latter we have observed that these processes are faster in the smaller micelles.[24]

The results with pyrene and xanthone show that PSS/DTB aggregates provide a nonpolar environment to these probes; however, the relocation of xanthone, the quenching by ions for a variety of probes, and the high yield of LATs in the case of benzophenone all seem to indicate that hydroxylic regions are readily accessible to the probe molecules. Thus, we suggest that water intercalates between the DTB islands or clusters and that in this sense, while the polymer has a coiled structure, it remains sufficiently open to allow water to penetrate in the system. This is not surprising in view of the fact that only about half of the charges have been neutralized.

The relocation of xanthone, presented in section B3, is believed to be the first example of its nature. In this sense it is important to note that xanthone is rather special only in that those changes are easily detectable, but the same type of phenomena may take place in many other systems. Quite frequently kinetic and equilibrium parameters for exit–entry processes in organized systems are measured for ground, singlet or triplet states and then used without any consideration for the type of electronic state. Our results indicate that solubility properties for ground and excited states may be quite different, particularly when significant changes in dipole moment occur upon excitation.

The behavior of radical pairs is quite similar to that observed in *small* micelles, with the competition between intersystem crossing and radical escape taking place in the hundreds of nanoseconds time domain.

Perhaps the most significant difference between the local DTB clusters in PSS/DTB aggregates, and conventional micelles, is that while the latter offer probe protection from *positive* quenchers, the PSS/DTB aggregates protect from *negative* species, thus reflecting the overall negative charge of the aggregates; in this sense, while local clusters seem to control the luminescent properties of the probes, static quenching phenomena, and radical-pair behavior, this is not the case of intermolecular processes involving species in the aqueous phase. These seem to be largely controlled by the total aggregate, particularly its charge.

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Registry No. ANS, 82-76-8; Eu^{3+}, 22541-18-0; $S_2O_3^{2-}$, 14383-50-7; poly(styrenesulfonate), 50851-57-5; dodecyltrimethylammonium bromide, 1119-94-4; phenanthrene, 85-01-8; pyrene, 129-00-0; xanthone, 90-47-1; 1-methylnaphthalene, 90-12-0; nitrite ion, 14797-65-0; 1,3-cyclohexadiene, 592-57-4; cupric ion, 15158-11-9; cupric sulfate, 7758-98-7; benzophenone, 119-61-9; dibenzyl ketone, 102-04-5; 1,4-cyclohexadiene, 628-41-1.

SAC–CI Calculations for Rydberg Levels of the Ammonium Radical

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Abstract: A highly accurate computational determination for Rydberg states of NH_4 is made with the cluster expansion of the wave function theory. The theory confirms the recent assignment of the Schüler band to $^2T_2(3p) \rightarrow {}^2A_2(3s)$. However, for the Schuster band, there is a 4510-cm^{-1} discrepancy between Herzberg's assignment and the present calculation.

The NH_4 radical is a molecule of special interest because its Rydberg states are expected to be bound and corresponding Rydberg spectra are the subject of wide recent discussion. In this paper a highly accurate computational determination for Rydberg states of NH_4 is made with cluster expansion of the wave-function theory.

The bands occurring in discharges through NH_3 have been observed by a number of investigators in the last 100 years, but none have obtained a definite identification.[1,2] Recent study by Herzberg[3-6] has established that the diffuse bands at 13040, 15390, 17630, 17730, and 18930 cm^{-1} are of the Rydberg spectrum of NH_4, and he has given them the name Schuster bands. He has assigned the Schuster band system to $^2T_2(3d) \rightarrow {}^2A_1(3s)$. A further band, the so-called Schüler band, is observed in the region 15050–15210 cm^{-1}. Herzberg tentatively assigns the Schüler band to $^2E(3d) \rightarrow {}^2T_2(3p)$. However, there exist serious conflicts between theoretical[7-9] and experimental results. There is a need for further improvement in the ab initio calculations with consideration of electron-correlation effects. Recently we have developed the symmetry-adapted-cluster (SAC) expansion theory and the SAC-CI theory[10,11] as an approach specifically designed to study the correlation effect both for the ground state and various excited states. Thus it seemed to be of particular interest to apply these theories to the NH_4 radical.

Table I. NH_4^+ Ground-State Energies (au)

	ground-state energy	correlation energy
SCF	−56.551275	
CI(S+D)	−56.664884	−0.113609
SAC	−56.669148	−0.117872

First we have performed the SAC calculation on the ground state of NH_4^+. We employed a basis set with the description

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Table II. Rydberg-State Energies for NH_4

state	HK[a]	Koopmans[b]	SAC-CI (A)	SAC-CI (B)	δn_k[d]
$1A_1(3s)$	−0.1465798	−0.1464083	−0.1615248	−0.1615655	1.2408
$1T_2(3p)$	−0.0934270	−0.0933872	−0.0986930	−0.0987262	0.7496
$2A_1(4s)$	−0.0611298	−0.0610438	−0.0645708	−0.0645931	1.2178
$2T_2(3d)$	−0.0597962	−0.0591816	−0.0624500	−0.0624938	0.1714
$1E(3d)$	−0.0563497	−0.0552163	−0.0557361	−0.0557050	0.0040
$3T_2(4p)$	−0.0448937	−0.0448684	−0.0465706	−0.0465911	0.7241
$4T_2(4d)$	−0.0337667	−0.0332738	−0.0350668	−0.0350978	0.2256
$2E(4d)$	−0.0317281	−0.0309826	−0.0311828	−0.0311827	0.0043
$3A_1(5s)$	−0.0334979	−0.0276228	−0.0303075	−0.0303250	0.9395
$4T_2(5p)$		−0.0217141	−0.0237762	−0.0238060	0.4170
$5T_2(5d)$		−0.0197486	−0.0206059	−0.0206361	0.0777

[a] Havriliak, S., King, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 4. Relative to −56.565547 au. [b] Relative to the SCF energy, −56.551275 au. [c] Relative to the SAC energy, −56.669149 au. [d] The quantum defect in the SAC-CI (B) approximation.

Table III. Frequencies and Transition Moments for NH_4[a]

	lower state				
upper state	$1A_1(3s)$	$1T_2(3p)$	$2A_1(4s)$	$2T_2(3d)$	$1E(3d)$
$5T_2(5d)$	30940	17144	9650	9189	7699
	30937	17143	9652	9186	7713
	0.241	0.006	0.739	0.440	0.275
$4T_2(5p)$	30243	16448	8954	8494	7003
	30241	16447	8956	8490	7016
	0.236	0.166	0.722	0.137	0.274
$3A_1(5s)$	28813	15017	7523	7062	5572
	28806	15013	7522	7056	5583
	0.001	0.806	0.000	0.266	0.000
$2E(4d)$	28624	14829	7335	6874	5384
	28615	14821	7330	6864	5390
	0.000	0.345	0.000	0.198	0.000
$4T_2(4d)$	27765	13969	6476	6014	4525
	27763	13969	6477	6012	4538
	0.082	0.027	0.542	0.605	0.107
$3T_2(4p)$	25241	11446	3952	3491	2001
	25237	11443	3952	3486	2012
	0.262	0.374	6.423	2.228	3.687
$1E(3d)$	23241	9445	1951	1490	
	23225	9431	1940	1474	
	0.000	2.925	0.000	0.679	
$2T_2(3d)$	21750	7955	461		
	21751	7957	466		
	0.206	3.091	1.112		
$2A_1(4s)$	21289	7494			
	21285	7491			
	0.001	2.915			
$1T_2(3p)$	13796				
	13794				
	2.959				

[a] For each entry the top number is the frequency in cm^{-1} in SAC-CI (A) approximation. The next entry is the frequency in SAC-CI (B) approximation. The third entry is the transition moments in SAC-CI (A) approximation in units of bohrs.

[8s6p4d/2s1p]. This set of 66 functions is obtained from the Huzinaga–Dunning basis set[12] by adding 4s, 4p, and 4d Rydberg functions[13] on nitrogen and one p on each hydrogen. All calculations have been done at the optimized geometry of the ground state of NH_4^+, R_{NH} = 1.0121 A with T_d symmetry. As a linked cluster we have included all single (S_1) and double (S_2) excitations from the reference function. The lowest occupied orbital was treated as frozen. As the disjoint clusters we have included the product of pair clusters $(1/2)S_2S_2$ for the SAC calculation. Table I shows the ground-state energy for NH_4^+. It also includes the SCF and single- and double-excitation CI results. The energy lowering due to the inclusion of the disjoint quadrupole excitations is 0.0043 au. Next the SAC-CI calculations have been carried out to get the electron affinities of NH_4^+. For electron-attached states, the single excitation operator (T_1) and double excitation operator (T_2) are considered as a linked cluster. In the first approximation (SAC-CI (A)) we have include triply excited configurations represented by the disjoint cluster of T_1S_2. In the second approximation (SAC-CI (B)) we consider the disjoint quadruply excited clusters of T_2S_2 in addition to T_1S_2.

The calculated Rydberg levels of NH_4 are given in Table II. The electron-correlation effects lead to greater energy lowering for low-lying Rydberg states. However, for upper states, the SAC-CI results are close to the Koopmans' values. This is due to the fact that the electron correlation in these electron-attached states is expected to be similar to that in the ground state since an electron is trapped in a very diffuse orbital. Comparing (A) and (B) approximations, we can conclude that the contribution due to the quadruply excited configurations is of little importance for NH_4.

Table III lists all transitions terminating in one of the five lowest Rydberg levels. Herzberg first assigned the Schüler band (15050–15210 cm^{-1}) to $^2E(3d) \rightarrow {}^2T_2(3p)$. This is in serious conflict with the present calculation which predicts this transition to occur at 9445 cm^{-1}. In view of the observed sizable spin doubling, the Schüler band must involve the $^2T_2(3p)$ state. Recently the rotational structure of the Schüler band of ND_4 has been fully assigned on the basis of the electronic transition $^2T_2(3p) \rightarrow 2A_1(3s)$.[14] Our cluster expansion theory predicts this transition to appear at 13796 cm^{-1}, corresponding to an error of 1200–1400 cm^{-1} (0.15–0.17 eV). The remaining error is probably about what should be expected from this level of theory. The present calculation confirms the recent assignment of the Schüler band. This then makes the assignment of the Schuster band the major problem in the interpretation of the spectrum.

The SAC-CI theory predicts that the Schuster band of $^2T_2(3d) \rightarrow {}^2A_1(3s)$ is very weak and occurs at 21750 cm^{-1}. There is a 4510-cm^{-1} discrepancy between theory and observation. The correlation effects make the disagreement worse. Watson[15] has pointed out that there are also other discrepancies between Herzberg assignment and ab initio computation, namely in rotational constants and Jahn–Teller constants. One of the $^2A_1(3s)$ and $^2T_2(3p)$ states must be the lower state for the transition since these two are the only Rydberg levels with ionization energies greater than 17000 cm^{-1}. It follows from the line widths that the Schuster band must involve a different lower state from that of the Schüler band. If it were $^2T_2(3p)$ then the upper state would have an unlikely high principal quantum number. One of the candidates is the $^2A_1(5s) \rightarrow {}^2T_2(3p)$, 15017 cm^{-1}. Raynor and Herschbach[8] have also suggested the Schuster band be assigned to $^2A_1(5s)$ or $^2A_1(6s) \rightarrow {}^2T_2(3p)$. At present the assignment of the Schuster band is not confirmed by other bands with common lower states. More extensive ab initio calculations are necessary.

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Registry No. NH_4, 14798-03-9.

Syntheses, Properties, and Molecular and Crystal Structures of $(Me_4N)_4[E_4M_{10}(SPh)_{16}]$ (E = S, Se; M = Zn, Cd): Molecular Supertetrahedral Fragments of the Cubic Metal Chalcogenide Lattice

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Contribution from the School of Chemistry, University of New South Wales, Kensington, NSW 2033, Australia. *Received October 24, 1983*

Abstract: The complexes $[S_4M_{10}(SPh)_{16}]^{4-}(Me_4N^+)$ (**3M**, M = Zn, Cd) and $[Se_4M_{10}(SPh)_{16}]^{4-}(Me_4N^+)$ (**4M**, M = Zn, Cd) are formed in 80–100% yield by the reactions of sulfur or selenium with the adamantanoid cages $[M_4(SPh)_{10}]^{2-}(Me_4N^+)$ (**2M**, M = Zn, Cd). Complexes **3M** and **4M** do not degrade to the metal chalcogenides, which also are not formed in the preparative reactions under varied conditions. All four complexes **3M** and **4M** are molecular, with the same $(\mu_3\text{-E})_4M_{10}S_{16}$ (E = S, Se) core structure, which is a supertetrahedral fragment of the cubic (sphalerite) ME lattice. In terms of expanding polyhedra the molecular structure is *octahedro*-M_6-*tetrahedro*-$(\mu_3\text{-E})_4$-*truncated tetrahedro*-$(\mu\text{-SPh})_{12}$-*tetrahedro*-M_4-*tetrahedro*-$(SR)_4$, with $\{(\mu_3\text{-E})_2(\mu\text{-SPh})_2\}$ coordination at the six inner metal atoms and $\{(\mu\text{-SPh})_3(SPh)\}$ coordination at the four outer metal atoms. The three-coordinate chalcogenide ions are located at the centers of the hexagonal faces of the $(\mu\text{-S})_{12}$ truncated tetrahedron. By inversion at the sulfur atoms of the 12 bridging thiolate ligands, 186 molecular configurational isomers can occur. Three different crystal structure determinations of **3M** (one Zn, two Cd) have revealed the occurrence of two isomers with $\bar{4}$ molecular symmetry. Crystal structure A (M = Cd), space group $I\bar{4}$, contains one isomer, while the other isomer occurs in crystal structure B (M = Zn), space group $P\bar{4}2_1c$, and crystal structure C (M = Cd), space group $I\bar{4}2m$, which is a mirror disordered form of structure B. Small distortions of the core geometry from idealized $\bar{4}3m$ (T_d) symmetry can be traced to weak repulsions between the phenyl substituents on the surfaces of the molecular anions. Low-frequency infrared and Raman data for **2M**, **3M**, **4M**, and $(Me_4N)_2[M(SPh)_4]$ are interpreted empirically. Crystal data for A: $I\bar{4}$ $a = 20.946$ (2) Å, $c = 14.779$ (2) Å, $Z = 2(\times C_{112}H_{128}Cd_{10}S_{20}N_4)$, 2971 reflections ($I > 3\sigma(I)$), Cu K$\alpha$, R (R_w) = 0.033 (0.045). B: $P\bar{4}2_1c$, $a = 19.783$ (4) Å, $c = 16.871$ (5) Å, $Z = 2(\times C_{112}H_{128}Zn_{10}S_{20}N_4)$, 1140 reflections, Mo K$\alpha$, R (R_w) = 0.044 (0.054). C: $I\bar{4}2m$, $a = 20.140$ (2) Å, $c = 16.896$ (1) Å, $Z = 2(\times C_{112}H_{128}Cd_{10}S_{20}N_4)$, 916 reflections, Mo K$\alpha$, R (R_w) = 0.042 (0.051).

Concentrated and systematic investigation during the past decade has provided detailed description of the formation and chemistry of the class of compounds $[S_wFe_x(SR)_y]^z$, anionic clusters of iron, sulfide (or selenide), and thiolate ions.[1,2] In stark contrast, comparable cluster compounds with metals other than iron were virtually unknown until 1982. The first preparations of $[Fe_4S_4(SR)_4]^{2-}$ (**1**) involved straightforward mixing of the component ions.[3] It was later shown that elemental sulfur[4] or selenium[5] could be used in the formation of **1** or its selenide analogues, in reactions such as (1) containing sufficient thiolate reductant.

$$4FeCl_3 + 14RS^- + 4S \rightarrow [Fe_4S_4(SR)_4]^{2-} + 5RSSR \quad (1)$$

More recently, Holm and co-workers[6] have examined in detail the formation of **1** and complexes $[Fe_2S_2(SR)_4]^{2-}$ from elemental sulfur and have demonstrated the intermediacy of $[Fe(SR)_4]^{2-}$ and $[Fe_4(SR)_{10}]^{2-}$ (**2Fe**). The latter complex ("ferromantane") is a member of a class $[M_4(SR)_{10}]^{2-}$ (**2M**), all with the adamantanoid cage structure.[7,8] The reaction of **2Fe** with sulfur to form **1** (reaction 2, R = Ph) proceeds cleanly, without detectable intermediates or other products, and with 100% yield based on sulfur.

$$[Fe_4(SR)_{10}]^{2-} + 4S \rightarrow [Fe_4S_4(SR)_4]^{2-} + 3RSSR \quad (2)$$

In 1982 we reported extension of the reaction of sulfur plus **2** to include the metals zinc and cadmium and the formation of

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