrational frequencies than given in previous assignments.^{8,9,11,12} Although the reliability of the present method in the calculation of force fields has not been established in detail, particularly in the case of ions, concurrent calculations on the lower fluorides of iodine and xenon (two elements adjacent to tellurium in the periodic table) yielded vibrational frequencies correct within 10–20%.²⁷ As shown in Table IV, a comparable agreement is found for the two firmest assignments, the Raman-active modes a_{1g} and b_{1g} . An apparently poorer agreement in the case of b_{2g} may be real, but here the experimental assignment is more speculative. Because no separate band identifiable with b_{2g} was found, it was assumed⁹ to lie under the intense a_{1g} band. More anomalous is the e_u stretch,^{11,12} the only infrared-allowed band associated with the D_{4h} point group. Although the pseudopotential force constant and frequency follow the experimental trend for e_u exhibited by S_4^{2+} and Se_4^{2+} (particularly when allowance is made for the tendency of the MO results to be slightly high for stretches), the experimental band assigned to e_u has only half the calculated frequency. It is as low in frequency as a bend and, indeed, is suspiciously close in frequency to the observed Raman-active bend b_{1g} .⁸ Perhaps, as observed for the b_{2g} mode in solid-state Se_4^{2+} ,⁶ interionic interactions in the crystal impart an infrared activity to the nominally symmetric deformation. The actual e_u stretch may be masked by bands in the vicinity of 200 cm^{-1} that belong to the tetrachloroaluminate anions also present.*

* In the infrared spectrum of crystalline $\text{Te}_4(\text{AlCl}_4)_2$ the peak at 130 cm^{-1} exhibits a splitting of 9 cm^{-1} . For the tentative e_u assignment,¹² the splitting was attributed to a removal of degeneracy. For an alternative b_{1g} assignment a factor group splitting could be involved (see, for example, ref. 28).

* The 18 closest chlorides were those with Te...Cl distances from 3.292 to 4.083 Å.

† Reference 25, pp. 255, 400, and 413.

Finally, the present calculations offer an estimate of the force constant and frequency for the b_{2u} mode, a mode inactive in the infrared and Raman spectra. The calculated frequency of 45 cm^{-1} is in line with the conjecture of Gillespie and Pez⁶ to the effect that the b_{2u} frequency of Se_4^{2+} lies below 100 cm^{-1} .

CONCLUSION

Pseudopotential calculations are both practical and fruitful for such heavy polyatomic ion as Te_4^{2+} , a system for which conventional all-electron *ab initio* computations would be prohibitive. Information of high enough quality pertaining to electronic and vibrational behavior was obtained to corroborate prior interpretations of certain spectra and to suggest alternative interpretations of others. Structural results for this heavy ion provided several insights.

The initial calculations on ground and excited states of the D_{4h} tetratellurium (II) ion, carried out at Vanderbilt University, were supported by the Air Force Office of Scientific Research under Grant AFOSR-77-3145. Subsequent calculations on the force field, on the ion with counterions, and on neutral Te_4 , performed at the University of Michigan, were supported by a grant from the National Science Foundation. The authors thank the Ethyl Corporation for support for M. J. R., and also gratefully acknowledge the generous allocation of computing time at the University of Michigan Computing Center.

Note added in proof: After submission of this manuscript, a paper presenting INDO-type molecular orbital calculations on S_4^{2+} , Se_4^{2+} , and Te_4^{2+} appeared.²⁹ Tanaka et al., who treated Te_4^{2+} as a C_{2h} system, obtained roughly similar orbital energies. They attributed the weak absorption in the optical spectrum at 420 nm to a weakly allowed $\pi(e_g) \rightarrow n^*(e_u)$ transition (written here as for a D_{4h} species) rather than to the $n \rightarrow \pi^*$ transition offered as a possibility in the present article. Both excitations must contribute to the spectrum in the vicinity of the observed band but the relative intensities are as yet unknown.

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