Electron spin resonance investigation of Sc$_2^+$ in neon matrices and assignment of its ground electronic state as $X^4 \Sigma^-$. Comparison with theoretical calculations

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The discandium radical cation, Sc$_2^+$, has been isolated in neon matrices at 4 K and studied by electron spin resonance (ESR) spectroscopy and theoretical methods. It was produced by the x-irradiation of neon matrix samples containing neutral Sc$_2$ which was formed by trapping the products generated from the pulsed laser vaporization of scandium metal. The experimental and theoretical findings indicate that Sc$_2^+$ has a $^4 \Sigma^-_u$ electronic ground state compared to an $X^2 \Sigma^-_u$ state for the neutral discandium radical. The large decrease in the $^{45}$Sc hyperfine interaction ($A$ tensor) going from Sc$_2$ to Sc$_2^+$ provides direct experimental information concerning the types of valence molecular orbitals that are involved in these diatomic radicals. The neon matrix magnetic parameters for $^{45}$Sc$_2^+$ are $g_{\perp}$ $\approx$ 2.00, $g_{\parallel}$ = 1.960(1), $|A_{\parallel}|$ = 28(6), and $|A_{\perp}|$ = 26.1(3) MHz; the $D$ value (zero field splitting) was 15 381(3) MHz. Ab initio configuration interaction (CI) calculations of the nuclear hyperfine interactions yielded results in reasonable agreement with the experimental observations.

I. INTRODUCTION

Neon matrix trapping at 4 K of scandium vapor generated from the pulsed laser vaporization of scandium metal produces an intense electron spin resonance (ESR) spectrum of the discandium radical, Sc$_2$. Previous neon and argon ESR matrix studies have shown that Sc$_2$ has an $X^2 \Sigma^-_u$ ground electronic state, derived essentially from a 4$s^2$4$\sigma^3$3$\delta^3$3$\pi^2$ configuration.1 This experimental result is also consistent with several theoretical studies conducted on Sc$_2$ discussed below,2-6 which further identify the ground state as $X^2 \Sigma^-_u$, deriving from a 4$s^2$4$\sigma^3$3$\delta^3$3$\pi^2$ configuration. The earlier experiments utilized a conventional high temperature effusion oven for scandium vaporization.1 In the present experiments, x irradiation of neon matrices containing neutral Sc$_2$ produced by laser vaporization yields a new scandium radical species which is assigned to the $X^4 \Sigma^-_u$ state of the high spin cation radical, Sc$_2^+$, with a 4$s^2$3$\delta^3$3$\pi^2$ configuration. The loss of 4$s$-type spin density in going from Sc$_2$ to Sc$_2^+$ is reflected in the large decrease in the magnitude of the $^{45}$Sc $I = 7/2$ hyperfine interaction ($A_1$ value) from 233 ± 3 to 26 ± 1 MHz. Theoretical calculations of the changes in the hyperfine interaction for Sc$_2$ and Sc$_2^+$, conducted as part of this experimental study, are consistent with this observed large decrease in $A$ for the cation radical.

The assignment of the observed ESR spectrum to the Sc$_2^+$ radical anion was given serious consideration. Theoretical calculations conducted on the two lowest lying $^4 \Sigma$ states of the anion indicated that one of these, the $^4 \Sigma^-_g$ state with the configuration 4$s^2$3$\delta^3$4$\sigma^5$3$\pi^2$, did in fact, have a small scandium $A_{bas}$ value and energy comparable to that calculated for the ground state of Sc$_2^+$. However, given the electropositive nature of scandium and the observed photobleaching characteristics of the scandium radical being observed, it was decided that the most reasonable ESR assignment is the discandium cation. Apparently no previous experimental or theoretical studies of Sc$_2^-$ have been reported. Photoelectron spectroscopy on mass selected beams of the following diatomic transition metal anions have been conducted: Cr$_2^-$, Fe$_2^-$, Co$_2^-$, Pd$_2^-$, and Re$_2^-$.11

In terms of electron count, Sc$_2^+$ is the simplest possible transition metal dimer cation. As such, it is especially important to determine its properties, so that other more complicated transition metal molecules can be understood. Other transition metal diatomic cation radicals studied experimentally by the matrix isolation ESR method include Mn$_2^+$,12,13 Co$_2^+$ and Ir$_2^+$,14,15 Nb$_2^+$,15 Cu$_2^+$,16 $\Lambda$Cr$_2^+$,17 and $\Lambda$W$_2^+$.16 A great deal of electronic structure information has been obtained from previous matrix ESR studies of neutral transition metal diatomics and clusters.17,18 Recent examples include MoCu, MoAg, MoAu, WCu, WAg, WAu,19 VNi,14 VPd,15 VPt,15 NbNi,20 ScNi, ScPd, YNi, YPd,21 ScCr,22 Co$_3$,23 Rh$_3$, Ir$_3$,14 and CrMn.13 Other small cation radicals recently studied in our laboratory include YAl$^+$ and YB$^+$,23 CH$_3$OH$^+$,24 C$_2^+$,25 $\Lambda$Pd$^+$,26 $\Lambda$Si$^+$,27 and Ge$^2^-$.27

For most of the cation radicals studied the isolated counter anion is not a radical, and thus cannot be detected by ESR; an example would be OH$^-$. Recent results in our laboratory show that CO$_2^-$ is also a fairly common background counter anion. We have conducted extensive $^{13}$C and $^{17}$O isotopic matrix experiments on this species (which can be detected by ESR) to determine optimum conditions for observing such isolated anion radicals.28 We have employed a variety of generation methods for studying matrix isolated anion and cation radicals, including x irradiation of the matrix after deposition, laser surface ionization, electron bombardment, and irradiation of the matrix using an
open tube neon resonance lamp during the deposition process. Other anion radicals studied include $\text{F}_2^-$, $\text{ClF}_2^-$, and $\text{HI}^-$. Electron transfer from sodium atoms has also been successfully employed for the generation of anion radicals in rare gas matrices.

In these scandium studies both the neutral dimer and the cation dimer have ground states that permit detection by ESR spectroscopy. This fortunate circumstance has not occurred in any of our previous ESR matrix ion studies for either the neutral-cation or the neutral-anion combination. An important experimental advantage of this situation is the ability to directly monitor the interconversion between the two radical types. Irradiation with x rays was shown to convert $\text{Sc}_2$ into $\text{Sc}^+$. Previous investigations in argon matrix experiments assigned certain absorption bands in the visible spectrum to electronic transitions of $\text{Sc}_2$. Resonance Raman spectroscopy provided $\text{Di}(\text{Sc}_2) = 0.79 \text{ eV}$, which corresponds to the electronic transition of $\text{Sc}_2$. Resonance Raman spectroscopy, provides $\text{Di}(\text{Sc}_2) = 0.79 \text{ eV}$, although this is not conclusive due to the limited number of vibrational levels observed, it is thought to provide a lower bound on the bond energy of $\text{Sc}_2$.

In one of the first theoretical studies of $\text{Sc}_2$, a local spin density calculation was performed on the series of homonuclear 3$d$ series diatomics. Although the predicted $\Sigma_1^-$ ground state was subsequently shown to be correct, this investigation predicted the ground states of all of the 3$d$ dimers to have extremely high spin multiplicities (predicting, for example, a $\Sigma_1^+$ ground state for $\text{Cr}_2$). Several subsequent calculations confirmed the identity of the ground state for $\text{Sc}_2$ as $\Sigma_1^-$, although this result is not universally nor unambiguously obtained.

In the most detailed calculation to date, Akeby, et al. have attempted to accurately determine the bond energy of $\text{Sc}_2$ through large scale internally contracted average coupled pair functional calculations which included the core 3$p$ orbitals in the correlation treatment along with estimates of relativistic corrections. This undoubtedly represents the most thorough ab initio treatment available for the $\text{Sc}_2$ molecule, and presumably provides the most accurate description yet available. In the most accurate version of this calculation, the $\Sigma_1^-$ ground state of $\text{Sc}_2$ was found to have values of the vibrational frequency, $\omega_v$, bond energy, $D_v$, and bond length, $r_g$, of 197 cm$^{-1}$, 0.77 eV, and 2.67 Å, respectively. Of these properties, only the vibrational frequency may be considered to be experimentally known, having the value $\omega_v = 239.9 \text{ cm}^{-1}$. The discrepancy between this gargantuan calculation and the measured vibrational frequency illustrates the theoretical difficulties in describing the properties of these types of molecules.

Previously studied small scandium radicals in rare gas matrices include $\text{ScCl}$, $\text{ScO}_2$, $\text{Sc}_3$, $\text{ScCl}_3$, $\text{ScH}_2$, $\text{ScF}_2$, and $\text{HSO}_2$. Experiments are currently under way in our laboratory to generate and characterize the high spin $\text{Sc}^{+1}$ and $\text{Sc}^{+2}$ cations, to determine if they are similar to the previously studied $\text{Y}^{+}$ and $\text{Y}^{+2}$ radicals.

II. EXPERIMENT

The ESR matrix isolation apparatus and the associated pulsed laser vaporization procedures used in our laboratory have been described previously. For these investigations, the copper matrix deposition surface was cooled to 4 K with a closed cycle helium refrigerator (APD 304 HS). Frequency doubled output from a Nd:YAG laser operating at 10 Hz and a typical energy of $\sim 20 \text{ mJ/pulse}$ was focused to a spot size of 0.5 mm on the scandium metal surface (Alfa; 99.9% foil). The focusing lens was continuously moved during the matrix deposition process to prevent the drilling of deep holes in the scandium target which was located 5 cm from the matrix deposition surface. A typical deposit was conducted in this manner for 45 min with a neon flow rate of 5 std cm$^3$ min$^{-1}$. See equipment diagram in Fig. 1 of Ref. 27.

Visible photolysis and x-irradiation of the matrix samples were conducted through a quartz window (5 cm diam and 3 mm thick) located 3 cm from the matrix sample. For the wavelength selective photolysis experiments, various Corning cutoff filters were mounted over this quartz access window. The x-irradiation equipment and procedure used in these scandium experiments have been described in a recent matrix ESR study of the methanol radical cation. The beryllium window of the x-ray source was positioned 2 cm from the quartz access window. The tungsten target in the x-ray tube was bombarded with 80 keV electrons.
and x irradiation of the deposited matrix samples was typically conducted for 40 min. The matrix depositions and the subsequent photolysis and x irradiation were conducted with the deposition target out of the X-band ESR cavity. Following these various procedures the matrix sample was lowered into the microwave cavity for recording the ESR spectral changes produced.

III. RESULTS

A. ESR analysis

ESR spectra recorded for the neon matrices containing laser vaporized scandium showed all the absorption features previously observed for the neutral Sc$_2$ radical which has an $X^1\Sigma^+$ electronic ground state. A segment of the Sc$_2$ ESR spectrum is shown in Fig. 1 for a neon matrix at 4 K. Similar laser vaporization experiments conducted with argon as the matrix did not produce the Sc$_2$ radical. The reduced diffusion rates of atoms in argon relative to neon is probably responsible for the lack of Sc$_2$ formation under these laser vaporization conditions. Higher scandium atom concentrations employed in the earlier argon experiments using a conventional high temperature effusion oven did produce Sc$_2$ in argon matrices. The magnetic parameters for Sc$_2$ in neon and argon matrices are practically identical.

Each fine structure transition of Sc$_2$ is split into fifteen $M_J$ hyperfine groups (J = 7/2 nuclei). Since the $A_J$ value for Sc$_2$ is large (233 MHz), the $M_J$ groups are spread over a wide magnetic field range. The inner groups show stronger order splittings since these $M_J$ groups have different J origins where J is the quantum number representing the coupling of the two $I = 7/2$ nuclei. For example, as shown in Fig. 1, the $M_J = 5$ group of the $XY_2$ (perpendicular) fine structure transition centered near 2215 G exhibits three equally intense lines since $M_J = 5$ can originate from $J = 7$, 6, and 5.

The substantial reduction in intensity of the Sc$_2$ ESR lines following x irradiation of the neon matrix sample is shown in the lower trace of Fig. 1. The Sc$_2$ spectra before and after x irradiation were recorded under the same instrumental conditions and no temperature change of the copper deposition surface occurred during the x-irradiation procedure.

As the neutral Sc$_2$ ESR signals grew weaker with x irradiation, a new 15 line hyperfine pattern shown in Fig. 2 centered near 1772 G appeared and became more intense as x irradiation continued, provided not all of the Sc$_2$ radicals had been consumed. These signals, which are assigned to the isolated Sc$_2^+$ radical in a $^4\Sigma^+$ electronic ground state, were not present prior to x irradiation. The relative intensity distribution of this new 15 line pattern which has a small $A_1$ value of 10 G is that expected for two equivalent $I = 7/2$ nuclei, namely $1:2:3:4:5:6:7:8:7:6:5:4:3:2:1$. In this case, the higher order splittings of the inner $M_J$ components were not resolved since the $A$ value is small. Other x-ray induced changes included the appearance of H$_2$O$^+$ and weak N$_2$ ESR signals in the $g$ magnetic field region. The neon matrix ESR spectra of these commonly occurring background radical cations, which are nearly always produced under ionizing conditions, have been previously assigned.$^{29-31}$ Isolated nonradical counter anions are probably produced by the x-irradiation treatment but not detected by ESR as discussed previously.

Extensive ESR scans under high gain/high sensitivity conditions between 0 and 9000 G also revealed a weak phase down absorption feature near 7760 G. This high field line shown in Fig. 3 appeared under the same experimental conditions required for the generation of the low-field 15 line pattern assigned to Sc$_2^+$. Its microwave power response and photolysis effects described below also provided additional evidence that this high field line is part of the Sc$_2^+$ ESR spectrum. We assign this high field line to an off-angle (OA) absorption feature of Sc$_2^+$ as illustrated in the simulated ESR spectrum and accompanying $H_{\text{RES}}$ vs $\Theta$ plots in Fig. 4. Efforts to detect the weaker $XY_2$ transition that lies at a higher magnetic field than the OA line were unsuccessful. The $XY_2$ designation refers to the various perpendicular (\(\Theta = 90^\circ\)) fine structure transitions that can be observed for a given high spin radical with the $N$ subscript ordering these from low to high magnetic fields.$^{25}$

An analysis of these observed ESR features which are assigned to Sc$_2^+$ in a ground $^4\Sigma^+$ state was conducted by an exact diagonalization of the following spin Hamiltonian:

$$\hat{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - S(S+1)/3] + \mathbf{I} \cdot \tilde{A} \cdot \mathbf{S},$$

where all symbols have their standard meanings.$^{25}$ Our computer programs, which provide exact line fitting solutions to this Hamiltonian and produce simulated ESR spectra and $H_{\text{RES}}$ vs $\Theta$ plots, have been previously described.$^{25,30,31}$ By systematically varying $g_\|$, and $D$ (the
The OA transition and the OA absorption feature at \( \theta = 25^\circ \) are shown in the bottom ESR spectrum. Note that the linewidth, phase, and line shape of the simulated absorption exhibit close agreement with the observed spectrum.

Since the scandium hyperfine splitting on the OA line at \( \theta = 25^\circ \) is determined by both \( A_1 \) and \( A_\| \), it was possible to estimate \( A_\| \) by carefully comparing simulated line-widths and line shapes with the observed line. The good agreement with the observed spectrum.

FIG. 3. An expanded scale presentation of the OA (off-angle \( \theta = 25^\circ \)) absorption feature of Sc\(^{2+} \) in a neon matrix sample at 4 K is shown in the top ESR spectrum. See overall spectrum in Fig. 4. A computer simulation of this OA feature is shown in the bottom ESR spectrum. Note that the linewidth, phase, and line shape of the simulated absorption exhibit close agreement with the observed spectrum.

B. Photolysis

Visible photolysis of the neon matrix samples reduced the ESR signals of Sc\(^{2+} \) and Sc\(^{3+} \) by at least 95\% over a 30 min period. Such visible photolysis also sharply reduced the ESR lines of the isolated cation background radicals, namely, \( \text{H}_2\text{O}^+ \) and \( \text{N}_2^+ \). Based upon previous studies of numerous matrix isolated radicals, it is unusual for neutral radicals to be photodestroyed by visible light. The photobleaching of charged radicals is a well established criteria for isolated ions. The photolytic energy typically exceeds the ionization energy of most of the isolated counter anions. The liberated electrons can easily diffuse throughout the rare gas lattice and neutralize the various cation radicals. For chemically bound or adjacent ion pairs (as opposed to isolated ions), photolysis in the visible region does not usually result in photodestruction.

In a separate series of matrix experiments, Corning cutoff filters were employed to determine the approximate wavelengths required to photodestroy these two scandium radicals. The ESR signal responses for Sc\(^{2+} \) and Sc\(^{3+} \) as a function of the various filters employed are presented in Fig. 5. The number of Sc\(^{2+} \) radicals present, as monitored by the \( XY_2 \), \( M_y = 5 \) ESR signals, is seen to decrease dramatically even when a CS-2-64 filter was used. This filter has a 50\% transmittance \( (T) \) at \( \sim 665 \text{ nm} \) and 1\% \( T \) below 650

FIG. 4. The overall simulated ESR spectrum of Sc\(^{2+} \) in its \( ^4 \Sigma \) ground state is shown directly above its \( H_{\text{RRS}} \) vs \( \Theta \) plot, where \( \Theta \) is the angle between the molecular axis and the applied magnetic field. These simulations do not include the small \( ^{45}\text{Sc} \) nuclear hyperfine interaction. Expanded scale presentations of the \( XY_1 \) perpendicular (\( \Theta = 90^\circ \)) fine structure transition and the OA absorption feature at \( \Theta = 25^\circ \) are shown in Figs. 2 and 3, respectively.

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irradiation at 647 nm would have photobleached a species such as \( \text{ScF}^+ \) since it would be expected to have a small ionization energy. The absence of photodestruction at this wavelength strongly supports the cation assignment.

### C. Calculations

*Ab initio* calculations were performed on the neutral scandium dimer \( \text{Sc}_2 \), the cation \( \text{Sc}_2^+ \), and the anion \( \text{Sc}_2^- \) in order to evaluate the relative energies of the electronic states of each species and to predict their hyperfine coupling constants. Considering the complexity of this problem we were constrained to use a rather small basis set in what must be considered only a preliminary theoretical analysis of these scandium radicals. The basis set chosen was a double zeta contraction (8s5p3d) of Wachters (14s9p5d) set augmented by an additional \( p \) function with an exponent of 0.0548 giving a final basis of (8s6p3d). This exponent was chosen so as to minimize the energy of the \(^{5}P\) excited state of the atom.

Geometry optimization for each electronic state was performed with the MELDF (Ref. 49) suite of programs at the self-consistent field (SCF) level in a point by point fashion. Relative energies of the electronic states and their hyperfine coupling constants were evaluated with single point Hartree–Fock single and double configuration interaction (HFSDCI) calculations at the optimized geometries. In the configuration interaction (CI) calculations all single excitations from the reference configurations were kept but only those double excitations which exceeded a threshold energy, evaluated by a perturbation theory approach, of \( 1 \times 10^{-6} \) a.u. were retained. The results of these calculations are presented in Table I.

Our calculations show that the ground state of \( \text{Sc}_2 \) is \(^{5}\Sigma_u^-\) with an electron configuration of \( 4s^22d^44s4p^2\) in agreement with the earlier work of others.\(^5\)-\(^6\) The unpaired electron in the \( 4s0_{\text{u}}^1 \) orbital, which is mainly com-

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<th>State</th>
<th>Configuration</th>
<th>( r_e (\text{Å}) )</th>
<th>Energy (a.u.)</th>
<th>( ^{4}\text{Sc} ) hyperfine coupling (MHz)</th>
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<td>( \Sigma_u^- )</td>
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<td>-1519.8299 ( (0.89) )</td>
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<tr>
<td>( \Pi_u )</td>
<td>( 4s^22d^44s4p^2 )</td>
<td>3.08</td>
<td>-1519.2239</td>
<td>-1519.8450 ( (0.91) )</td>
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\( \text{All calculations were conducted with the MELDF suite of programs (Ref. 49).} \)

\( \text{A description of the "estimated full CI" calculation approach is given in Ref. 50.} \)
posed of atomic 4s atomic orbitals, results in a large calculated value of $A_{iso}$ of 211 MHz, in reasonable agreement with the experimental value of 252 (11) MHz. This is apparently the first comparison of a calculated $A_{iso}$ value with the earlier experimental measurements for Sc$_2$.

As the ESR results have unequivocally shown that the discandium radical being observed has a quartet electronic state, only the low lying 4$^+_g$ and 2$^+_g$ states were investigated in detail for Sc$_2^+$ and Sc$_2^-$. It was found that the lowest lying 2$^+_g$ and 2$^+_u$ states were less stable than these quartet states, although it is difficult to make such a comparison for the two different spin manifolds given the problem of properly treating the correlation energies for states of different spin multiplicity. As shown in Table I, at the SCF and HF$SDCI$ levels the calculations show the 4$^+_g$ state to be more stable than either of the two 4$^+_g$ states of Sc$_2^+$. The energy gap between the lowest 4$^+_g$ state and the 4$^+_g$ state becomes significantly smaller with the inclusion of CI, and the estimated full CI energy of the 4$^+_g$ state is slightly lower than that of the 4$^+_u$ state. A description of the “estimated full CI” calculation method has been described in previous theoretical studies. Hence we assign the ground state of Sc$_2^+$ to the 4$^+_g$ state with a 4$^+_g$ ground state. The calculated value of the Sc hyperfine of $-32$ MHz for this state is in reasonable accord with our experimental value of 26 MHz (the sign of the hyperfine coupling cannot be determined from these FSR results alone). The other 4$^+_u$ state is predicted to be slightly less stable (by 1600 cm$^{-1}$ using the estimated full CI energies) and to have a large value of $A_{iso}$ = 378 MHz, which is not consistent with the ESR measurements. The 4$^+_u$ state would not be observed by matrix isolation ESR due to large $g$ tensor anisotropy, thus eliminating this state as the ground state of Sc$_2^+$. Since it is possible that Sc$_2^-_g$ could form under our experimental conditions, calculations were also performed on the anion radical. These HF$SDCI$ calculations summarized in Table I, give the ground state of Sc$_2^-$ to be a 4$^+_g$ with a 4$^+_g$ ground state, which has a large $A_{iso}$ value of 211 MHz, which is also consistent with our ESR experimental results. The other 4$^+_u$ state arising from a 4$^+_u$ ground state is less stable by 0.05 a.u. (11 000 cm$^{-1}$) and has a large scandium $A_{iso}$ value of 236 MHz. Hence, it is not possible from these theoretical calculations alone to determine whether the discandium molecule being observed is the cation or anion radical. However, given the electro-positive nature of scandium and the higher photolytic energies required for photobleaching, it is much more likely that the Sc$_2^+$ ion is being observed rather than the Sc$_2^-$.

IV. DISCUSSION

In the present study the ground state of Sc$_2^+$ has been shown to be 4$^+_g$, deriving from the 4$^+_g$ electronic configuration. Similar ground electronic configurations have been found for many of the other early 3d series transition metal molecules that have been investigated, in the sense that they possess two 4$^+_g$ and no 4$^+_u$ electrons. Thus Ti$_2^+$ has been shown to have a 3$^+_d$ ground state deriving from a 4$^+_g$ 3$^+_d$ electronic configuration. TIV has a 3$^+_d$ ground state deriving from a 4$^+_g$ 3d$^6$ electronic configuration. V$_2$ has a 3$^+_g$ ground state deriving from a 4$^+_g$ 3d$^5$ electronic configuration, and Cr$_2$ has a 3$^+_g$ ground state which at least nominally derives from a 4$^+_g$ 3d$^5$ electronic configuration.

In contrast to these molecules, Sc$_2$ and ScCr are somewhat unusual, having significant contributions from 4$^+_g$ 4s$^0$ configurations. In the case of Sc$_2$, the large hyperfine splitting associated with the ground 4$^+_g$ state identifies it as primarily 4$^+_g$ 4s$^0$ 3d$^5$ state in character, while an ESR investigation of ScCr (which possesses a 4$^+_g$ + ground state) has shown it to consist of a mixture of the 4$^+_g$ 4s$^0$ 3d$^5$ state, and 4$^+_g$ 4s$^0$ 3d$^5$ 4s$^0$ 3d$^5$ configurations. Without a doubt, the importance of 4$^+_g$ 4s$^0$ configurations in scandium-containing neutral molecules derives from the high promotion energy associated with the neutral scandium atom. The lowest energy 3$^+_d$ 4s$^1$ state of this atom lies 11 520 cm$^{-1}$ above the 3d$^4$ 4s$^2$, 2$^+_d$ ground state, making promotion of both scandium atoms energetically quite unfavorable for the ground state of Sc$_2$. In contrast, only 6557 and 2112 cm$^{-1}$, are required to excite titanium and vanadium atoms to their 4s$^1$ configurations, respectively, making 4$^+_g$ 4s$^0$ 4s$^0$ configurations quite achievable in the ground states of Ti$_2$, TIV, and V$_2$. In ScCr, on the other hand, the ground state of Cr is 3$^+_d$ 4s$^1$, which is ideally set up for bonding. However, 11 520 cm$^{-1}$ is still required to promote the single Sc atom to the 3$^+_d$ 4s$^1$ configuration, and the smaller size of the 3d orbitals in chromium makes them less accessible for chemical bonding than the 3d orbitals of scandium. Furthermore, the high spin 3$^+_d$, 6$^+$ of chromium is strongly stabilized by favorable exchange interactions, and interaction with a 3$^+_d$ 4s$^1$ scandium atom would lead to loss of exchange energy as $d-d$ bonds are formed. Apparently the bonding energy to be gained by promoting the scandium atom to the 3$^+_d$ 4s$^1$ configuration is insufficient to make up for the energetic cost of this promotion in the ScCr molecule.

Although Sc$_2^+$ possesses a 4$^+_g$ 4s$^0$ 3d$^5$ electronic configuration, the promotion energy associated with this configuration is much less than that required for a 4$^+_g$ 4s$^0$ 3d$^5$ configuration in neutral Sc$_2$. Promotion of both Sc atoms to 3$^+_d$ 4s$^1$ configurations in Sc$_2$ requires 2$\times$11 520 = 23 040 cm$^{-1}$, while for Sc+Sc$, the 3$^+_d$ 4s$^1$, 2$^+_d$ and 3$^+_d$ 4s$^1$, 2$^+_d$ separated atom asymptote lies only 4803 cm$^{-1}$ above ground state atoms. The low energy of this favorable separated atom asymptote probably makes Sc$_2^+$ considerably more strongly bound than Sc$_2^+$, and implies that the ionization potential of Sc$_2$ is probably considerably less than that of the scandium atom.

We also note that Y$_2$ seems to be rather different than Sc$_2$. Although numerous attempts were made, no ESR spectra could be obtained for Y$_2$, Y$_2^+$, or Y$_2^-$, despite the observation of strong matrix ESR signals due to the doublet ($\Delta = 1/2$) radical, Y$_2$. The energetics of the $d^2$, $d^3$, and $d^5$ manifolds are similar for yttrium and scandium, and the two atoms are similar in ionization poten-
tial has electron affinity as well, making it difficult to rationalize why the corresponding yttrium and scandium molecules should have different electronic ground states. Perhaps the single most significant difference between the two atoms is that the ratio of the nd to the (n+1)s orbital radii (as obtained for the d^2 configuration in a relativistic Dirac–Fock self-consistent field method) is much larger for yttrium (r_{4d}/r_{5s}=0.596) than for scandium (r_{3d}/r_{4s}/r_{5s}=0.429). This makes the d orbitals of yttrium much more accessible for chemical bonding than those of scandium, since they are not so deeply buried in the outer s orbital. The greater strength of the 4d orbital contributions to the bonding in Y$_2$ could then lead to a ground state of 5s\sigma_0^24d\sigma_0^24p\pi^-\Sigma^+_g; or possibly even 5s\sigma_0^24d\pi^-\Sigma^+_g (in all cases we note that the \sigma orbitals probably involve a significant amount of so–do hybridization). Similar speculations would apply to the Y$_2^-$ and Y$_2^-$ molecules, except in these cases the inability to observe the molecule by ESR methods is more definitive, since the molecules have an odd number of electrons, and therefore a \Sigma state (whether it is \Sigma^-, \Sigma^+, \Sigma^0, etc.) should be observable. In contrast, it is conceivable that if the ground state of Y$_2$ were \Sigma or \Sigma^0, it might be unobservable by ESR methods if the zero-field splitting were large.

We now turn to the photodestruction behavior of Sc$_2^+$, which could in principle provide information about the Sc$_2$ bond energy. As shown in Fig. 5, the neutral scandium dimer is destroyed upon photolysis by exposure to light with \lambda<665 nm, which corresponds to a photon energy \hbar\nu>1.86 eV. It seems reasonable that the molecule is destroyed by a photodissociation process, so this implies \Delta_{\text{diss}}(\text{Sc}_2^+)<1.86 eV, which is in accord with all previous estimates of the bond strength. The absorption spectrum of Sc$_2$ isolated in an argon matrix, shows a strong absorption at 662 nm, and it is probably absorption into the tail of this band that causes photodissociation in the present experiments.

The characteristic ESR spectrum of Sc$_2^+$ can likewise be destroyed by photolysis, but in this case irradiation with wavelengths to the red of 647 nm is ineffective in destroying the molecule, while wavelengths in the range of 625–647 nm successfully convert the characteristic ESR spectrum of Sc$_2^+$ to that of Sc$_2$. Presumably a photon energy of 1.95±0.03 eV (corresponding to 625–647 nm light) is required to release an electron trapped on a matrix isolated anion, enabling it to neutralize the Sc$_2^+$ cation. The measurement of a threshold for this process then gives no information about the Sc$_2^+$ molecule itself.

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