depletion.

No transitions for the equatorial fluorine conformer were assigned although a search was made for them. It is clear that the axial conformer is the predominant form. This is in contrast to the preference for the equatorial site by methyl groups in other ozonides.[6d] This contrast seems attributable to the anomeric effect and has analogies in other haloheterocyclic systems.[13-16]

Acknowledgment. The authors are grateful to the National Science Foundation for the support of this work.

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(8) Several explosions occurred during workup of the reaction products. They occurred when handling shock sensitive solid residues, while venting some samples, and upon syringing the products isolated in a −78° trap for GC analyses. The GC inlet was then modified to accept gases directly from the vacuum line. A 15% Dow 710 silicone column was used at slightly elevated temperatures (~30°).

(9) Mass spectrum (intensities in parentheses): 94 (0.35), 66 (0.25), 65 (0.02), 64 (0.07), 62 (0.08), 49 (0.05), 48 (0.2), 47 (0.1), 46 (0.9), 45 (0.15), 44 (1.0). IR (prominent Q branch listed, ±5 cm^{-1}): 3010 (vw), 2910 (w), 1390 (w), 1350 (w), 1300 (vw), 1112 (vs), 1078 (s), 1050 (s), 1005 (m).

(10) The number of MW transitions assigned followed by A, B, C (in MHz): normal species, 24 transitions, 6774.0, 3916.3, 3122.7; ^{18}O-ether, 11 transitions, 6534.6, 3912.9, 3071.7; cis-D, 6 transitions, 6582, 3791, 3040.

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Discandium and Dititanium, Their Synthesis and Optical Spectra in Low Temperature Argon Matrices

Sir:

Besides the reaction of titanium atoms and benzene,[1] which at 10-70 K yields the electron rich 16-electron complex bis(benzene)titanium(0), little else is known about the reactivity of the early transition elemental vapors towards other reactive partners. Indeed, the even more fundamental question, as to the fate of these metal atomic vapors when cocondensed at low temperatures in the presence of a nonreactive partner, remains to be ascertained. This kind of information is crucial for designing efficient syntheses using metal vapor techniques.[2]

In a continuing effort to try to understand the intricate details associated with the surface and bulk diffusion properties and aggregation processes of metal atoms when cocondensed with reactive as well as inert partners at low temperatures,[2,3] we have recently turned our attention to the highly active metals on the left of the transition block.

Our preliminary studies with Sc($4s^2 3d^1$) and Ti($4s^2 3d^2$) have revealed a surprisingly facile matrix dimerization process in Ar. In this brief report we would like to present our optical data for the Sc/Ar and Ti/Ar systems as a function of total metal concentration which serve to identify, for the first time, matrix isolated Sc_2 and Ti_2.

Our experimental techniques and apparatus have been described elsewhere.[4] The crucial aspect of the method involves the precise control and measurement of the rate of metal atom deposition onto the cooled optical window. This was achieved with the aid of a quartz crystal microbalance incorporated into the furnace-cryostat assembly.[5]

Monatomic scandium and titanium (99.99%) were generated by directly heating a thin filament (0.010 in.) of the metal. Argon was deposited at a rate of 2.2 mmol h^{-1}. Uv-visible spectra were recorded on a standard Unicam SP8000 instrument in the range 200-700 nm, the sample being condensed onto a NaCl plate cooled to 10 K by means of an Air Products Displex refrigerator.

Scandium. Several authors have reported on the electronic spectra of atoms trapped in low temperature matrices, which generally show lines shifted to higher energy than in the spectra of the gaseous atom.[2,6] The electronic spectrum of atomic Sc isolated in a low temperature matrix has not previously been published, although Weltner et al.[7] in their work on matrix isolated ScO briefly mention that two lines at 3896 and 3748 Å could be attributed to absorptions of Sc atoms.

When Sc atoms were cocondensed with Ar at high dilutions (Sc/Ar $\simeq 1/10^5$) the optical spectrum shown in Figure 1A was obtained. Table I lists the observed frequencies together with the corresponding gas phase absorptions from a $^2D_{3/2}$ ground state.[8] Noteworthy is the blue shift of the order of 500-1000 cm^{-1} for all absorptions of the isolated atom compared with those for the atom in the gas phase. For high energy transitions this shift can be as large as 3000-5000 cm^{-1} so that for absorptions with energies larger than 40 000 cm^{-1}, no correlation with the gas phase data was attempted.

When the rate of metal deposition at constant gas deposition

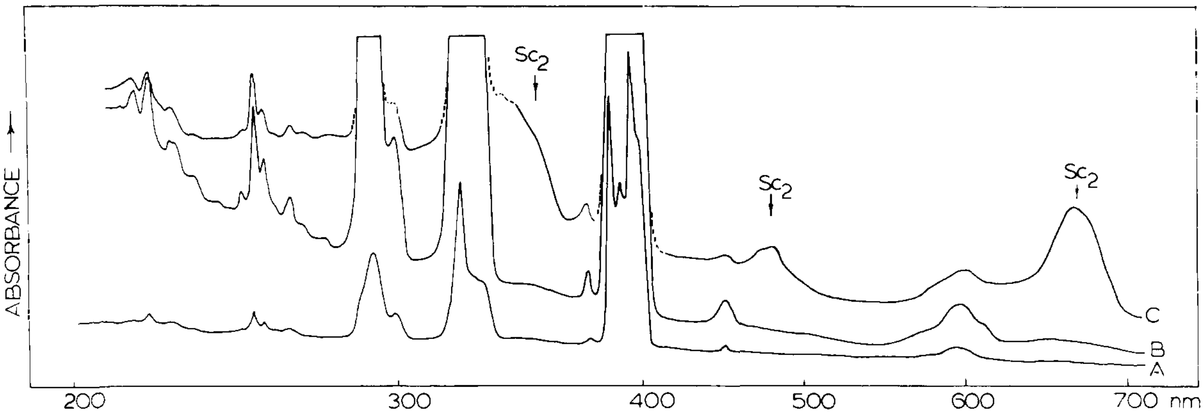

Figure 1. The uv-visible spectrum of (A) atomic Sc isolated in solid Ar at 10 K at high dilutions (Sc/Ar $\simeq 1/10^5$), (B) the same as (A) but on 5× scale expansion, and (C) the same total metal concentration as (B) but deposited at Sc/Ar $\simeq 1/10^4$ showing the growth of absorptions attributable to Sc_2 (also on 5× scale expansion).

Table I. The Uv-Visible Absorption Spectrum of Sc Atoms ($3d^14s^2$; $^2D_{3/2}$) Isolated in an Argon Matrix, Compared to the Gas Phase

λ_{matrix}[a]	ν_{matrix}[b]	ν_{gas}[b]	($\nu_{gas} - \nu_{matrix}$)[b]
596	16 778	16 022	−756
590	16 949	16 097	−852
450	22 222	21 033	−1189
400	25 000	24 657	−343
395	25 316	24 866	−450
388	25 773	25 014	−759
382	26 178	25 585	−593
366	27 322		
326	30 674	30 573	−101
319	31 347	30 707	−640
298	33 557	33 154	−403
292	34 246	33 615	−631
288	34 722	33 707	−1015
265	37 735		
257	38 910	36 934	−1976
253	39 525	37 126	−2399
250	40 000		
228	43 859		
222	45 045		
217	46 082		

[a] In nm units. [b] In cm^{-1} units.

Table II

	Orbital	Orbital exponent	H_{ii} (eV)	Interatomic distance (Å)
Sc	3p	3.135	−40.89	2.30[13]
	3d	2.373	−5.60	
	4s	1.158	−6.15	
	4p	1.050	−2.95	
Ti	3p	3.367	−46.05	2.30[14]
	3d	2.713	−5.00	
	4s	1.204	−5.90	
	4p	1.100	−3.35	

rate is increased, *three* new absorptions can be observed to grow in at 662, 475, and 335 nm (15 100, 21 050, and 29 850 cm^{-1}, respectively). Figure 1B shows this spectral region displaying only atom lines and Figure 1C shows the same region exhibiting the new lines under conditions where roughly 25% of the atoms have formed new species.

We have previously demonstrated that under these circumstances, the formation of trimer and higher aggregates is negligible and are expected to be still unobservable.[3] On these grounds we can therefore attribute the three new absorptions to the formation of discandium, Sc_2. Preliminary, quantitative Sc concentration studies confirm this view and moreover lead to the conclusion that the extinction coefficient of Sc_2 is of the same order of magnitude as that for the Sc atom in keeping with the trend observed for $\epsilon_{V_2}/\epsilon_V$, $\epsilon_{Cr_2}/\epsilon_{Cr}$, and $\epsilon_{Cu_2}/\epsilon_{Cu}$[3]

Titanium. As a result of an extremely thorough investigation by Gruen et al.[9] the absorption spectra of Ti atoms isolated in low temperature matrices have been well established. Our data for atomic Ti are completely in accord with theirs.

When Ti atoms are cocondensed with argon at a ratio of $1/10^5$, the optical spectrum in Figure 2A for the low energy region is obtained. On increasing the rate of metal deposition at constant gas deposition rate, *three* new absorptions can be observed at 624, 546, and 430 nm (16 020, 18 310, and 23 250 cm^{-1}, respectively) as seen in Figure 2B. Using arguments similar to those delineated for the case of Sc_2, we attribute these three new absorptions to the formation of Ti_2 in the argon matrix. Preliminary quantitative metal concentration studies put the value of $\epsilon_{Ti_2}/\epsilon_{Ti}$ also close to unity.

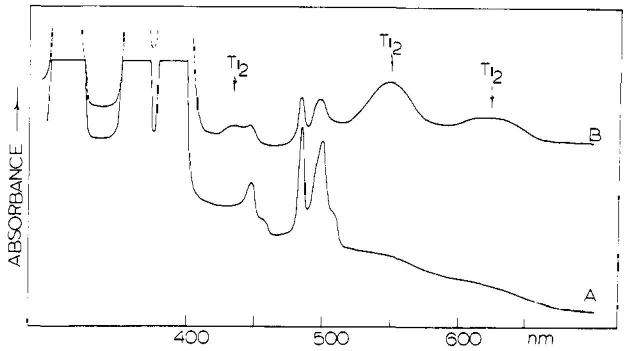

Figure 2. The uv-visible spectrum of (A) atomic Ti isolated in solid Ar at 10 K at high dilutions (Ti/Ar ≃ $1/10^5$) and (B) the same total metal concentration as (A) but deposited at Ti/Ar ≃ $1/10^4$ showing the growth of absorptions attributable to Ti_2 (both spectra are shown on 5× scale expansion).

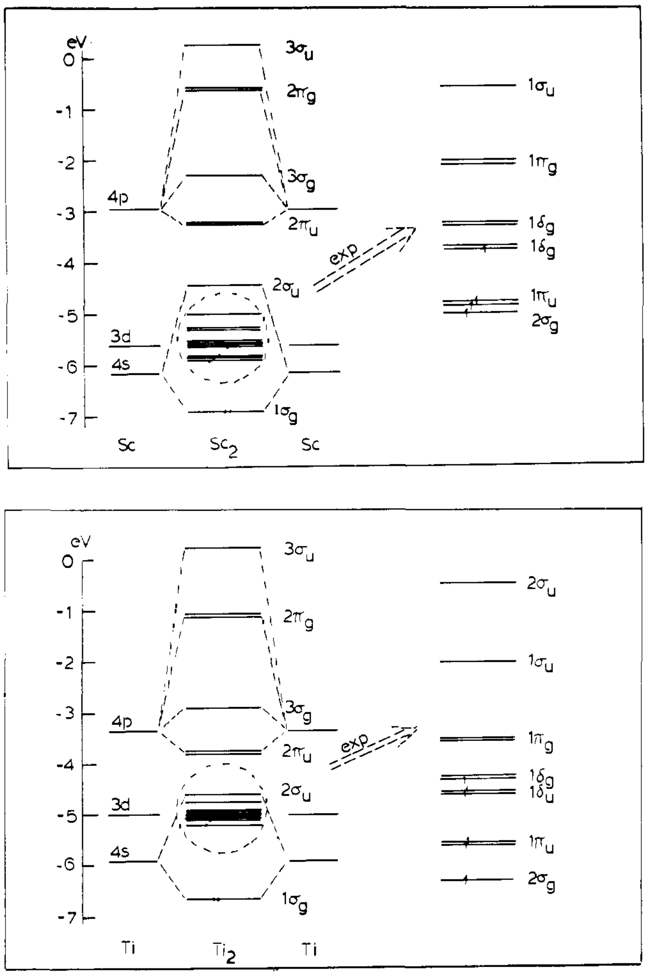

Figure 3. Computed extended Huckel molecular orbital energy level schemes for Sc_2 and Ti_2 (see text for notation and parameters used in the calculation).

Extended Huckel molecular orbital calculations for Sc_2 and Ti_2, using the 3p, 3d, 4s, and 4p orbitals of atomic Sc and Ti, Clementi-Raimondi coefficients,[10] the Cusach's approximation,[11] and known approximate values for the Coulomb integrals,[12] result in the schemes shown in Figure 3. The parameters required to reproduce these calculations are tabulated in Table II.

For Sc and Ti the 4s orbital is lower in energy than the 3d orbital. Under these circumstances the bonding is adequately described by a strong 4s-4s σ-interaction.

The optical spectra for Sc_2 and Ti_2, within the spectral range of our uv-visible instrument, can then be anticipated as shown in Table III.

Table III

	Optical transition	Obsd ($\mathrm{cm^{-1}}$)	Calcd ($\mathrm{cm^{-1}}$)
Sc_2	$1\sigma_g \rightarrow 1\sigma_u$	15 100	15 492
	$1\sigma_g \rightarrow 2\sigma_u$	21 050	19 880
	$1\sigma_g \rightarrow 2\pi_u$	29 850	29 558
Ti_2	$1\sigma_g \rightarrow 1\sigma_u$	16 020	15 355
	$1\sigma_g \rightarrow 2\sigma_u$	18 310	16 654
	$1\sigma_g \rightarrow 2\pi_u$	23 250	23 307

Matrix uv-visible and molecular orbital investigations of the first transition series diatomic molecules Sc_2 through to Zn_2 are currently underway in our laboratories and full details will be reported soon.

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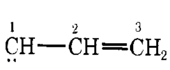
Vinylmethylene and the Ring Opening of Cyclopropene. Ab Initio Generalized Valence Bond and Configuration Interaction Studies

Sir:

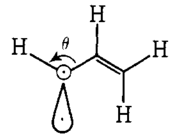
Vinylmethylenes (e.g., **1**) have been suggested as intermediates in both the ring opening of cyclopropenes[1] and in the decomposition of vinyl diazo compounds.[2] Recent ESR experiments[2] have detected two forms of **1**.

We report herein theoretical studies of the planar (**2**) and twisted (**3**) forms of vinylmethylene, along with the corresponding calculation on cyclopropene (**4**), of sufficient accuracy to be compared directly with experimental results. All calculations[3] used a "double-zeta" basis of contracted Gaussian functions[6] which was augmented with a set of d-polarization functions (α = 0.6769) on each carbon for the final calculations. Hartree–Fock (HF), generalized valence bond (GVB),[7] and configuration interaction (CI) wave functions were used. In the initial step of the GVB calculations (referred to as GVB2) all but four electrons (three π and one σ) were in doubly occupied orbitals (that is, uncorrelated C_{1S}, CH bond, and CC σ bond pairs). In the final set of GVB calculations (referred to as GVB4), two additional pairs, corresponding to the CC sigma bonds, were correlated. With both the GVB2 and GVB4 wave functions, CI calculations were carried out allowing all configurations involving the correlated orbitals and, in addition, all double excitations from those orbitals into π virtuals. This led to from 176 to 205 spin configurations (677–1260 determinants) of appropriate spin and spatial symmetry.

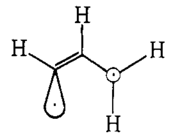


$$\overset{1}{\underset{\cdot\cdot}{\mathrm{C}}}\mathrm{H}-\overset{2}{\mathrm{C}}\mathrm{H}=\overset{3}{\mathrm{C}}\mathrm{H_2}$$

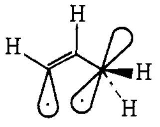
1



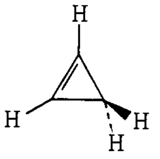
2a (^{3}A″ and ^{1}A″)



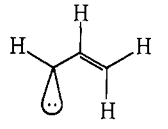
2b (^{3}A″ and ^{1}A″)



3 (^{3}A′ and ^{1}A′)



4 (^{1}A$_1$)



5 (^{1}A′)

It has generally been assumed that planar vinylmethylene can be represented by a resonance hybrid of **2a** and **2b**, much as in the allyl radical. However, the GVB calculation shows quite conclusively that in the triplet state (^{3}A″), the double bond is largely *localized* to the region between C-2 and C-3; i.e., the structure is basically that of a triplet methylene as in **2a** alone. The first $\sigma\pi$ singlet state (^{1}A″) also has a localized double bond, but in this case the GVB calculations show that it is localized in the C-1 and C-2 region; i.e., the structure is basically that of a singlet 1,3-biradical as in **2b**. This result of localized bonds is due to the nondegeneracy of the two resonance contributors (**2a** and **2b**) resulting from the exchange interactions. In allyl the two resonance contributors analogous to **2a** and **2b** are degenerate, and the mixing of the two states is strong.[8] We can represent the energy of each configuration of **2** as the sum or difference of a basic energy term, E_0, and an exchange term, $K_{\sigma\pi}$, which describes the interaction between the two unpaired electrons. The triplet state is stabilized by the exchange term as in eq 1, while the singlet state is *destabilized* by $K_{\sigma\pi}$ as in eq 2.

$$E_T = E_0 - K_{\sigma\pi} \qquad (1)$$

$$E_S = E_0 + K_{\sigma\pi} \qquad (2)$$

The *magnitude* of the exchange term $K_{\sigma\pi}$ is related to the proximity of the orbitals. Thus for **2a** (where the electrons are located on the same carbon), it is large (0.9 eV) but for **2b** (where the electrons are well separated) it is small (0.05 eV). Thus eq 1 shows that, in the triplet state, localized structure **2a** will be lower than **2b** by ~0.8 eV, but from eq 2 in the singlet case state **2b** will be lower than **2a** by the same amount. With such energy separations the two configurations mix (resonate) only slightly, and the wave function for each final structure is dominated by the lower-energy (localized) configuration.

ESR experiments[2] on **1** lead to *D* values comparable to that[8b] in :CφH and :Cφ_2 and much smaller[8a] than in CH_2. This has been interpreted as indicating nearly complete delocalization of the π system in **1**. Such extensive delocalization would be in conflict with our wave functions. We have included all important correlation effects involving the σ and π orbitals of the CCC region and consider our wave functions to be quite reliable. (We should note that at the Hartree–Fock level the π orbitals are delocalized (due to the extra ionic character forced in the wave function) but that inclusion of electron correlation leads to the localization discussed above.) For this