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Gas-Phase Ion Chemistry of Zinc Atoms and Ions

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Thermally generated zinc atoms in an ICR spectrometer have a proton affinity between that of NF_3 and hexafluoroacetone. When ionized by electron impact, Zn^+ abstracts fluorine from NF_3 to make ZnF^+, and when translationally excited, forms ZnO^+ from N_2O. No sulfur abstraction from a variety of species is observed. Thermochemical parameters are derived from these data, and periodic trends in bond strengths are analyzed.

There has been considerable recent interest in the gas-phase chemistry of metal ions, due to the remarkable reactivity observed for such unsolvated species. Direct insertion into C–C and C–H bonds[1] and catalytic transfer of groups[2] have been observed, and quantitative ligand-binding energies have been measured.[3] Much of this work has focused on the mid transition metals, with relatively little attention paid to other metals, however. Similarly, while there have been numerous investigations of the gas-phase chemistry of metal atoms with neutral organic molecules,[4] there are only a few reports of the gas-phase chemistry of neutral metal atoms reacting with ionic species.[5] In this work, using ion cyclotron resonance (ICR) spectrometry, we report some gas-phase chemistry of zinc atoms reacting with a variety of ionic species by proton transfer, as well as some reactions of Zn^+. This oxidation state of zinc, while not unknown in solution, has chemistry primarily dealing with transient species produced by radiolysis.[6]

Experimental Section

The ion cyclotron resonance spectrometer used for this work has been previously described.[7] Zinc atoms were volatilized by passing ca. 3–4 A of direct current through a brass filament (33% Zn, 67% Cu) adjacent to the ICR cell. No zinc signals were obtained when a pure zinc filament was substituted for the brass filament. Inspection of the surface of the brass filament after several weeks of intermittent operation revealed the surface to be pitted and no longer shiny. We believe that the zinc atoms are volatilized thermally from the surface of this filament, and then undergo ionization in the electron beam. The lack of a Zn^+ signal when the electron energy is less than 9.4 eV rules out ion production via surface ionization on the hot rhenium filament that generates the electron beam.[8] When other chemicals were present in the spectrometer, the largest Zn^+ signals were obtained when the ionizing electron beam was operated at an electron energy of 14 eV. This is presumably due to the relative cross sections for ionization of the zinc atoms and the polyatomics used in this electron energy range. Zinc ion signals are observed in abundance only under unquenched conditions,[9] where the electron beam is operated continuously, and ions are never ejected from the cell save by their own space-charge repulsion. This allows ions that are the products of reactions that are very slow, due either to a small rate constant or to a low concentration of the neutral precursor, to build up in the cell over several minutes. Only very small signals, normally buried in base line noise but brought out by extensive signal averaging, could be detected in the normal quenched-mode operation. On the basis of the slow rise time for these signals and the ionization cross section for zinc,[10] we estimate the number density of zinc atoms in the cell to be on the order of 10^5 cm^{-3} (10^{-11} torr). The necessity of operating in unquenched mode unfortunately rules out measurement of any kinetic parameters but allows certain inferences to be made concerning the chemical pathways of zinc atoms or ions reacting with any other chemical species admitted into the spectrometer. If a primary electron-impact ion of some species reacts away rapidly (e.g., in less than 100 collisions) with its own neutral species, then that ion will not persist long enough to react with a zinc atom. Only those ions that are the end products of an ion/molecule reaction sequence will be present for a sufficient time under unquenched conditions to react with the very low concentration of zinc atoms present.

Other chemicals were obtained commercially and subjected to the usual freeze–pump–thaw cycles before being admitted to the ICR spectrometer.

Results

A spectrum obtained at a background pressure of 10^{-9} torr is shown in Figure 1. The peak ratios are within 0.5% of the natural isotope abundance,[11] which is on the order of the accuracy of the detection electronics used in our instrumentation.[7] Various gases were admitted to the vacuum system to further probe the reactivity of these ions and their precursor neutrals.

Alkanes. When 2×10^{-7} torr of methane is present in the spectrometer, both Zn^+ and ZnH^+ are observed under typical conditions. The protonated ion has 10–20% of the intensity of the atomic ion, depending on the exact experimental conditions. Double-resonance techniques indicate that the ion ZnH^+ arises from CH_5^+ and not from $C_2H_5^+$, in agreement with the results of Porter and co-workers,[5e] thus placing the basicity of Zn between 128.2 and 163 kcal/mol.[12] Double

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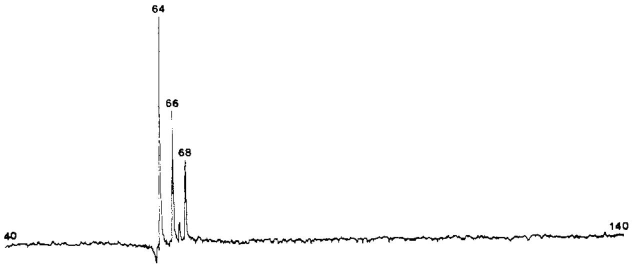


Figure 1. Mass spectrum of Zn^+ in the ICR spectrometer (10^{-9} torr, 15-eV electron-impact energy). Scale is in amu.

resonance also indicates that Zn^+ is not derived from either of these organic ions and must therefore be a primary product. Dissociative charge transfer as in reaction 1 is calculated to

$$CH_5^+ + Zn^0 \rightarrow Zn^+ + H + CH_4 \qquad (1)$$

be 31 and 62 kcal/mol endothermic for CH_5^+ and $C_2H_5^+$, respectively, ruling them out as sources of Zn^+. With ethane or pentane at 2×10^{-7} torr in the spectrometer, no zinc-containing ions are seen, other than Zn^+ itself. Although ethane has a proton affinity less than that of zinc (see below),[12] unlike methane, it does not undergo an autoprotolysis reaction in the gas phase so that there is no $C_2H_7^+$ to react with the zinc.

Nitrous Oxide. When nitrous oxide is present at 2×10^{-7} torr in the spectrometer, the only zinc-containing peaks are Zn^+ and ZnO^+. The latter is a product of Zn^+, and not N_2O^+, NO^+, or O^+, by double resonance. Zn^+ is not derived from any other ion in the spectrum by double resonance. We note that reproducibility problems exist with observing ZnO^+; its production is a sensitive function of electron energy, filament current, plate voltages, detection rf level, and sweep rate of the rf. If reaction 2 is the source of the ZnO^+ signal and is

$$Zn^+ + N_2O \rightarrow ZnO^+ + N_2 \qquad (2)$$

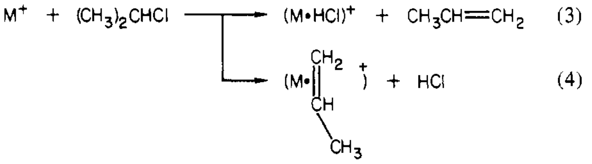
exothermic, the Zn^+–O bond strength must be greater than that of N_2–O at 39 kcal/mol.[13] This is in direct contrast to the work of Kappes and Staley,[14] where Zn^+ ions created in an ICR spectrometer by laser desorption/ionization from a cold metal surface were not reactive with N_2O. If 2×10^{-8} torr of methane is admitted to the spectrometer in addition to the N_2O, then N_2OH^+ becomes a prominent ion in the spectrum, and ZnH^+ also appears. Double resonance indicates that the protonated nitrous oxide is the source of the protonated zinc, placing a lower bound on the proton affinity (PA) of zinc of 135.6 kcal/mol.[12]

Carbon Monoxide. With 2×10^{-7} torr of CO present, no ZnO^+, $ZnCO^+$, or ZnC^+ ions are observed, although Zn^+ is present. Added methane results in a large HCO^+ signal, which by double resonance is shown to be the precursor to the ZnH^+ ion that also appears. This places a lower limit on the PA(Zn) of 139 kcal/mol.[12,15]

Nitrogen Trifluoride. With 2×10^{-7} torr of NF_3 present, NF_3^+ and NF_2^+ are the principal primary ions. Both Zn^+ and ZnF^+ are observed; double resonance indicates that the latter arises from Zn^+ and not from NF_3^+ or NF_2^+. This places the Zn^+–F bond strength at >59 kcal/mol.[15] The appearance of ZnF^+ is not dependent on electron energy, occurring at all energies where Zn^+ is observed. With 2×10^{-8} torr of added methane, HNF_3^+ becomes an appreciable ion in the spectrum and by double resonance gives rise to the ZnH^+ signal also observed. Unfortunately, the PA of NF_3 is at present only bracketed as 147 ± 4 kcal/mol by the PA sequence[16] $CO < NF_3 < CH_3F < C_2H_2$ so that this allows only a rough increase in the lower limit for PA(Zn).

Hexafluoroacetone. CF_3^+, CF_3CO^+, and the parent cation are the principal ions observed here along with Zn^+. No ZnF^+ is seen, nor any other zinc-containing species. A trace amount of methane results in an appreciable $(CF_3)_2COH^+$ signal, as well as ZnH^+. Double resonance indicates that the protonated ketone is not a source of ZnH^+, thus placing the upper limit to the proton affinity of Zn as 160.4 ± 0.7 kcal/mol.

Other Gases. No zinc-containing ions are formed when Zn^+ is in the presence of CO_2, OCS, CS_2, elemental sulfur, SO_2, or 2-chloropropane. The last species is used as a standard derivatizing reagent for gas-phase metal ions, as in reactions 3 and 4.[1,17] Under the unquenched conditions, the possible



precursor ions to any zinc-containing ions arising from Zn^0 are the self-chemical ionization products of 2-chloropropane, isopropyl cation and the diisopropylchloronium ion. Both charge exchange and proton transfer (see below) to zinc from the isopropyl cation are calculated to be endothermic, by 42 and 30 kcal/mol, respectively.[15] For diisopropylchloronium ion, taking the binding strength of isopropyl cation to chloromethane[18] as that for isopropyl bound to 2-chloropropane, dissociative proton transfer to Zn^0 to give propene, 2-chloropropane, and ZnH^+ is calculated to be ca. 48 kcal/mol endothermic, and dissociative electron transfer, 70 kcal/mol endothermic. The lack of zinc atom reactions under our conditions with these species is therefore not surprising. If the nonobservation of reaction 2 or 3 is taken as a thermochemical threshold, the bond strength of Zn^+ bound to HCl or propene is <18 kcal/mol.[15]

Discussion

Proton Affinity of Zn. There are several previous values for PA(Zn). The report by Porter and co-workers[5e] involves an experimental bracketing of PA(Zn) between that of CH_4 (current best value 128.2 kcal/mol)[15] and that of $CH_2{=}CH_2$ (PA = 162.6 ± 0.5 kcal/mol);[16] using high-pressure mass spectrometry. This yields a direct experimental value of PA(Zn) = 145.7 ± 17.0 kcal/mol. They also derive a value for PA(Zn) of 6.8 ± 0.2 eV (156.8 ± 4.6 kcal/mol) from the spectroscopic bond strength for Zn^+–H of 2.5 eV given by Herzberg,[19] plus the appropriate ionization potentials of Zn and H. An uncertainty of 0.2 eV is placed on this PA, presumably from the upper experimental bound involving no proton transfer from $C_2H_5^+$ to Zn, with no rationale for the same lower limit. No explicit uncertainty is given by Herzberg for the original spectroscopic bond strength, though generically 9 times the last decimal place is stated as a probable bound.[19] A value of 164 ± 10 kcal/mol can be derived for PA(Zn) from the appearance potential, with no kinetic shift correction, for ZnH^+ formed from $Zn(CH_3)_2$ in an electron-impact mass

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spectrometer.[20] A molecular orbital calculation has given the Zn^+–H bond strength as 35 kcal/mol.[21]

The present work experimentally brackets PA(Zn) between those of NF_3 at 147 ± 5 kcal/mol,[16] and hexafluoroacetone at 160.4 ± 0.7 kcal/mol[16] for an average of 154^{7}_{-12} kcal/mol. This places the Zn^+–H bond strength at 57^{+7}_{-12} kcal/mol, compared to the spectroscopic value of 58 kcal/mol. A $\Delta H_f°(ZnH^+)$ of 242.8^{+7}_{-12} kcal/mol is similarly derived. It would be desirable to have more bases in this region to enable a more precise bracketing of the PA; however, there are relatively few known. AsF_3 and CH_3F both have basicities between those of NF_3 and $(CF_3)_2CO$,[16] but the protonated species of these, $HAsF_3^+$ and $HFCH_3^+$, react away in their neutral vapors, so that the protonated base is not available under unquenched conditions to react with zinc.

The Zn^+–H bond is stronger than the Zn–H bond of 20 ± 2 kcal/mol.[19] This bond strength increase upon ionization is due to the presence of a total of three s electrons from Zn and H, with the third having to occupy an antibonding orbital in ZnH; ionization of ZnH results in the stronger two electron bond.

ZnO^+. There is a striking contrast between the results of the present work, that zinc ions will abstract oxygen from nitrous oxide, and the corresponding lack of reaction of N_2O with laser-generated Zn^+.[14] One possible explanation is the presence of an electronically excited state of Zn^+; the first excited state of Zn^+ is at 15.4 eV above Zn^0,[22] near where the best Zn^+ signals are observed. Such excited species have been invoked in other transition-metal ion/molecule chemistry to explain apparently endothermic reactions.[1g,1k,3d] The instances cited in the literature, however, all involve excited states of multiplicity different from that of the ground state, so that relaxation will be slow, relative to the collision rate. The radiative lifetime of the $(Zn^+)^*$ state at 15.4 eV is ca. 3 ns, since the excited and ground states are both doublets.[23] This is far too fast for chemistry to be attributed to a free $(Zn^+)^*$ in the ICR spectrometer.

A preferable explanation is based on chemistry observed by Beauchamp and co-workers, who have measured the excess translational energy needed to drive reactions 5 and 6, using

$$M^+ + O_2 \rightarrow M^+\text{–}O + O\cdot \qquad (5)$$

$$M^+ + N_2O \rightarrow M^+\text{–}O + N_2 \qquad (6)$$

an ion beam apparatus, for a number of transition-metal ions.[24] They find that a kinetic barrier exists for exothermic oxygen transfer to the metal ions from nitrous oxide, compared to an endothermic, but barrier-free, transfer from oxygen. This is ascribed to multiplicity differences: oxygen dissociating from MO^+ correlates with the triplet state, while dissociation from N_2O correlates with the singlet state. The resulting singlet–triplet crossing on one of the potential surfaces results in a barrier to oxygen transfer at the thermochemical onset. A similar reduction in rate constant for Zn^+ reacting with N_2O is observed in aqueous solution, relative to Zn^+ reacting with other species.[6] The appearance of ZnO^+ in our spectrometer, as noted above, is not easily reproducible. This is interpreted as due to the nature of the unquenched mode and the intermediate-passage method in ICR spectrometry. Detection of Zn^+ in the ICR spectrometer is due to translational excitation, and since Zn^+ is not removed from the cell after detection (as is usual in pulsed ICR spectrometry) but allowed to remain, it may undergo endothermic reactions. If the balance of rf level, power absorption, ion loss by diffusion, and N_2O pressure are just right, the oxygen transfer is facilitated by the excess energy of the Zn^+. The ZnO^+ so formed is detected on the next frequency scan. Thus, lack of thermal reactivity with N_2O cannot be taken as an upper thermochemical limit in assigning bond strengths here, due to possible kinetic problems. Even the use of CO_2 and COS as upper limits to oxygen transfer cannot be taken as necessarily valid since a similar singlet–triplet correlation problem exists there.[24]

Charge Transfer. No charge transfer to zinc is detected by double resonance for any of the cations present; all zinc ions are observed to arise by primary electron impact. For atomic ions, this is consistent with the lack of a rotational or vibrational sink for the excess energy, if the charge transfer is not a resonant process and if the collision complex is weakly coupled translationally due to long-range electron transfer. None of the atomic ions that arise from the nonmetallic species used have recombination energies closer to the ionization potential of zinc than 2eV.[15] For diatomic and larger cations, nonresonant charge transfer could occur due to rotational and vibrational coupling in the long-lived collision complex, as well as due to translational disposal of energy.[25] For the di-, tri-, and tetratomics used here, such transfer is in general not observed. The only case where such a transfer might have occurred is with the S_n^+ ions, n = 2–8, which have recombination energies within 0.5 eV of the IP of zinc at 9.394 eV.[15] These ions are depleted from the S_8 spectrum when zinc atoms are present, and a much larger than usual Zn^+ signal is observed. Of the usual sulfur ions, only S^+ is present. The lack of signals for these S_n^+ ions precludes double-resonance detection of this possible change transfer.

Other Thermochemistry. It is risky to infer thermochemical stability from a lack of reaction, save when dealing with a homologous series where the reacting sites are constant. For ion/molecule reactions, kinetic barriers, as noted above for N_2O, can result in reactions that proceed at much less than collision rate even though they are thermochemically favored.[24] With this caveat, several upper bounds on bond strengths will be derived here for some zinc-containing species. The lack of sulfur transfer from CS_2, elemental sulfur, or OCS to Zn^+ implies a Zn^+–S bond strength of less than 34 kcal/mol. A hard–soft acid–base analysis predicts a weaker Zn^+–S bond than Zn^+–O, but the lack of good data for the latter precludes further evaluation. The lack of chlorine transfer from 2-chloropropane to Zn^+ implies that the Zn^+–Cl bond strength is less than 83 kcal/mol, in agreement with $DH(Zn^+\text{–}Cl)$ = 54 ± 6 kcal/mol based on the appearance potential of $ZnCl^+$ from $ZnCl_2$.[26]

In no case were any transfers of cationic species from other ions to Zn^0 observed, other than proton transfer. On the basis of a reasonable range for the Zn^+–O bond strength of 30–70 kcal/mol and the ionization potentials of Zn and O, O^+ transfer from XO^+ to Zn^0 should be endothermic for all the oxide cations used in this work save for N_2O^+. In that case, O^+ transfer should be exothermic by >75 kcal/mol. Since this reaction is not observed, there must be a kinetic barrier. Such a rate reduction is not a result of different collision rates since, due to polarizability differences, Zn^0 should collide with N_2O^+ at a 24% greater rate than for Zn^+ colliding with N_2O.[27] The lack of reaction may be due to a multiplicity argument as given for N_2O above: N_2O^+ is a doublet, and correlates

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1880 *Inorg. Chem.* **1984**, *23*, 1880–1885

Table I. Bond Strengths of Transition-Metal Compounds[a]

metal	IP[b]	PA[c]	M^+–H	M^+–O	M^+–Me	M^+–Cl	M^+–F
Cr	6.77	193 ± 4	35 ± 4	77 ± 5	37 ± 7		
Mn	7.44	196 ± 3	53 ± 3	57 ± 3	>48		76 ± 12[d]
Fe	7.87	189 ± 5	58 ± 5	68 ± 3	68 ± 4	77 ± 12[d]	125 ± 12[d]
Co	7.86	184 ± 5	52 ± 4	65 ± 3	61 ± 4		
Ni	7.64	181 ± 2	43 ± 2	45 ± 4	48 ± 5		
Cu	7.73	150[l]	15[l]	33 ± 7[i]		>83[j]	95 ± 14[d]
Zn	9.39	154^{+7}_{-12}[e]	57^{+7}_{-12}[e]	33 ± 7[i]	68 ± 3,[f] 67.3 ± 1.0[k]	54 ± 6[g]	>59[e]
Ga	6.00			49 ± 12[d]			62 ± 12[d]
Cd	8.99	152 ± 20[h]	46 ± 7[h]	54 ± 3[d]	54.6 ± 1.0[k]		
Hg	10.44	126 ± 20[h]	53 ± 20[h]		69 ± 3,[d] 68.2 ± 1.0[k]	71 ± 7[d]	

[a] Reference 3c, unless otherwise stated; kcal/mol. [b] Ionization potential, eV, ref 11. [c] Proton affinity, DH(M–H^+), kcal/mol. [d] From data in ref 13, 15. [e] This work. [f] Reference 20. [g] Reference 26. [h] Reference 19. [i] Reference 14; value is a lower limit, see text. [j] Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* 1980, *102*, 3794. [k] Reference 28. [l] Predicted from data in ref 3c.

with doublet O^+, 77 kcal/mol up from the ground quartet state.[15] If this is taken as an upper limit, then DH(Zn–O^+) $\geqslant$ 117 kcal/mol and DH(Zn^+–O) $\geqslant$ 19 kcal/mol. The only instance in this work where ion transfer to Zn^0 was observed is for H^+ from the various protonated bases; the "closed-shell" nature of the transferred ion precludes multiplicity problems in this reaction.

Periodic Trends. Certain other thermochemical data are available from the literature and are compiled in Table I. These include data from ion-beam experiments, appearance and photoionization potentials, and ion/molecule reactions. Across the row, a general decrease in PA(M) is observed, with Zn having a lower PA than the first-row transition metals. Unfortunately, the only data for the neighboring elements Cu and Ga are the estimate for PA(Cu) based on promotion energy[3c] and the fact that GaH^+ does not appear to have been observed. It is noteworthy regarding the latter species that unless PA(Ga) is greater than 175 kcal/mol (considerably larger than for Zn), then DH(Ga^+–H) will be negative and GaH^+ therefore unstable with respect to dissociation. The relatively strong Zn^+–H bond is consistent with Zn^+ being an s^1 configuration.[3c] The Zn^+–F bond strength of >59 kcal/mol derived here can be regarded as a relatively low bound; DH(Cu^+–F) = 95 ± 14 kcal/mol[15], and on the basis of the promotion energy argument of Beauchamp and co-workers,[3c] it should be weaker than Zn^+–F. These halide bonds are considerably more polar than the M^+–H and M^+–CH_3 bonds discussed in ref 28, but for Cu vs. Zn, the electronegativity difference reinforces the bond strength ordering. The Ga^+–F bond strength of 62 ± 12 kcal/mol[15] is weak for a metal–fluoride bond, but the bonding may involve p orbitals, so that the promotion-energy correlation[3c] is not applicable. The chloride vs. fluoride bond strengths for Zn^+ parallel the general order DH(M^+–Cl) <DH(M^+–F) observed for the first-row transition metals.[15] For the 2B elements Zn, Cd, and Hg, the uncertainties in the M^+–H bond strengths are large, but the order Cd^+–H < Zn^+–H < Hg^+–H[28] can be taken to be a mixture of electronegativity change and the lanthanide contraction. This order is not reflected in the neutral ordering Zn–H > Cd–H > Hg–H, where the unpaired antibonding electron affects the stability.[19] Similarly, the groups capable of sharing one electron in a bond, such as H· and Cl·, have neutral Zn–X bonds[19] weaker than their ionic counterparts, while oxygen, requiring a two-electron donation from the metal, has stronger neutral bonds, compared to the ionic analogues, for the 2B elements. On the basis of periodic trends, we predict that DH(Zn^+–O) should be ca. 30 kcal/mol.

Conclusions

Zinc atoms and ions are relatively unreactive, in terms of atom abstraction or oxidative insertion, compared to the first-row transition metals, in spite of Zn^+ having the strongest metal ion to one-electron-donor ligand bond strengths of the first long series. This is a reflection of the filled-d-shell nature of Zn and Zn^+, with the bonding being primarily due to the s electrons.

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Registry No. Zn, 7440-66-6; Zn^+, 15176-26-8; ZnH^+, 41336-21-4; CH_5^+, 15135-49-6; N_2O, 10024-97-2; ZnO^+, 60131-08-0; CH_4, 74-82-8; N_2OH^+, 76412-54-9; CO, 630-08-0; HCO^+, 17030-74-9; NF_3, 7783-54-2; ZnF^+, 19624-01-2; HNF_3^+, 64709-84-8; $(CF_3)_2CO$, 684-16-2; $(CF_3)_2COH^+$, 79999-78-3; F_2, 7782-41-4; S, 7704-34-9; Cl_2, 7782-50-5; O_2, 7782-44-7.

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Vanadium(II) Pair Excitations in $CsMg_{1-x}V_xCl_3$

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Mixed crystals $CsMg_{1-x}V_xCl_3$ with x between 1% and 15% were prepared by the Bridgman technique. Single and double excitations to the ^2E, $^2T_1$, and $^2T_2$ states of $V_2Cl_9^{5-}$ dimers were studied by optical absorption and Zeeman spectroscopy. The ground-state exchange parameter is $2J = -187 \pm 5$ cm^{-1}. From an analysis of singly excited ^2E pair states the following orbital exchange parameters were derived: $2J_{a_1a_1} = -570$ cm^{-1}, $2J_{ee} = -195$ cm^{-1}. $J_{a_1a_1}$ is the dominant antiferromagnetic pathway as expected on the basis of overlap arguments.

1. Introduction

The exchange in the quasi-one-dimensional (1D) antiferromagnets $CsVX_3$ (X = Cl, Br, I) is unusually strong. Intrachain $2J$ values estimated from high-temperature magnetic susceptibility data are −160, −110 to −120, and −75 to −95 cm^{-1}, respectively.[1] The coupling constants between the chains

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