Cadmium Benzenethiolate Clusters of Various Size: Molecular Models for Metal Chalcogenide Semiconductors

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The optical and electrochemical properties of three cadmium benzenethiolate clusters, Cd(SPh)42-, Cd4(SPh)12-, and Cd10S5(SPh)16-, are studied as function of the cluster size. The Cd4 clusters (n = 1, 4, 10) which may represent molecular models for the semiconductor CdS show structured absorption spectra that are assigned to both ligand-to-metal charge-transfer (LMCT) and intraligand transitions. The absorption and emission bands of Cd4 are red-shifted compared to those of Cd10 and Cd16. The emission of the Cd4 clusters (n = 4, 10) is ascribed to a LMCT transition as suggested by the short luminescence lifetimes and the red shift with increasing cluster size. Illumination of the Cd4 clusters yields thianthrenes, dibenzothiophenes, and benzenethiols, the rate of photodegradation depending on the cluster size. Electrochemical studies of Cd4 show that, with increasing cluster size, the oxidation potential is shifted negative while the reduction potential is shifted positive. Both Cd4 and Cd16 form charge-transfer complexes with methyl viologen. However, steady-state illumination of these clusters in the presence of methyl viologen does not result in the formation of the methyl viologen radical cation.

Introduction

The electronic properties of bulk inorganic semiconductors are collective properties that result from the periodic arrangement of a large number of atoms or molecules in a crystal lattice. As the diameter of the semiconductor crystal size is successively decreased in the nanometer range, a gradual transition from the bulk semiconductor to the properties of very small particles (size quantization effect) occurs. This transition leads to substantial changes in both the optical and photocatalytic properties, as well as in the electrochemical behavior. A further reduction of the crystallite size finally yields molecular dimensions.

Several approaches involving colloidal semiconductor have been described in order to observe the transition region between semiconductor and molecular properties. However, the relatively broad particle distribution of most colloids complicates the quantitative correlation of the photophysical properties of the semiconductor with the crystallite size. Such a correlation is improved through rigorous control of the semiconductor particle size and dispersity. New methods for preparing and isolating semiconductor crystallites with a very narrow size distribution have been recently developed involving the synthesis of particles in vesicles, zeolites, and polymers, surface modification procedures, biosynthesis, and separation (according to size) by chromatography. The synthesis of monodisperse inorganic clusters of various sizes represents another approach. The advantage of these synthetic clusters over conventional semiconductor colloids is their well-defined size and structure. Furthermore, molecular properties such as structural rearrangements in the excited state are observed in these species. Suitable candidates for the investigation of molecular clusters are polymeric cadmium benzenethiolate complexes such as Cd(SPh)42-, Cd4(SPh)12-, and Cd10S5(SPh)16-. The crystal structures of these Cd4 clusters (n = 1, 4, 10) imply that they are well-suited as molecular models for CdS, one of the best studied semiconductors. Many structural features, i.e., the coordination environment of Cd and S, the Cd-S and Cd-C bond distances, and bond angles, are very similar in the clusters and in the bulk semiconductor.

According to these considerations the optical properties of molecular clusters of this type should be of considerable interest. We explored this possibility and selected the clusters Cd7(SPh)16, Cd9(SPh)12, and Cd10(SPh)16 as reference compounds for the present study. In addition, some relevant observations on the electrochemistry and photochemistry are also reported.

Experimental Section

Materials. Benzenethiol, cadmium nitrate tetrahydrate, triethylamine, tributylamine, tetramethylammonium chloride, sulfur, tetraethylammonium hexafluorophosphate, methyl viologen di-3
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The Journal of Physical Chemistry, Vol. 96, No. 9, 1992 3819

chloride hydrate, thianthren, and dibenzothiophene were used as received from Aldrich. All photochemical studies were carried out with spectroscopic grade solvents. The Cd₄, clusters (n = 1, 4, 10) were synthesized following the procedure described by Dance et al. and characterized by elemental analysis and FTIR spectroscopy. Methyl viologen was used as a perfluorophosphate salt.

Methods. Absorption spectra were recorded on a Hewlett-Packard 8451A single-beam spectrophotometer. Steady-state luminescence spectra were measured on an SLM Aminco 500 C spectrofluorometer. For emission measurements at room temperature, solutions of Cd₄ in CH₃CN were used, whereas luminescence measurements at 77 K were carried out with Cd₄ in the solid state (powders). Photolysis of Cd₄ in CH₃CN was carried out with a 1000-W high-pressure mercury lamp. The lamp intensity was attenuated by using calibrated metal screens.

High-resolution mass spectra (EI) were recorded on a VG Analytical mass spectrometer (ZAB 2-E). The photolyzed Cd₄ solutions were evaporated to dryness and directly analyzed by mass spectrometry (MS). Electrochemical measurements were performed with a Princeton Applied Research 175 universal programmer and a Model 173 potentiostat. The signal was recorded on a Houston Instruments 2000 X–Y recorder. A conventional single-compartment electrochemical cell equipped with either a Pt disk (oxidation) or a hanging mercury drop electrode (HMDE) (reduction), working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode was used. Tetrabutylammonium hexafluorophosphate (0.13 M) was used as supporting electrolyte and spectrograde CH₃CN (dried over molecular sieves) as solvent. All electrochemical studies were carried out under N₂.

Time-resolved emission measurements with Cd₄ (n = 4, 10) in CH₃CN were performed via time-correlated single photon counting (SPC) using a mode-locked, frequency-doubled Nd:YAG laser (Quantronix Model 416) synchronously pumping a cavity-dumped dye laser (Coherent Model 701-3D; Rhodamine 6G). The dye laser output (at 586 nm) was frequency doubled using an angle-tuned KDP crystal to produce pulses at 293 nm. The instrument response function was ca. 70 ps fwhm (full width at half-height of the maximum). The decay profiles were fit to a multi-exponential decay function using standard least-squares deconvolution techniques. The shortest lifetime which could be determined was 25 ps. The quality of the fits was evaluated by x² test and the randomness of the distribution of the residuals. The emissions of Cd₄ and Cd₁₀ were monitored at 500 and 545 nm, respectively. All measurements were carried out with air-saturated solutions at room temperature. For each luminescence lifetime, an average deviation of ±5% was observed.

The luminescence lifetimes of the Cd₄ powders were measured at 77 K using the transient diffuse reflectance spectroscopic technique. The samples were excited at 266 nm with a frequency-quadrupled Nd:YAG laser (pulse width 11 ns).

Results and Discussion

Absorption Spectra of Cd₁₀, Cd₄, and Cd₁₀. The absorption spectra of Cd₄ in CH₃CN are shown in Figure 1. Cd₄, which contains only terminal benzenethiolate ligands, exhibits an absorption band at 282 nm (ε₉₀ = 20 300 M⁻¹ cm⁻¹), whereas two maxima are observed for both Cd₄ (275 nm (ε₉₀ = 11 5900 M⁻¹ cm⁻¹) and 249 nm (ε₉₀ = 170 400 M⁻¹ cm⁻¹))² and Cd₁₀ (292 nm (ε₉₀ = 138 400 M⁻¹ cm⁻¹) and 235 nm (ε₉₀ = 178 400 M⁻¹ cm⁻¹)). Cd₄ and Cd₁₀ consist of two different types of benzenethiolate ligands, i.e., bridging and terminal benzenethiolates. Each bridging benzenethiolate ligand is bound to two Cd atoms via the lone electron pair of the benzenethiolate sulfur, whereas the terminal benzenethiolates are attached to one Cd. The pure ligand, benzenethiolate (303 nm; ε₉₀ = 13 600 M⁻¹ cm⁻¹), displays a significantly different absorption spectrum. For related anionic ligands such as phenolate, coordination with the lone electron pair is usually accompanied by a blue-shift of the intraligand absorption bands. Cd₁₀ additionally, contains some S²⁻ ligands. However, the absorption spectra of the Cd₄ clusters are most likely a composite of intraligand and ligand-to-metal charge-transfer (LMCT) transitions. Since S²⁻ and SPh⁻ have certainly very similar electronegativities (S²⁻ to and SPh⁻ to Zn²⁺), LMCT transitions should occur at comparable energies. A LMCT assignment is further supported by the apparent metal-to-ligand charge-transfer (MLCT) emission of Cd₄ and Cd₁₀. (See emission spectra and lifetimes below.)

For a series of mononuclear alkyl thiolate complexes of cadmium, absorption spectra similar to that of Cd₄ showing a broad absorption band in the 240–290-nm region with extinction coefficients in the 30 000–40 000 M⁻¹ cm⁻¹ range have been previously reported. The absorption bands of these alkyl thiolate complexes were assigned to LMCT transitions. The bulk semiconductor CdS has a band gap of 2.4 eV (onset of absorption, λ₁/₂ = 516 nm). In a molecular picture, this band gap transition can be also regarded as a LMCT transition since the filled sulfide 3p valence orbitals form the valence band of CdS, whereas its conduction band is composed of the empty Cd²⁺ 5s orbitals. The number of interacting sulfide and Cd²⁺ orbitals affects the energy of the band gap, or LMCT transition, in such a way that an increase in the number of interacting atoms, i.e., an increase in the crystallite size, leads to a red-shift of the band gap or LMCT transition. Since Cd₄(SPh)₂, a 55-atom 10-Å cluster, may be the smallest cadmium–sulfur cluster yet reported which is assumed to show both the bulk sphalerite structure and a sharp absorption band at 351 nm. A further growth of the crystallite causes a steady bathochromic shift of both the absorption onset and the luminescence as shown for thiophenol-capped size-quantized CdS particles.

![Figure 1. Absorption spectra of (a) 2.5 X 10⁻⁴ M Cd₄, (b) 6.9 X 10⁻⁴ M Cd₄, and (c) 4.9 X 10⁻⁴ M Cd₁₀ in CH₃CN at room temperature (1-cm cell).](image-url)
The absorption spectra were obtained after different illumination times: temperature phosphorescence at Kunkely, H.; Vogler, of 390 and Stokes shift of the emission was observed for tetranuclear clusters lifetimes of CdlO

5.2

min.

3

Figure 3. Photolysis of 7.4 \times 10^5 M Cdl in CH_3CN in aerated solution. The absorption spectra were obtained after different illumination times: (a) before photolysis, (b) after 2 min, (c) after 5 min, and (d) after 60 min. Excitation was always at 290 nm. The observed changes in luminescence intensity may be caused by both an inner filter effect and different luminescence quantum yields of the photoproducts.

clusters, the emission at room temperature is ascribed to an (allowed) MLCT transition as suggested by both the short lifetimes and the red-shift of the emission bands with increasing cluster size.

Photodecomposition of Cdl, Cdl, and Cdl. Illumination of Cdl in CH_3CN leads to a strong decrease of the absorption bands with time (Figure 3). Concomitantly, the luminescence of the cluster at 500 nm disappears and a new broad emission band with a maximum at 355 nm and a shoulder at 440 nm occurs (Figure 4). Oxygen does not influence the photodecomposition of the Cdl cluster: nearly identical decomposition rates are obtained with N_2, air, and O_2-saturated solutions. Furthermore, the short luminescence lifetimes of Cdl and Cdl imply that a bimolecular photoreaction with O_2 should not occur.

Cdl and Cdl exhibit photochemical behavior similar to Cdl, and the same photoproducts are most likely obtained for all the Cdl clusters as suggested by the similar absorption (Figure 3, spectrum d) and luminescence spectra (Figure 4, spectrum d) observed at long illumination times. However, the photodecomposition rates of the Cdl clusters, i.e., their photostability, are clearly affected by cluster size: Cdl decomposes twice as fast as Cdl, and photodegradation of Cdl is ca. 10 times faster than that of Cdl. This effect may be attributed to a higher degree of electronic delocalization in the bigger cluster, i.e., less probability of bond cleavages in the series Cdl, Cdl, Cdl.

Interestingly, in the case of the Cdl clusters, oxygen does not influence the photodecomposition, in contrast to previous observations with colloidal CdS which undergoes photocorrosion only in the presence of oxygen yielding H_2O_2, SO_2^-, and Cd^{2+}, which are formed in the case of the Cdl clusters, indicating that the formation of thianthrene (m/e = 216), dibenzo-thiophene (m/e = 184), and benzenethiol (m/e = 110), which were formed in comparable

(27) For Cdl in CH_3CN, a similar emission at 530 nm has been reported by Herron et al. 14


(30) The relative photodegradation rates are estimated from the illumination times from a fixed illumination source required to decrease the absorption of Cdl by 50% at the same extinction.


wave which is chemically irreversible at all scan rates up to 200 V s⁻¹. The average deviation is determined to be ±10%. *Pt-disk working electrode. †HMDE working electrode. ‡Scanned to −2.8 V vs Ag/AgCl.

yields. Absorption and emission measurements were carried out with thiannethre, dibenzoenthieno, and benzenethyl in CH₂CN in order to determine whether the absorption and emission spectra of the photolyzed Cd₄ solutions may be attributed to a superposition of the absorption and emission spectra of these compounds. Thiannethre, dibenzoenthieno, and benzenethyl all absorb at λ < 330 nm and show structured absorption spectra. However, a superposition of their absorption spectra matches the absorption spectrum of the Cd₄ photodecomposition (Figure 3d). Furthermore, a superposition of the emission spectra of thiannethre and dibenzoenthieno similarly matches the emission spectrum of the photolysis mixture formed upon illumination of Cd₄ (Figure 4d): thiannethre and dibenzoenthieno emit at 350 and 445 nm, respectively, following excitation at 290 nm. Benzenthionol shows no measurable emission. Furthermore, a yellowish precipitate was formed during the photolysis. According to ESCA, it was not CdS, but the possibility that elemental Cd was present could not be excluded.

Thus, from the MS, absorption, and emission data, we conclude that photolysis of Cd₄ leads to the formation of thiannethre, dibenzoenthieno, and benzenethyl. The insensitivity of the photodecomposition of the Cd₄ clusters toward oxygen is consistent with the observation that none of the photoproducts contain oxygen.

The photolysis is certainly not a simple process as indicated by the product analysis. However, some reasonable assumptions can be made. The related compound Hg(SPh)₂ photodecomposes to mercury and SPh⁺ radicals.54 Owing to the LMCT nature of the reactive excited state, the Cd(SPh)₂ moiety may undergo a similar reaction as primary photoprocess. The secondary reactions could lead to product formation by the following overall stoichiometries:

Cd(SPh)₂ → Cd + H₂ + thiannethre
Cd(SPh)₂ → Cd + H₂S + dibenzoenthieno

This suggestion is not unreasonable since Zn and Cd sulfur compounds are well-known to photocatalyze the dehydrogenation and subsequent carbon-carbon coupling of organic compounds.55 The formation of thiophenol may result from hydrogen abstraction of the primary thiophenolates radicals.

Electrochemical Behavior of Cd₄: Redox Potentials as a Function of Cluster Size. The redox potentials of Cd₄ are determined as a function of cluster size by cyclic voltammetry. For Cd₄, the oxidation is most likely sulfur centered and the reduction metal centered.31,32,36 All the Cd₄ clusters show a broad oxidation wave which is chemically irreversible at all scan rates up to 200 V s⁻¹. The potential at which the oxidation occurs clearly depends on the cluster size (Table I): the oxidation peak potential is shifted

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<td>Cd₄</td>
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<td>Cd₄⁺</td>
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<td>Cd₄²⁻</td>
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*Ag/AgCl reference electrode. Scan rate = 200 mV/s. Both oxidation and reduction waves were chemically irreversible at all scan rates up to 200 V s⁻¹. The average deviation is determined to be ±10%. †Pt-disk working electrode. ‡HMDE working electrode. §Scanned to −2.8 V vs Ag/AgCl.

to less positive values with increasing cluster size. A similar size dependence is observed for the reduction waves of Cd₄ which are also chemically irreversible and rather broad: an increase in cluster size leads to a shift of the reduction peak potential to less negative values. Since the electrochemistry was irreversible, the significance of the data is not quite clear. However, the observed shifts in the redox potentials of Cd₄, with cluster size are consistent with the size dependence of the optical properties of these clusters and in good agreement with theory.1,36

Reaction with Methyl Viologen: Formation of Charge-Transfer Complexes. Both Cd₄ and Cd₄⁺ form ground-state charge-transfer (CT) complexes with methyl viologen (MV²⁺) in CH₂CN as evidenced by the occurrence of a new broad absorption band upon addition of methyl viologen (Figure 5). The formation of ion-pair complexes between MV²⁺ and several anionic electron donors has been previously reported.97 For Cd₄/MV²⁺, the maximum of the CT complex is at ca. 470 nm, whereas Cd₄⁺/MV²⁺ exhibits a maximum at ca. 440 nm (Figure 5). In view of the redox potentials of the clusters (Table I), this observation seems to be surprising. However, this influence may be overcompensated by the outer-sphere reorganization energy which also depends on the size of the redox centers.37,38 This energy should increase from Cd₄ to Cd₄⁺. Furthermore, a charge effect may be important as the ground-state charge for Cd₄/MV²⁺ (2+/2+) is different from that of Cd₄⁺/MV²⁺ (4+/2+). A similar blue-shift in the absorption maximum of the CT complex upon increasing the (ground state) charge of the anionic electron donor has been recently reported for a series of CT complexes between methyl viologen and naphthalene derivatives of different charge.40 In the case of Cd₄, the methyl viologen radical cation (MV⁺⁺) is formed, either by thermal electron transfer or by photodecomposition of the extremely light-sensitive complex and subsequent reaction of the photoproducts with MV²⁺ yielding MV⁺⁺.41

Cd₄ forms a 1:1 complex with MV²⁺. The complex formation equilibrium constant and the extinction coefficient (at 470 nm) of Cd₄/MV²⁺ are determined to be 5400 ± 500 M⁻¹ and 880 M⁻¹ cm⁻¹, respectively, applying the Benesi–Hildebrand method.42 For Cd₄⁺/MV²⁺, precipitation occurs for c(MV²⁺) > c(Cd₄⁺). The complexation of Cd₄⁺ (ground-state charge 4−) with a second MV²⁺ molecule yielding a 1:2 complex leads to a charge neutralization of the adduct and subsequently to its precipitation. A

| Table I: Redox Potentials of Cd₄ in CH₂CN as a Function of Cluster Size †
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†Ag/AgCl reference electrode. Scan rate = 200 mV/s. Both oxidation and reduction waves were chemically irreversible at all scan rates up to 200 V s⁻¹. The average deviation is determined to be ±10%. †Pt-disk working electrode. ‡HMDE working electrode. §Scanned to −2.8 V vs Ag/AgCl.

Figure 5. Charge-transfer complexes of Cd₄ (counterion Me₄N⁺) and Cd₄⁺ (counterion Me₄N⁺) with MV²⁺ (counterion PF₆⁻) in aerated CH₂CN: (a) absorption spectrum of Cd₄, c(Cd₄) = 2.7 × 10⁻⁵ M; (b) absorption spectrum of Cd₄/MV²⁺, c(Cd₄) = 2.7 × 10⁻⁵ M and c(MV²⁺) = 1.0 × 10⁻⁴ M; (c) absorption spectrum of Cd₄⁺/MV²⁺, c(Cd₄⁺) = 5.2 × 10⁻⁵ M and c(MV²⁺) = 4.5 × 10⁻⁵ M.

(33) MS of Cd₄ was carried out as a control experiment and yielded different compounds: biphenyl-1,1'-diol or phenyl disulfide (m/e = 218), biphenyl-4-thiol (m/e = 186), biphenyl (m/e = 154), and benzenethyl (m/e = 110). Thus, besides benzenethyl, MS of the Cd₄ clusters leads to different products than are formed during photodecomposition. This suggests that benzenethyl might also be photochemically formed.

(38) The exact positions of the maxima of the CT complexes are obtained from the second derivative of the absorption spectra of Cd₄/MV²⁺ and Cd₄⁺/MV²⁺.
similar behavior, i.e., precipitation upon charge neutralization, is observed for many metal oxide colloids. For Cd_{10}, the extinction coefficient of the 1:1 complex at 440 nm is determined to 1250 M^{-1} cm^{-1}, assuming complete conversion of Cd_{10}. Steady-state excitation of the CT complexes (\lambda_{ex} = 450 nm) of Cd_{4} and Cd_{10} does not lead to the formation of MV^{2+}, which is presumably caused by fast back electron transfer.

Conclusions

Three cadmium benzenethiolate clusters Cd_{n} (n = 1, 4, 10) of well-defined size and structure have been examined as molecular models for the semiconductor CdS and have been characterized by spectroscopic and electrochemical methods. Cd_{4} display structured absorption spectra which are assigned to both LMCT and intraligand transitions. For the polynuclear Cd_{n} clusters (n = 4, 10), the position of the absorption maxima clearly depends on cluster size; i.e., the absorption bands of Cd_{10} are red-shifted compared to those of Cd_{4}. Similarly, Cd_{10} emits at longer wavelengths than Cd_{4}. Emission from Cd_{4} is not observed. The emission bands of Cd_{4} and Cd_{10} are ascribed to MLCT transitions as suggested by their short luminescence lifetimes and the red-shift of the luminescence with increasing cluster size. The electrochemical properties of these Cd_{n} clusters show a similar dependence on cluster size: an increase in cluster size leads to both a shift of the oxidation wave to less positive potentials and a shift of the reduction wave to less negative potentials. The size-dependent optical and electrochemical properties of the Cd_{n} clusters are qualitatively in good agreement with theory.

Photodecomposition of Cd_{4}, which is not affected by oxygen, yields thianthrene, dibenzoazophene, and benzenethiol. The rate of photodegradation also depends on cluster size; i.e., the photostability of the Cd_{4} clusters is enhanced with increasing cluster size. Cd_{4} and Cd_{10} form ground-state charge-transfer complexes with the cationic electron acceptor methyl viologen, the position of the CT band depending on the size and charge of the anionic electron donor (the Cd_{4} cluster). However, steady-state illumination of the CT complexes does not lead to the formation of the methyl viologen radical cation.

Acknowledgment. We thank F. Sabin for help with the synthesis of the Cd_{4} clusters, Dr. J. Merker for help with the electrochemical measurements, D. J. Kiserow and Dr. S. J. Atherton for help with the time-resolved emission measurements, and Drs. S. M. Hubig and B. A. Gregg for stimulating discussions. Financial support of the work at the University of Regensburg by the Deutsche Forschungsgemeinschaft and at the University of Texas by the U.S. Army Research Office is gratefully acknowledged. Initial SPC measurements were made at the Center for Fast Kinetics Research, a facility jointly supported by the National Institutes of Health and the University of Texas.

A Local Dielectric Constant Model for Solvation Free Energies Which Accounts for Solute Polarizability

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A model for treating solute polarizability in solvation processes is presented. The model, which requires little computation compared to atomic detail simulations, is based on a classical electrostatic treatment, whereby the solute polarizability is represented by local dielectric constants (LDC) rather than the usual point inducible dipoles. Point inducible dipoles and local dielectric constants are shown to be formally equivalent ways of representing solute polarizability for a simple spherical, point dipolar solute. For more realistic solute representations, however, there are some advantages to the local dielectric model. The solvation energy, change in solute dipole moment upon polarization, and the polarization energy in the LDC model are obtained self-consistently from one set of calculations involving solutions to the Poisson equation. Calculated solvation energies are compared to experimental data for water and 12 small polar solutes.

Introduction

Most available force fields that are used in molecular simulations do not treat electronic polarizability explicitly. This is due in large part to the computational expense associated with accounting for nonadditive pairwise interactions and to the theoretical difficulties associated with developing a valid model. Polarization effects are treated implicitly in that force-field parameters, such as charge and atomic radius, are generally chosen so as to reproduce experimental properties, but nevertheless, the neglect of polarizability imparts a degree of uncertainty to the conclusions that can be derived from simulations. In recent years a number of polarizable water models have been reported and have been used primarily to study pure water and ion-water interactions. However, the same effort has not yet been invested in the treatment of solute polarizability. Since it is known that dipole moments change significantly in transfers from the gas phase to polar solvents, electronic polarizability makes an important contribution to solvation free energies. In this paper we develop a treatment of solute polarizability which is based on solving the Poisson equation for a solute molecule embedded in a solvent represented as a continuous medium.

Our treatment is based on classical dielectric models which treat the solute as a cavity embedded in a dielectric medium. However, in contrast to earlier work, it is now possible to use numerical methods to account for the shape and charge distribution of the solute in atomic detail. Comparisons with experiment and with the results of microscopic simulations of the solvent suggest that the continuum treatment offers comparable accuracy for many problems with orders of magnitude less computer time. This has opened up the possibility of a simple, fast,