Raman Spectroscopic Measurements and ab Initio Molecular Orbital Studies of Cadmium(II) Hydration in Aqueous Solution

Wolfram W. Rudolph*,†

Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X5

Cory C. Pye

Department of Chemistry, University of Calgary, Calgary AB, Canada T2N 1N4

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The weak, polarized Raman band assigned to the ν_1 CdO$_6$ mode of the hexaaquo Cd (II) ion (O_h symmetry for the CdO$_6$ unit, T_h with H-atoms) has been studied over the temperature range from 25 to 152 °C. The isotropic scattering geometry in R format was employed in order to measure the true vibrational contribution of the band and account for the Boltzmann temperature factor B and frequency factor. The band profile as a function of temperature has been examined analytically to extract the parameters: position of band maximum, full width at half-height (fwhh), integral intensity of the band, and relative molar scattering coefficient, S_h, over the temperature range measured. The dependence on concentration has also been measured. The 358 cm^{-1} stretching mode of the hexaaquo Cd(II) shifts only 3 cm^{-1} to lower frequencies but broadens about 32 cm^{-1} for a 127 °C temperature increase. Two depolarized modes at 235 and 185 cm^{-1} could be assigned to $\nu_2(e_g)$ and $\nu_5(f_{2g})$, respectively. The Raman spectroscopic data suggest that the hexaaquo Cd(II) ion is thermodynamically stable in perchlorate solution over the temperature and concentration range measured. These findings are in contrast to CdSO$_4$ solutions, recently measured by one of us, where sulfate replaces a water molecule of the first hydration sphere. Ab initio geometry optimizations of [Cd(OH$_2$)$_6$$^{2+}$] were carried out at the Hartree−Fock and second-order Møller−Plesset levels of theory, using various basis sets up to 6-31+G*. The global minimum structure of the Cd(II) hexaaquo ion corresponds with symmetry T_h. The vibrational frequencies of the [Cd(OH$_6$$^{2+}$]cation were also calculated. The unscaled frequencies of the CdO$_6$ unit are lower than the experimental frequencies (ca. 16%), but scaling the calculated Hartree−Fock/MP2 vibrational frequencies (HF/6-31G*, HF/6-31+G*, and MP2/6-31G* levels) reproduces the measured frequencies. The theoretical binding energy for the hexaaquo Cd(II) ion was calculated and accounts for ca. 66% of the experimental hydration enthalpy of Cd(II). Frequency calculations are also reported for a Cd-(OH$_2$)$_{18}$$^{2+}$ cluster with 6 water molecules in the inner sphere and 12 water molecules in the outer sphere. The global minimum of this cluster corresponds with symmetry T. The ν_1 CdO$_6$ mode (unscaled) occurs at 335 cm^{-1}, quite close to the experimental value. The water molecules of the first sphere form strong H-bonds with the water molecules in the second hydration shell because of the polarizing effect of the cadmium ion. The importance of the second hydration sphere is discussed.

1. Introduction

Raman spectroscopy has been extensively used to elucidate the spectroscopic characteristics of hydrated cations in aqueous solution. However, the strong quasi elastic Rayleigh wing, which extends well over 500 cm^{-1}, prohibits the clear detection of the weak low-frequency modes of the metal aquo ions.[1,2] To circumvent this difficulty, Raman difference spectroscopy has been developed.[3−5] The subtraction of a synthetic background has also been employed to obtain base line corrected Raman spectra.[6−8]

It is well-known that dissolved ions (especially anions) alter the low-frequency Raman spectrum of water.[9] Therefore, the Raman difference spectra obtained by subtracting the spectrum of pure water from the spectrum of an aqueous solution must

be viewed with caution as pointed out in previous papers.[10,11] On the other hand, it is not necessary to employ Raman difference spectroscopy or to subtract a synthetic Rayleigh wing from the aqueous electrolyte spectra in order to obtain base line corrected spectra. It has been recently shown[12] that for accurate relative intensity measurements it is essential to normalize the low-frequency Raman data for the Bose−Einstein temperature factor, B, and a frequency factor in order to present the data in a spectral form that is directly related to the relative molar scattering factor, $S_Q(\bar{\nu}) \propto (\partial\alpha/\partial Q_i)^2$, where Q_i is the mass-weighted normal coordinate.

The reduced or $R_Q(\bar{\nu})$ spectrum was constructed after eq 1:

$$R_Q(\bar{\nu}) = I(\bar{\nu})\cdot(\bar{\nu}_0 - \bar{\nu}_i)^{-4}\cdot\bar{\nu}_i\cdot B \qquad (1)$$

Equation 1 is valid under the condition that the normal coordinates are taken to be harmonic and the polarizability expansion is terminated after the first-order term (i.e., the double

Cadmium(II) Hydration in Aqueous Solution

J. Phys. Chem. B, Vol. 102, No. 18, 1998 **3565**

harmonic approximation). The $R_Q(\bar{\nu})$ spectrum has been related to the vibrational density of states spectrum and may also be considered as the energy absorbed in a scattering process (see ref 12 and references therein).

In this study, Raman spectra of cadmium perchlorate solutions were obtained as a function of concentration and temperature in order to draw conclusions about the thermodynamic stability of the hexaaquo complex. It is well-known that perchlorate does not penetrate the first hydration sphere, which allows a vibrational characterization of the hexaaquo cadmium species. Additionally, we modeled the vibrational spectra of hexaaquo Cd(II) ion using ab initio calculations. Ab initio calculations, whose utility for predicting structural and vibrational characteristics are already well-established,[10,11] were performed on the Cd(II) hexaaquo species in order to support the spectroscopic data. For this purpose, Hartree−Fock and second-order Møller−Plesset levels of theory were employed with several different basis sets. The geometry of the hexaaquo cadmium(II) ion was optimized as explained in detail in the experimental section below.

2. Experimental Details and Data Analysis

The $Cd(ClO_4)_2$ stock solution was prepared by dissolving CdO with a stoichiometric amount of $HClO_4$. The solution was analyzed for cadmium by colorimetric titration with standard EDTA.[13] The perchlorate concentration was determined by passing a portion of a solution through a column with a cation exchanger (Dowex 50W-X8) and titrating the eluate with standardized NaOH solution. Densities were determined with a pycnometer (5 mL) at 25 °C. The stock solution was 2.51 mol/L (2.59 mol/kg).

A deuterated solution was prepared by dissolving the Cd-$(ClO_4)_2$ in D_2O (Cambridge Isotope Laboratories, 99.9%) and evaporating the water off in a vacuum distillation apparatus. This process was repeated three times. The deuteration grade, checked by Raman spectroscopy (in the OD and OH region), was better than 99.5%.

The solutions were filtered through a 0.22-μm Millipore filter into a 150-mm i.d. quartz tube.

Raman spectra were obtained with a Coderg PHO Raman spectrometer using the 488.0-nm argon ion laser line with a power level at the sample of about 0.9 W. The slit widths of the double monochromator were set normally at 1.8 cm^{-1}. The Raman scattered light was detected with a PMT cooled to −20 °C, integrated with a photon counter, and processed with a boxcar averager interfaced to a personal computer. Two data points were collected per wavenumber. To increase the signal-to-noise ratio, six data sets were collected for each scattering geometry ($I_{\parallel}$ and $I_{\perp}$). A quarter wave plate before the slit served to compensate for grating preference. $I_{\parallel}$ and $I_{\perp}$ spectra were obtained with fixed polarization of the laser beam by changing the polaroid film at 90° between the sample and the entrance slit to give the following scattering geometries:

$$I_{\parallel} = I(Y[ZZ]X) = 45\bar{\alpha}'^2 + 4\beta'^2 \qquad (2)$$

$$I_{\perp} = I(Y[ZY]X) = 3\beta'^2 \qquad (3)$$

Further spectroscopic details about the high-temperature measurement, the band fit procedure, and details about R-normalized Raman spectra are described in previous publications.[14−17]

For quantitative measurements, the perchlorate band, ν_1 ClO_4^- at 935 cm^{-1}, was used as an internal standard. From the R_{iso} spectra, the relative isotropic scattering coefficient $S(\nu_1$ $CdO_6)$

was obtained. The use of S values instead of J values has the advantage that these relative scattering coefficients can be put on an absolute scale if an absolute standard reference is considered. For further details about S values cf. ref 15.

Ab initio Hartree−Fock calculations with the STO-3G,[18] 3-21G,[19] and 6-31G*[20] basis sets were employed. Huzinaga's (433321/43211*/421) basis set was used for cadmium[21] in conjunction with the 6-31G* water basis set. The geometry was optimized with the MUNGAUSS program[22] using Davidon's optimally conditioned (OC) method,[23] and for incompletely converged geometries, the structure was further optimized with a version of Pulay's DIIS method.[24] The calculations were performed on a Silicon Graphics Indigo 2 workstation. Vibrational frequencies were computed at the 3-21G and 6-31G* levels with GAMESS-US[25] and/or Gaussian 92 (DEC AXP version).[26] The T_h structure was shown to correspond to a local minimum. To examine the effect of the basis set extension and correlation upon our structures and vibrational frequencies, Gaussian 92 was used to optimize the structure at the levels described below. First, the s shell of cadmium corresponding to the 4s orbital was split in order to determine the effect of the outermost core. This cadmium basis set (4332121/43211*/421) will be denoted cs-6-31G*. Second, a diffuse sp shell was added to the oxygen to give the standard 6-31+G* (no diffuse functions were added to cadmium since the cationic nature of cadmium renders them unnecessary). Finally, Møller−Plesset perturbation theory was used to approximate correlation effects (as MP2/6-31G* and MP2/6-31+G*). Frequency calculations could not be carried out at the MP2/6-31+G* level because of computational restrictions.

3. Results and Discussion

3.1. Raman Spectra of $Cd(ClO_4)_2$ Solution. The overall Raman spectrum of an aqueous $Cd(ClO_4)_2$ solution was analyzed between 70 and 1300 cm^{-1}. The "free" ClO_4^- ion possesses T_d symmetry and has nine modes of internal vibrations spanning the representation $\Gamma_{vib}(T_d) = a_1 + e + 2f_2$. All modes of vibration are Raman-active, but in IR only the f_2 modes are active. The spectrum of a 2.51 mol/L $Cd(ClO_4)_2$ solution shows the predicted four Raman-active bands for the tetrahedral ClO_4^-. An overview Raman spectrum in R_{iso} format at 25 °C is given in Figure 1a and in Figure 1b the expanded wavenumber region from 50 to 850 cm^{-1} is given. The ν_1 ClO_4^- band centered at 935 cm^{-1} is totally polarized ($\rho = 0.006$) (the asymmetry on the low-frequency side at 924 cm^{-1} is due to Fermi resonance of the overtone of the $\nu_2(e)$ ClO_4^- bending mode, which occurs at 464 cm^{-1}, with the fundamental $\nu_1(a_1)^{27}$), whereas $\nu_3(f_2)$ ClO_4^- centered at 1114 cm^{-1} is depolarized as are the deformation modes $\nu_4(f_2)$ ClO_4^- at 631 cm^{-1} and $\nu_2(e)$ ClO_4^- at 464 cm^{-1}.

The Raman spectra of the $Cd(ClO_4)_2$ solution were measured at three different temperatures in the wavenumber range from 70 to 800 cm^{-1}. The Raman spectra in R format were calculated for both orientations in order to get the isotropic spectrum. In the low-frequency region, it is absolutely necessary to use the R spectrum (see experimental section). In addition to the ClO_4^- bending modes $\nu_2(e)$ at 464 cm^{-1} and $\nu_4(f_2)$ at 631 cm^{-1} of the tetrahedral anion, there are two additional bands observable, namely, one at 358 ± 2 cm^{-1} (fwhh = 58 cm^{-1}) and a very weak broad band centered at 180 ± 10 cm^{-1}. The band around 190 cm^{-1} is also seen in pure water and is moderately intense but slightly polarized. This band has been assigned as a restricted translation mode of the H-bonded water molecules, and the band is anion- and concentration-dependent (cf. ref 10
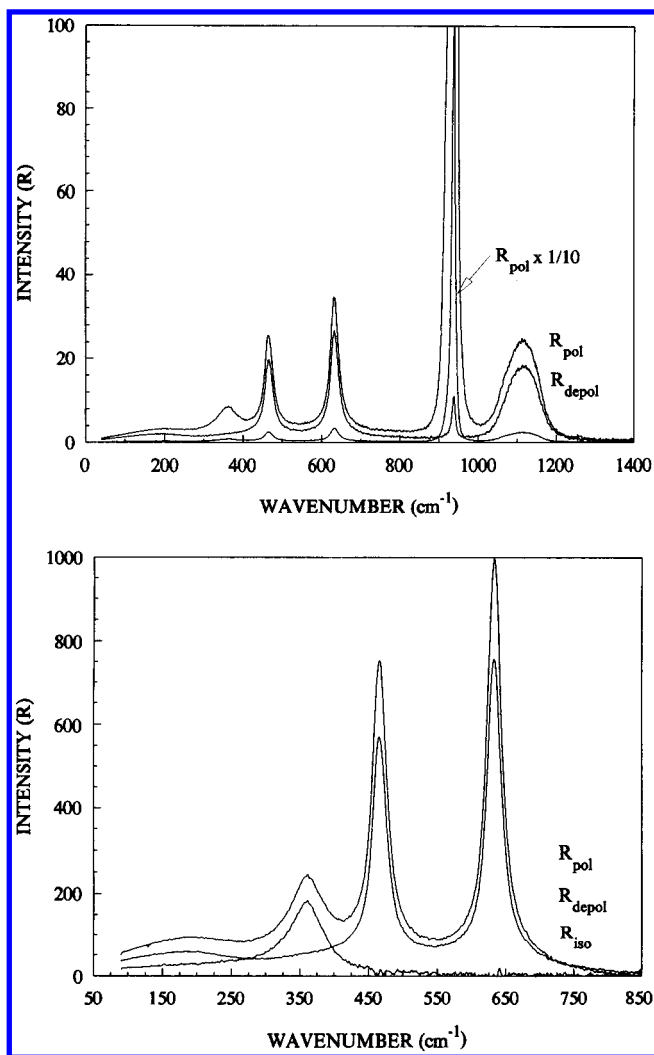
Figure 1. (a, top) Overview Raman spectrum (R_{pol} and R_{depol}) of a 2.51 mol/L Cd(ClO$_4$)$_2$ solution at 25 °C. (b, bottom) R_{iso}, R_{pol}, and R_{depol} Raman spectrum of a 2.51 mol/L Cd(ClO$_4$)$_2$ solution at 25 °C in the wavenumber range from 50 to 850 cm^{-1}.

and references therein). In concentrated Cd(ClO$_4$)$_2$ solutions other H-bonds are important, namely HOH···OClO$_3^-$. The intensity of the band due to HOH···OClO$_3^-$ is very weak in the isotropic spectrum. Because perchlorate forms a weaker hydrogen bond with water, the intermolecular H-bond stretching mode does not shift the frequency to higher wavenumbers compared to pure water.[10] It should be mentioned that ClO$_4^-$(aq) also gives rise to a new polarized band at 3595 cm^{-1} in the O−H stretching region of water. This band has been assigned to a O−H vibration of a water molecule weakly H-bonded to ClO$_4^-$(aq) (cf. ref 2 section 7.2.3 and references therein). The polarized band at 358 cm^{-1} is due to the Cd^{2+}−oxygen symmetric stretching mode of the [Cd(OH$_2$)$_6$]$^{2+}$ cation, ν_1(a$_{1g}$) CdO$_6$. The vibrational modes of the CdO$_6$ unit possess O_h symmetry under the assumption that the water molecules are treated as point masses. This assumption is certainly sufficient enough in aqueous solutions. The 15 normal modes of the CdO$_6$ unit span the representation $\Gamma_{vib}(O_h)$ = a$_{1g}$ + e$_g$ + 2f$_{1u}$ + f$_{2g}$ + f$_{2u}$. The modes ν_1(a$_{1g}$) (polarized), ν_2(e$_g$), and ν_5(f$_{2g}$) (both depolarized) are Raman-active and the modes ν_3-(f$_{1u}$) and ν_4(f$_{1u}$) are IR-active, while the mode ν_6(f$_{2u}$) is not observable in solution spectra. The following depolarized modes at 235 ± 5 and 185 ± 5 cm^{-1} could be assigned to ν_2-(e$_g$) and ν_5(f$_{2g}$), respectively. The frequency of ν_1(a$_{1g}$) CdO$_6$ does not show a significant shift with increasing temperature,
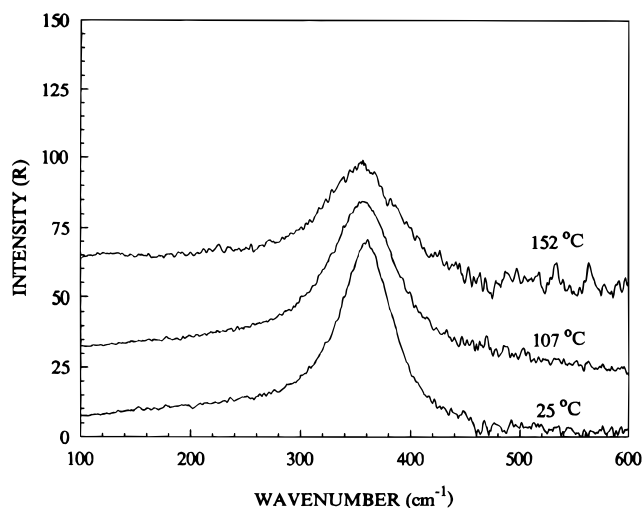

Figure 2. R_{iso} Raman spectra of a 2.51 mol/L Cd(ClO$_4$)$_2$ solution at 25, 107, and 152 °C in the wavenumber range from 100 to 600 cm^{-1}.

TABLE 1: Temperature Dependency of the ν_1 CdO$_6$ Band Parameters (Peak Maxima and fwhh in cm^{-1}) of the Hexaaquo Cadmium(II) Ion of a 2.51 mol/L (2.59 mol/kg) Aqueous Cd(ClO$_4$)$_2$ Solution

T (°C)	peak maximum (cm^{-1})	fwhh (cm^{-1})
25	358 ± 2	58 ± 2
107	356 ± 2	76 ± 4
152	355 ± 2	90 ± 4

but the half-width increases. Furthermore, the band symmetry persists, indicating that the perchlorate does not penetrate into the inner sphere of the water molecules. The frequencies and half-width for the symmetric stretch of the cadmium hexaaquo complex (ν_1 CdO$_6$) as a function of temperature are given in Table 1. These Raman spectroscopic results show, clearly, that over the applied temperatures the hexaaquo complex remains stable, in contrast to the sulfate system, in which a sulfate−water exchange is taking place.[14]

The position of the symmetric stretching mode of [Cd-(OH$_2$)$_6$$^{2+}$], ν_1 CdO$_6$ for a 2.51 mol/L Cd(ClO$_4$)$_2$ at 25 °C, is 358 cm^{-1} (fwhh = 58 ± 2 cm^{-1}), at 107 °C is 356 cm^{-1} (fwhh = 76 ± 4 cm^{-1}), and at 152 °C is 355 cm^{-1} (fwhh = 90 ± 4 cm^{-1}). The R_{iso} spectra of the 2.51 mol/L Cd(ClO$_4$)$_2$ solution at these three different temperatures are given in Figure 2.

For low-frequency vibrations the excitation of "hot bands" must be considered. At the lowest temperature investigated, 12% of the molecules occupy the $v = 1$ level of ν_1 CdO$_6$, and this fraction increases about 22% over the temperature range. Thus transitions 2 ← 1 must be contributing to the observed band profile. The small 3 cm^{-1} shift to lower frequencies of the band maximum may arise from these transitions, but the anharmonicity of the potential surface cannot be large, as can be deduced from this small frequency shift as a function of temperature.

Most Raman lines are homogeneously and inhomogeneously broadened, due to the time dependence of fluctuation of the probe molecule's surrounding interaction, and are observed as an ensemble average. Only a few systems such as N$_2$ and CCl$_4$ are solely homogeneously broadened. Separation of the homogeneous and inhomogeneous broadening contributions to the total vibrational line width was first performed by the combined study of spontaneous isotropic Raman scattering and picosecond coherent scattering by Laubereau at al.[28] Most theoretical models have concentrated on the mechanism of dephasing relaxation, like the description by Schweizer and Chandler

Cadmium(II) Hydration in Aqueous Solution

J. Phys. Chem. B, Vol. 102, No. 18, 1998 **3567**

(SC).[29] The $\nu_1 CdO_6$ mode in aqueous solution is certainly strongly inhomogeneuosly broadened like other modes in H-bonded systems (it should be mentioned that also the mode in non-H-bonded systems are inhomogeneously broadened; cf. Harris and co-workers.[30]). The broadening mechanisms in systems with preferentially homogeneously broadened modes described by Griffiths et al.,[31] namely, increase in collisional frequency and vibrational energy transfer, are certainly playing a role as well. The processes: $2M(v = 1) \rightarrow M(v = 0) + M(v = 2)$ and $M'(v = 1) + M(v = 0) \rightarrow M'(v = 0) + M(v = 1)$ would decrease the mean lifetime in the excited state, τ, and increase the full width at half-height (fwhh). The fwhh ($\Gamma_{1/2}$) is related with the mean lifetime, τ, through $\Gamma_{1/2} = (\pi c \tau)^{-1}$, assuming the line width is measured in the pure isotropic scattering orientation (R_α). The isotropic spectrum in R format is independent of reorientational changes, and thus contributions to the profile from such motions can be neglected as well as the temperature influence, the fourth power scattering factor, and the frequency factor (see experimental section). The band profile in I format is not appropriate at the low-frequency range as pointed out earlier.[10,11]

The exchange rate of the water molecules for Cd(II) is fast (ca. 10^8 s^{-1}, cf. Petrucci[32]), but even with increase in temperature the exchange rate will be still slow compared with the time scale of vibrational spectroscopy (cf. results of ultrafast exchange and influence on half width of Raman lines[33] and an application of ultrafast H_3O^+ exchange in aqueous phosphoric acid solution[34]). Certainly the inhomogeneous broadening due to strong intermolecular interactions plays the major role for the $\nu_1 CdO_6$ mode in this H-bonded system (cf. the results of our ab initio calculations in Section 3.3, which demonstrate the strong H-bonding between first- and second-sphere water molecules). Both factors (homogeneous and inhomogeneous broadening) will be temperature-dependent, but theories such as the SC theory mentioned above are only valid for homogeneously broadened lines and therefore cannot be applied for the $\nu_1 CdO_6$ mode in aqueous solution.

In the $Cd(ClO_4)_2$–D_2O system, this band is observable at 342 cm^{-1} in accordance with the expected isotope shift:

$$\nu_1[(Cd(OD_2)_6^{2+}] = \sqrt{18.02/20.03} \cdot \nu_1[(Cd(OH_2)_6^{2+}]$$

$$= 0.948 \cdot 358 \text{ cm}^{-1} = 340 \text{ cm}^{-1} \qquad (4)$$

Relative intensity measurements for three different $Cd(ClO_4)_2$ solutions as a function of concentration (2.51, 1.00, and 0.5 mol/L) yield a relative scattering coefficient for the ν_1 Cd–O mode, $S_h = 0.041$. The perchlorate band, $\nu_1(a_1)$ ClO_4^- at 935 cm^{-1}, served as the reference band. The S_h value is defined as the corrected relative scattering efficiency of the $[M(OH_2)_n]^{m+}$ aqueous metal hydrates in ref 2 (it should be noted that the S_h values in ref 2 are compared to $\nu_1(a'_1)$ NO_3^- and are taken as percentage). Furthermore S_h is defined in the pure isotropic R spectrum. For the ν_1 Zn–O mode, a S_h value of 0.032[16] was found and for the ν_1 Hg–O mode a value of 0.143,[35] reflecting the increase in the softness of these group IIb metal ions with increase in the periodic number. It should be mentioned that Cd^{2+} forms strong complexes with halide ions (CdX^+, CdX_2, CdX_3^-, and CdX_4^{2-}, X = Cl^-, Br^-, and I^-) in order of increasing complex stability from Cl^- to I^- (cf. for instance, Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley: New York, 1988; p 608, Table 16-7.).

As a summary, these Raman spectroscopic data show clearly that over the applied temperature range the hexaaquo complex remains stable. However, in the sulfate system, a water–ligand

TABLE 2: Optimized Geometry of Hexaaquo Cd(II)

	Cd–O (Å)	O–H (Å)	H–O–H (deg)	$-E$ (hartrees)
HF/STO-3G	2.158	0.980	104.4	5861.440 983
HF/3-21G	2.291	0.968	109.6	5893.514 809
HF/6-31G*	2.353	0.954	106.5	5916.759 302
HF/cs-6-31G*	2.350	0.953	106.5	5916.763 839
HF/6-31+G*	2.359	0.954	106.6	5916.780 850
MP2/6-31G*	2.327	0.974	105.9	5917.981 003
MP2/6-31+G*	2.338	0.977	105.9	5918.029 098

TABLE 3: Predicted Geometry and HF/MP2 Energy for Monomeric Water[a]

H_2O	H–O bond length (Å)	H–O–H (deg)	energy (au)
HF/6-31G*	0.9473	105.50	−76.010 746 5
HF/6-31+G*	0.9476	106.52	−76.017 743 2
MP2/6-31G*	0.9687	103.97	−76.196 847 8
MP2/6-31+G*	0.9709	105.47	−76.209 776 6

[a] Geometrical parameters of water determined by microwave spectroscopy: O–H = 0.9572 ± 0.0003 Å; HOH = 104° 31′ ± 3′ (taken from: Benedict, W. S.; Gailar, N.; Plyler, E. K. *J. Chem. Phys.* **1956**, *24*, 1139).

exchange takes place.[14] However, it should be mentioned that, in highly concentrated $Cd(ClO_4)_2$ solutions ($m_{Cd-perchlorate} \geq 8$ mol/kg), the perchlorate ion is forced to penetrate the first hydration sphere of Cd(II) because of a lack of water for complete hydration. (Cf. the solubility curve of $Cd(ClO_4)_2$ (in wt %) as a function of temperature is given in *Gmelin-Handbuch für Anorganische Chemie*, Nr. 33, Cd Erg., Verlag Chemie: Weinheim/Bergstrasse; p 514, Figure 131).

3.2. Ab Initio Calculations of $[Cd(OH_2)_6^{2+}]$. The results of our ab initio calculations for $[Cd(OH_2)_6^{2+}]$ and for comparison for monomeric water are given in Tables 2–5. Tables 2 and 3 present the results of our geometry optimization for $[Cd(OH_2)_6^{2+}]$ and H_2O, respectively. Tables 4 and 5 present the predicted frequencies, intensities, and force constants for the Cd(II) hexaaquo complexion and monomeric water. Our ab initio calculations demonstrate that the cadmium–hexaaquo complex is a stable species and the global minimum is in accordance with T_h symmetry (for a model, see Figure 3). The equilibrium cadmium–oxygen distance, r_e, of 2.35 Å at the 6-31G* level is in agreement with the diffraction result of 2.31 ± 0.02 Å.[36] (It has to be noted that diffraction measurements give r_a, the averaged position of atoms at the temperature of experiment, and not r_e.) However, the calculated frequency (HF/6-31G*) is almost 58 cm^{-1} (ca. 16%) smaller than the observed symmetric stretching mode, ν_1 CdO_6 at 358 cm^{-1}. This poor agreement could be due to a deficiency of the theory (such as an inadequate basis set or neglect of correlation). This is not thought to be the case, as HF/6-31G* is usually sufficient for describing the geometry and (scaled) frequencies. Nevertheless, the effect of extending the basis set was examined in order to rule out this possibility. Splitting the core decreased the Cd–O distance by only 0.002 Å and barely changes the vibrational frequencies. The addition of diffuse functions to oxygen has a larger effect, increasing the Cd–O distance by almost 0.007 Å and decreasing the frequency of ν_1 CdO_6 to 293 cm^{-1}. The effect of correlation was then ascertained by performing MP2/6-31G* and MP2/6-31+G* calculations. The Cd–O bond shortens to 2.3380 and 2.3266 Å, respectively, improving the agreement with the experiment. The MP2 frequencies were calculated only with the 6-31G* basis set (ν_1 CdO_6 to 312 cm^{-1}, cf. results in Table 4), as 6-31+G* frequencies proved too difficult. We may estimate them by assuming a linear relationship holds between Cd–O bond length and the vibrational frequency. This relationship holds if we consider the frequen-

TABLE 4: Unscaled HF/6-31G*, HF/6-31+G*, and MP2/6-31G* Frequencies (in cm^{-1}), Intensities and Force Constants of the Modes of the Hexaaquo Cd(II) Ion; $\Gamma_{vib} = 3a_g(R, tp) + a_u(n.a.) + 3e_g (R, dp) + e_u(n.a.) + 5f_g(R, dp) + 8f_u (IR)^a$

HF/6-31-G* ^{b}			HF/6-31+G* ^{b}			MP2/6-31G* ^{c}				
freq.	I	f.c.	freq.	I	f.c.	freq.	I	f.c.	mode	activity
64.9	0.036	0.0116	73.7	0.033	0.015	38.6		0.004	δ O−Cd−O(f$_g$)	Ra
49.8	3.07	0.0066	55.3	2.37	0.008	45.2	5.45	0.006	δ O−Cd−O(f$_u$)	IR
71.4	0.75	0.0175	76.5	0.91	0.020	62.4	0.06	0.014	δ O−Cd−O(f$_u$)	i.a.
174.4		0.018	193.5		0.022	185.6		0.020	τ HOH(e$_u$)	n.a.
231.5	3.7	0.032	250.4	1.039	0.038	237		0.034	τ HOH(f$_g$)	Ra
231.9	0.047	0.185	227.5	0.02	0.178	243.4		0.202	ν_{as}Cd−O(e$_g$)	Ra
279.2	1.5	0.291	275.0	0.16	0.295	286.9	43.2	0.192	ν_{as}Cd−O(f$_u$)	IR
298.6	0.16	0.312	292.9	0.22	0.301	311.5		0.340	ν_s Cd−O(a$_g$)	Ra
337.5		0.068	358.7		0.076	351.7		0.073	τHOH(a$_u$)	n.a.
393.4	4.47	0.103	411.8	1.77	0.113	334.7		0.073	ωHOH(f$_g$)	Ra
423.1	447	0.122	437.8	415	0.130	360.8	456	0.097	ωHOH(f$_u$)	IR
534.1	0.217	0.193	535.8	0.008	0.194	504.1		0.174	ρHOH(f$_g$)	Ra
534.8	539	0.196	537.3	522	0.198	508.6	415	0.180	ρHOH(f$_u$)	IR
1831.2	539	2.149	1824.8	3.3	2.134	1726.8		1.916	δHOH(e$_g$)	Ra
1832.0	283	2.148	1825.5	298	2.133	1728	237	1.915	δHOH(f$_u$)	IR
1837.3	0.39	2.155	1831.2	0.032	2.140	1734		1.920	δHOH(a$_g$)	Ra
4018.6	47	9.947	4005.7	38	9.883	3744.7		8.632	ν_sOH(e$_g$)	Ra
4020.1	291	9.957	4007.0	273	9.891	3745.6	233	8.638	ν_sOH(f$_u$)	IR
4027.9	266	10.00	4014.1	329	9.933	3751.2		8.670	ν_sOH(a$_g$)	Ra
4110.3	71	10.79	4098.1	55	10.731	3848.2		9.453	ν_{as}OH (f$_g$)	Ra
4110.9	484	10.80	4098.7	490	10.735	3848.6	402	9.455	ν_{as}OH(f$_u$)	IR

^{a} R = Raman active with tp = totally polarized and dp = depolarized; IR = infrared active and n.a. mode not active. ^{b} For each individual basis set/level of theory, the IR activities (km/mol) and the Raman intensities (Å^4/au) are given (because of the mutual exclusion rule only modes with subscript g are Raman active and modes with subscript u IR active); in the third column, the force constants (mdyn/Å) are given. ^{c} For MP2 calculations, no Raman activities were calculated.

TABLE 5: Predicted Harmonic Frequencies (cm^{-1}), the IR (km/mol) and Raman (Å^4/amu) Intensities and Force Constants (mdyn/Å) of Water

	HF/6-31G*				HF/6-31+G*				MP2/6-31G*			MP2/6-31+G*		
mode	freq.	IR	R	f.c.	freq.	IR	R	f.c.	freq.	IR	f.c.	freq.	IR	f.c.
ν_3(b$_2$)	4188.7	5.1	39.1	11.19	4190.2	58.1	39.1	11.21	3916.2	38.7	9.771	3893.6	70.5	9.672
ν_1(a$_1$)	4070.4	18.2	75.5	10.21	4071.1	23.4	74.8	10.20	3774.8	5.5	8.773	3747.9	11.6	8.644
ν_2(a$_1$)	1826.5	107	5.70	2.128	1796.6	119	3.0	2.060	1735.5	88.6	1.922	1681.8	106	1.806

^{a} Experimental frequencies for water are 3756, 3657, and 1595 cm^{-1}, and their harmonic values are 3943, 3832 and 1649 cm^{-1}. The data were taken from: Hoy, A. R.; Mills, I. M.; Strey, G. *Mol. Phys.* **1972**, *24*, 1265. Note that the MP2 frequencies reproduce the harmonic experimental frequencies quite well, while the frequencies at the HF level are by ca. 10% too high.
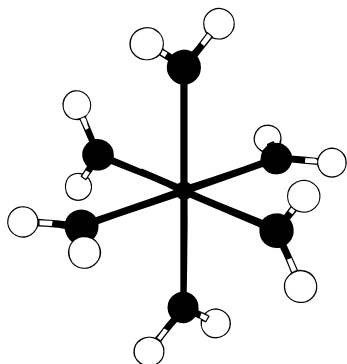
Figure 3. Structural model for Cd(OH$_2$)$_6^{2+}$, Cd[6 + 0].

cies and geometries at HF/3-21G, HF/6-31G*, and HF/6-31+G*. The MP2/6-31G* frequency falls underneath this line by several wavenumbers, so a second line with the same slope through the MP2/6-31G* point was used. The estimated MP2/6-31+G* frequency is thus 304 cm^{-1}. Considering either our best actual values or the estimated value, ν_1 CdO$_6$, the total symmetric stretching frequency of the hexaaquo complex is underestimated. Clearly, the theory is not to blame. The only conclusion reachable from the above data is that the cluster model used to calculate the frequencies is insufficient. (It is known that even the strongest bonds include anharmonic contributions. The dilemma is that for the weak CdO$_6$ mode

no such data are available, while for monomeric water, the anharmonicity corrections are well-known and therefore the ab initio frequencies, which can at best reproduce harmonic frequencies, can be compared directly to (harmonic) experimental frequencies. From literature compilations, it can be deduced that the harmonic frequency of ν_1 CdO$_6$ should be ca. 10 cm^{-1} higher than the measured one (cf. Jones, L. H. *Inorganic Vibrational Spectroscopy*; Marcel Dekker: New York, 1971; Vol. 1, Chapter 1) and therefore the anharmonicity cannot be the deeper reason for the above-described deviation. Compare also the small temperature influence of ν_1 CdO$_6$, as described in Section 3.1.) The six water molecules represent only the first hydration shell. In solution, these water molecules form strong H-bonds with the water molecules in the second hydration shell because of the polarizing effect of the cadmium ion. The only other recent calculations on [Cd(OH$_2$)$_6^{2+}$] are given in refs 37−42. Strömberg and co-workers[37] use in-house effective core potentials (ECPs) and split-valence basis sets for Cd (Kr core) and O. With a frozen-water geometry, a Cd−O bond length of 2.32 Å and frequencies for the a$_g$ and e$_g$ modes at 312 and 184 cm^{-1}, respectively, were obtained. Probst[38] uses the Hay-Wadt ECP for Cd and the Stevens ECP for O, with SVP-quality basis sets. Here, the Cd−O bond length was calculated to be 2.331 Å. The symmetry for the Cd hexaaquo ion was assumed to be D_{2d}, clearly in contrast to our result, and no frequency calculations were performed to confirm that

Cadmium(II) Hydration in Aqueous Solution

J. Phys. Chem. B, Vol. 102, No. 18, 1998 **3569**

TABLE 6: Structural Parameters, Energy (hartrees), and Thermodynamic Parameters (ΔE_B, Binding Energy, at 0 K, and $\Delta H^\ominus$, the Enthalpy of the Cluster Formation at 298.15 K) Calculated for the Cd(OH$_2$)$_{18}^{2+}$ Cluster Denoted Cd[6 + 12]

	HF/3-21G	HF/6-31G*	HF/6-31+G*
bond length (in Å)			
Cd—O (first water sphere)	2.276	2.332	2.341
Cd—O (second water sphere)	4.276	4.482	4.513
O—H (first water sphere)	0.975	0.957	0.957
O—H(A) (second water sphere)	0.983	0.956	0.956
O—H(B) (second water sphere)	0.966	0.950	0.950
HO1···H bond length	1.776	1.936	1.951
angle Θ (deg)			
HOH angle (first water sphere)	113.5	108.77	108.7
HOH angle (second water sphere)	111.8	107.01	107.2
energy (hartrees)	−6801.105 947 9	−6829.214 709 3	−6829.293 53 3
ΔE_B (0 K) (kJ/mol)	−3056.11	−2064.79	−1941.08
$\Delta H^\ominus_{298}$ (kJ/mol)	−2867.33	−1920.38	−1845

this structure was a minimum. Therefore the claimed global minimum turns out to be a saddle point. Garmer and Krauss[39] use the small-core Stevens Cd and O ECPs with the DZP basis set and obtained a Cd—O length of 2.37 Å. Garmer and Gresh[40,41] use the Stevens small-core ECPs and basis sets for Cd and O with a DZ2P basis set and obtained a Cd—O bond length of 2.36 Å. Åkesson et al.[42] use a Hay—Wadt large-core Cd ECP with a DZ+ diffuse-p basis set for O, giving a Cd—O distance of 2.308 Å and a ν_1 CdO$_6$ frequency of 322 cm^{-1}. These literature data[37,40−42] are consistent with our all-electron HF/3-21G and HF/6-31G* results and also underestimate the ν_1 CdO$_6$ frequency.

Comparison with our earlier study of the lithium tetraaquo ion[11] suggests that the model is indeed the problem for the reason cited above (it does not represent the effect of the second hydration sphere on the symmetric stretching mode of Cd—O). In the case of lithium ion, including the second hydration sphere, denoted [Li(H$_2$O)$_4^+$](H$_2$O)$_4$, or more concisely, [4 + 4], the frequency of the ν_1 LiO$_4$ mode by 18 cm^{-1} (7%), relative to the [4 + 0] species. Obtaining a more accurate ν_1 CdO$_6$ frequency necessitates the inclusion of an explicit second solvation sphere in the ab initio calculation.

Our preliminary calculations (HF/6-31G*) of the magnesium [6 + 12] aquo complex[43] corrects the ν_1 MgO$_6$ frequency for the effect of strong hydrogen bonding to the second hydration sphere, clearly a result of the strong polarization of the hydrogens of the inner-sphere water molecules, and reproduces the ν_1 MgO$_6$ frequency almost perfectly. (The H···O hydrogen bond distance is 1.889 Å compared with 2.021 Å in the water dimer.[44]) Other metal aquo complexes exhibit the same behavior, namely, Zn^{2+}, Be^{2+}, Ga^{3+}, In^{3+}, and Al^{3+}.[45] Recently, we could manage an ab initio calculation at the HF/3−21G, HF/6-31G*, and HF/6-31+G* levels of a octadeca aquo Cd(II) cluster with 12 water molecules in the second and 6 waters in the first hydration sphere. The local minimum of the cluster corresponds to T symmetry. Structural parameters calculated at the HF/3-21G, HF/6-31G*, and HF/6-31+G* levels are given in Table 6. The Cd—O distances for Cd[6 + 0] are 2.291, 2.353, and 2.359 Å at the HF/3-21G, HF/6-31G*, and HF/6-31+G* levels, respectively, and for Cd[6 + 12] the corresponding distances (bond length between Cd(II) and the oxygen of the first-sphere water, Cd—O$_{first sphere}$) are 2.276, 2.332, and 2.341 Å, respectively. For the latter species, the Cd—O distances between Cd(II) and the oxygen of the second sphere (Cd—O$_{second sphere}$) are 4.276, 4.482, and 4.513 Å, respectively. These Cd—O$_{second sphere}$ bond lengths are primarily determined by H-bond distances between water molecules of the first and second sphere of 1.776, 1.936, and 1.951 Å, respectively. These results illustrate the inadequacy of the HF/3-21G basis set. It is well-known that the 3-21G basis set overestimates the strength

of the H-bonds.[45] The slight, but subtle, decrease in Cd—O distance in the first hydration sphere of the cluster Cd [6 + 12] arises because the water molecules in the second sphere polarize the waters in the first shell, so that the interaction of Cd^{2+} and the first-shell water molecules is enhanced. HF/6-31+G* results of the octadeca cluster are also included in Table 6. Although the geometries are very similar to the HF/6-31G* results, the energies are much improved, since the addition of diffuse functions largely eliminates basis set superposition error (BSSE). It should be noted that the Cd(II) cluster described in this paragraph is to the best of our knowledge the first report of ab initio calculations, which explicitly introduces a complete second hydration sphere for a hexahydrate. The ν_1 CdO$_6$ frequency equal to 335 cm^{-1} (HF/6-31G* level) reproduces the measured frequency much better, and the predicted frequencies for the Cd[6 + 12] cluster are given in Table 7. The structural model of the Cd(H$_2$O)$_{18}^{2+}$ cluster is given in Figure 4.

A more tractable solution, using only the Cd[6 + 0] cluster results, would be to scale the frequencies for the influence of the second hydration sphere. The scaling of the HF frequencies is a widely employed procedure, especially for organic molecules, and has its value for big molecules, which cannot be calculated by high-level theory/basis set level. Typically Hartree—Fock frequencies are scaled by an empirical factor of 0.9 in an attempt to reproduce experimentally observed values. This scaling factor is used to account for the deficiency of the Hartree—Fock model. The HF/6-31G* scale factors for both high and low frequencies are similar.[46] For water at HF/6-31G*, we found an optimal scaling factor of 0.895 through standard least-squares fitting.

Two other scaling models are considered. The first approach employing eq 5

$$\nu_{exptl} = \nu_{HF} \cdot e^{-\alpha \cdot \nu_{HF}} \tag{5}$$

was used for zinc hydrates[47] with different basis sets. Our agreement with α is good ($\alpha = 3.05 \times 10^{-5}$ cm), but the errors in the predicted frequencies are unacceptably large. The second approach employing eq 6

$$\nu_{exptl} = A \cdot \nu_{HF} \cdot e^{-\alpha \cdot \nu_{HF}} \tag{6}$$

where $\alpha = 1.2 \times 10^{-5}$ cm and $A = 0.855$, gave much smaller errors but may be unsuitable for the low-frequency modes.

In Table 4, the unscaled HF/6-31G*, HF/6-31+G*, and MP2/6-31G* frequencies of the hexaaquo cadmium(II) ion are given. This ion possesses T_h symmetry, and the 51 normal modes having the representation $\Gamma_{vib} = 3a_g + a_u + 3e_g + e_u + 5f_g + 8f_u$. The vibrational modes of the CdO$_6$ unit can also be treated as having O_h symmetry under the assumption that the water

TABLE 7: Unscaled HF/6-31G* Frequencies, Intensities (IR, Raman), and Force Constants of the Octadecaaquo Cadmium(II) (Γ_{vib} = 13a (R) + 13e (R) + 40f (IR, R) and Γ_{CdO6} = a (R) + e (R) + 4f (IR, R))[a]

freq.	IR	Raman	f.c.	char.	assignment
21.3	0.027	0.0814	0.0013	f	$(H_2O)_3$ twist
35.6	0	0.156	0.0080	a	$(H_2O)_3$ twist
37.5	0	0.237	0.0045	e	$(H_2O)_3$ trans
41.0	6.50	0.018	0.0067	f	$(H_2O)_3$ trans
49.0	0.221	0.029	0.0125	f	$(H_2O)_3$ trans
66.6	2.67	0.0004	0.0171	f	translational mode + CdO_6 def.
85.4	0.150	0.040	0.0272	f	translational mode + CdO_6 def.
113.8	6.13	0.017	0.066	f	CdO_6 def, coupled
115.8	0	0.192	0.039	e	$(H_2O)_3$ rock
128.3	1.44	0.114	0.052	f	$(H_2O)_3$ rock
140.2	0	0.004	0.067	a	$(H_2O)_3$ H-bond sym. + CdO_6 sym. str.
150.1	0.061	0.20	0.0596	f	$(H_2O)_3$ H-bond asym.
171.9	38.54	0.057	0.093	f	$(H_2O)_3$ H-bond asym.
175.1	0	0.098	0.092	e	$(H_2O)_3$ H-bond asym
196.8	0.256	0.0117	0.117	f	$(H_2O)_3$ H-bond sym
198.2	0	0.051	0.113	a	$(H_2O)_3$ H-bond sym
227.8	0.002	0.000	0.156	f	CdO_6 def.
235.2	2.18	0.051	0.148	f	CdO_6 def.
282.9	0	0.107	0.178	e	CdO_6 stretch + H_2O (2) lib.
315.5	0.565	1.773	0.097	f	H_2O (2) lib.
318.5	42.143	0.200	0.072	f	H_2O (2) lib.
330.9	0.34	3.25	0.124	f	CdO_6 stretch
331.9	0	0.057	0.081	e	H_2O (2) lib.
335.0	0	0.315	0.204	a	CdO_6 stretch
376.2	113.9	1.93	0.109	f	H_2O (2) lib.
398.0	0	0.002	0.106	a	H_2O (2) lib. + CdO_6 stretch
418.3	48.52	0.77	0.112	f	H_2O (2) lib.
442.9	278	1.105	0.125	f	H_2O (2) lib.
447.4	0	0.76	0.126	e	H_2O (2) lib.
476.9	4.30	0.443	0.142	f	H_2O (2) lib.
481.7	1.715	1.71	0.143	f	H_2O (2) lib.
490.2	0	1.56	0.149	e	H_2O (2) lib.
528.3	447	0.24	0.182	f	H_2O (2) lib.
544.5	0	0.21	0.190	a	H_2O (2) lib.
547.8	143	2.45	0.189	f	H_2O (1) wag
570.0	0	0.022	0.208	a	H_2O (1) twist
628.4	1.067	0.71	0.249	f	H_2O (1) twist
636.3	0	0.147	0.251	e	H_2O (1) twist
701.2	1013	2.78	0.314	f	H_2O (1) wag
754.0	261.3	0.182	0.353	f	H_2O (1) rock
812.4	457.5	0.814	0.417	f	H_2O (1) lib.
840.3	61.8	0.258	0.440	f	H_2O (2) lib
840.4	0	0.163	0.460	e	H_2O (1) rock + H_2O (1) lib
1826.3	122.8	0.506	2.117	f	HOH bending outer sph.
1826.4	0	9.85	2.117	e	HOH bending outer sph.
1827.0	94.3	2.154	2.116	f	HOH bending outer sph.
1837.7	127.5	0.656	2.137	f	HOH bending outer sph.
1837.8	0	0.684	2.144	a	HOH bending outer sph.
1865.5	0	1.724	2.208	e	HOH bending inner sph.
1872.3	289.7	0.014	2.221	f	HOH bending inner sph.
1887.0	0	0.0086	2.250	a	HOH bending inner sph.
3920.7	0	46	9.466	e	OH str. sym. inner sph.
3927.5	287.8	46	9.503	f	OH str. sym. inner sph.
3950.7	0	940	9.653	a	OH str. sym. inner sph.
3956.0	211	9.04	9.715	f	OH str. asym. inner sph. + sym. outer sph.
3962.6	0	14.14	9.712	a	OH str. asym. inner sph. + sym. outer sph.
3973.5	119	0.10	9.908	f	OH str. asym. inner sph. + sym. outer sph.
3994.1	1777.5	17.9	9.9273	f	OH str. asym. inner sph. + sym. outer sph.
4000.6	0	72	9.901	e	OH str. asym. inner sph. + sym. outer sph.
4023.5	539	112.3	10.304	f	OH str. asym. inner sph. + sym. outer sph
4024.8	12.8	7.12	10.237	f	OH str. asym. inner sph. + sym. outer sph
4125.4	30.5	58	10.816	f	OH str. asym. outer sph.
4126.1	647	3.58	10.822	f	OH str. asym. outer sph.
4126.2	0	124.3	10.823	e	OH str. asym. outer sph.
4127.8	87.2	6.52	10.817	f	OH str. asym. outer sph.
4128.4	0	159	10.820	a	OH str. asym. outer sph.

[a] Harmonic frequencies in cm^{-1}; IR = infrared intensities in km/mol; Raman scattering activities in Å^4/au; force constants in mdyn/Å.

molecules are seen as point masses. This assumption is certainly sufficient enough in aqueous solutions, and as an example the vibrational analysis of the $[Al(OH_2)_6]^{3+}$ ion (AlO_6 unit) was carried out on the basis of O_h symmetry (compare results in ref

48). The 15 normal modes of the CdO_6 unit (O_h symmetry) span the representation Γ_{vib} = a_{1g} + e_g + 2f_{1u} + f_{2g} + f_{2u}. The modes $\nu_1(a_{1g})$ (polarized), $\nu_2(e_g)$, and $\nu_5(f_{2g})$ (both depolarized) are Raman-active and the modes $\nu_3(f_{1u})$ and $\nu_4(f_{1u})$ are IR-active,
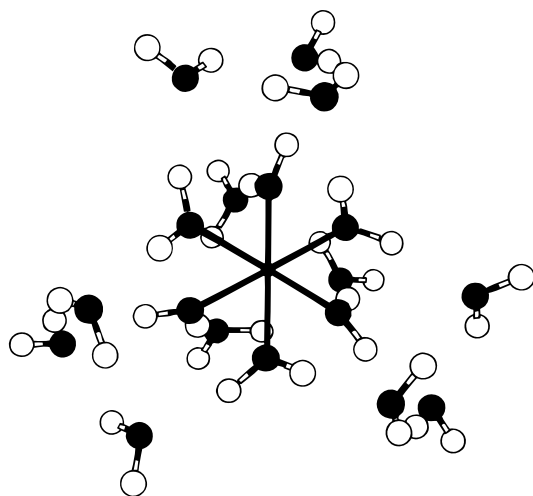
Cadmium(II) Hydration in Aqueous Solution

J. Phys. Chem. B, Vol. 102, No. 18, 1998 **3571**

Figure 4. Structural model for $Cd(OH_2)_{18}^{2+}$, Cd[6 + 12].

TABLE 8: CdO_6 Skeleton Modes (CdO_6 Unit Possesses O_h Symmetry), Experimental Frequencies, and Calculated HF/6-31G*, HF/6-31+G*, and MP2/6-31G* Frequencies (Scaled) in Aqueous $Cd(ClO_4)_2$ Solution

assignment and activity	exptl freq. (cm^{-1})	HF/6-31G* scaled freq. (cm^{-1})	HF/6-31+G* scaled freq. (cm^{-1})	MP2/6-31G* scaled freq. (cm^{-1})
$\nu_1(a_{1g})$ Ra	358 ± 2^a	358	358	358
$\nu_2(e_g)$ Ra	235 ± 5^b	275	278	280
$\nu_3(f_{1u})$ IR	330^c	335	336	330
$\nu_4(f_{1u})$ IR	not observed	85	94	72
$\nu_5(f_{2g})$ Ra	185 ± 5^b	78	90	45
$\nu_6(f_{2u})$	not active	60	68	52

^{a} Isotropic Raman frequency ($\rho = 0.01$). ^{b} Depolarized Raman frequency. ^{c} IR frequency, taken from Adams, D. M. *Metal−Ligand Vibrations and Related Vibrations*; Edward Arnold: London, 1967.

while the mode $\nu_6(f_{2u})$ is not observable. The experimental frequencies, the scaled Hartree−Fock frequencies, and the vibrational assignment are given in Table 8. The calculated HF/6-31G*, HF/6-31+G*, and MP2/6-31G* frequencies for the vibrational modes of the CdO_6 unit were scaled with a factor of 1.20, 1.22, and 1.15, respectively. These scaling factors for the skeletal modes of CdO_6 are employed for a fundamentally different reason than the typical Hartree−Fock scale factor of 0.9. It corrects the frequencies of the gas-phase cluster for the influence of the second hydration sphere. From these results it becomes obvious that the MP2 frequencies are closer compared with the experimental results. An exception is the O−Cd−O modes, which are all at very low frequencies as compared with our experimental results. This fact shows again the lack of a second hydration sphere (which would shift these modes to higher frequencies owing to H-bonding between first- and second-sphere water molecules).

It should be pointed out that ab initio calculations of vibrational modes of aquo ions are a powerful tool in vibrational analysis (frequency predictions from first principles have the advantage that no assumptions have to be made, unlike GF force field calculations) in predicting modes that are neither Raman- nor IR-active (like $\nu_6(MO_6)$), which is useful in subsequent thermodynamic models.

The electronic binding energy of the hexaaquo ion, [Cd-$(OH_2)_6^{2+}$], was calculated according to

$$\Delta E_b = -E_{hexahydrate} + 6 \cdot E_{water} + E_{cation} \quad (7)$$

The binding energies of the hexaaquo complex, [$Cd(OH_2)_6^{2+}$],

TABLE 9: Calculated Electronic Binding Energies at 0 K and the Computed Enthalpies for the Cd(II) Hexaaquo Cluster, ΔH_b^{298} at 298.15 K (All Energies in kJ/mol) at Four Different Basis Sets/Levels of Theory

basis set/level of theory	ΔE_b^0	ΔH_b^{298}
HF/6-31G*	−1207.7	−1170.1
HF/6-31+G*	−1154.1	−1116.5
MP2/6-31G*	−1298.4	−1261.9
MP2/6-31+G*	−1221.0	−1186.1

ΔE_b^0 (at 0 K) were calculated and are given in Table 9. After zero-point vibrational energy, (thermally dependent) vibrational, translational and rotational energy corrections were made, the theoretical binding energy, ΔE_b^{298}, at 298.15 K could be obtained. Including the *PV* work term relates ΔH and ΔE. (The basis set superposition error, BSSE, for a split-valence basis set with diffuse functions is negligible.) The values for the binding energy contributions due to the formation of the hexaaquo ions, ΔH°_{298}, are also included in Table 9. The single-ion hydration enthalpy, ΔH°_{hyd}, for Cd(II) was measured to be 1807 kJ/mol (taken from ref 42). The calculated binding energies, ΔH°_{298}, account only for ca. 62−69% of the measured single-ion hydration enthalpy, ΔH°_{hyd}, at 298.15 K. This shows, again, the importance of the second hydration sphere (12 water molecules), which was recently demonstrated by Pappalardo and Marcos[49] employing Monte Carlo and MD calculations on a similar system $[Zn(OH_2)_6^{2+}] \cdot H_2O$.

The SCF binding energy at 0 K for the Cd[6 + 18] cluster was calculated to be −3056, −2065, and −1941 kJ/mol for HF/3-21G, HF/6-31G*, and HF/6-31+G*, respectively. The hydration enthalpy for the gas-phase reaction at 298.15 K, 18 H_2O + $Cd^{2+} \rightleftarrows Cd(OH_2)_{18}^{2+}$, follows: $\Delta H_{298} = \Delta E_{298} + \Delta PV$, where $\Delta E_{298} = \Delta E_b^0 + \Delta E_v^0 + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298}$, with the following definitions: ΔE_b is the computed difference in the electronic energies of reactants and product at 0 K. ΔE_v^0 is the difference between the zero-point vibrational energies of reactants and products at 0 K. $\Delta(\Delta E_v)^{298}$ is the change in the vibrational energy difference between 298 and 0 K. (This term arises primarily from thermal population of new low-frequency modes, librations, Cd−O skeletal modes, and intermolecular modes which appear in the cluster as already described). ΔE_r^{298} is the change in rotational energies between reactants and product. (Classically, this is equal to $(−1/2)RT$ for each degree of rotational freedom lost owing to cluster formation. So this term is equal to $(−51/2)RT$.) ΔE_t^{298} is the translational energy change due to the changes in the number of degrees of translational freedom. (In this reaction 3 times 18 degrees of freedom are lost, so this term is equal to $(−54/2)RT$.) Finally, the ΔPV is the *PV* work term. (Assuming ideal behavior, $\Delta PV = −18RT$, since 18 mol of gas are lost in the hydration reaction.) ΔH_{298} was calculated to be −1920.4 kJ/mol for the Cd[6 + 12] and is ca. 6% bigger than the single-ion hydration enthalpy, ΔH°_{hyd}, for Cd(II) (1807 kJ/mol at 298.15 K, taken from ref 42). Both values, the SCF binding energy at 0K and the gas-phase hydration enthalpy at 298.15 K, for the cluster formation are given in Table 6.

4. Conclusions

The weak, polarized Raman band previously assigned to the $\nu_1(a_{1g})$ CdO_6 mode of the hexaaquo Cd (II) ion (T_h symmetry for the whole complex ion or O_h symmetry for the CdO_6 unit) has been studied over the temperature range from 25 to 152 °C. The isotropic scattering geometry in R format was

Rudolph and Pye

employed in order to measure the true vibrational contribution of the band and account for the Boltzmann temperature factor B. The band profile as a function of temperature has been examined analytically to extract the parameters: position of band maximum, full width at half-height (fwhh), integral intensity of the band, and relative molar scattering coefficient, S_h, over the temperature range measured. The dependence on concentration has also been measured. The 358-cm^{-1} band of hexaaquo Cd(II) shifts only 3 cm^{-1} to lower frequencies and broadens about 34 cm^{-1} for a 127 °C temperature increase. The Raman spectroscopic data suggest that the hexaaquo Cd(II) ion is stable in perchlorate solution over the temperature range measured. These findings are in contrast to CdSO$_4$ solutions, recently measured by one of us, where sulfate replaces a water molecule of the first hydration sphere. (The inner-sphere Cd−sulfato complex formation is strongly concentration- and temperature-dependent. At 0 °C, and even in a saturated CdSO$_4$ solution, almost all sulfate appears in the outer sphere, or in other words, at this temperature almost all Cd(II) occurs as hexaaquo Cd(II) (with outer-sphere sulfate, which hardly influences the modes of CdO$_6$.))

Besides the polarized component at 358 cm^{-1}, two weak depolarized modes at 235 and 185 cm^{-1} were measured in the Raman effect. These two modes of the CdO$_6$ unit of the hexaaquo ion were assigned to $\nu_2(e_g)$ and $\nu_5(f_{2g})$, respectively. The infrared active mode $\nu_3(f_{1u})$ was measured to be at 330 cm^{-1} (taken from Adams, D. M. Metal−Ligand Vibrations and Related Vibrations; E. Arnold: London, 1967).

Ab initio geometry optimizations of [Cd(OH$_2$)$_6$$^{2+}$] were carried out at the Hartree−Fock and second-order Møller−Plesset levels of theory, using various basis sets up to 6-31+G*. The vibrational frequencies of the [Cd(OH)$_6$$^{2+}$] cation were also calculated. Scaling the Hartree−Fock vibrational frequencies (HF/6-31G*, HF/6-31+G*, and MP2/6-31G* levels) reproduced the measured frequencies of the CdO$_6$ unit, if scaled. The theoretical binding energy for the hexaaquo Cd(II) ion was calculated and accounts for ca. 62−69% of the experimental hydration enthalpy of Cd(II). The frequency calculations and the thermodynamic parameters for the Cd[6 + 12] cluster are given, and the importance of the second hydration sphere is stressed.

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Cadmium(II) Hydration in Aqueous Solution

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