A Theoretical Examination of the Solvent Dependence of the Metal-to-Ligand Charge-Transfer Band in Amino Ruthenium Complexes

Greg M. Pearl and Michael C. Zerner*

Contribution from the Quantum Theory Project, University of Florida, P.O. Box 118435, Gainesville, Florida 32611

Received June 8, 1998. Revised Manuscript Received November 9, 1998

Abstract: An examination is made of the electronic spectroscopy of the title complexes modeled in several solvents with ab initio and semiempirical quantum chemical techniques, generating structures by using a mixed quantum/classical (QM/MM) model. We obtain near-quantitative predictions of the spectra of these complexes, but the calculations indicate that considerable electron transfer is involved between the more polar solvents, as water, and the complex, and that accounting for this transfer is important in the prediction of the location of metal-to-ligand charge-transfer bands.

I. Introduction

The environment in which a molecule resides can greatly influence observed properties, and a proper theoretical modeling of solvent effects is crucial for predicting many properties, and especially molecular electronic spectroscopy. The current methods for modeling solvent effects can be classified into two groups: implicit and explicit. The implicit treatment of solvent effects generally invokes dielectric continuum theory[1−3] and the assumption that "local" solvent effects can be included by using "bulk" solvent properties. Implicit solvent models have flourished recently in quantum chemical calculations, mainly due to their simplicity and the observation that most important trends are well reproduced, if not quantitatively, often semiquantitatively. Explicit solvent methods include the solvent "explicitly". These models have the major drawback of being computationally expensive. The additional expense arises from two factors: first, the system being modeled has increased in size, and second, stochastic methods are required to properly reproduce "bulk" thermodynamic properties that are parametrized in the empirical models.[4,5] Nevertheless, such explicit consideration of the solvent is required whenever bonding between solute and solvent is greater than *kT* (thermal energy), and whenever there is charge transfer or exchange interactions between the solute and solvent.

There has been considerable experimental and theoretical interest in determining the origin of the solvent dependence of the Metal-to-Ligand Charge-Transfer (MLCT) band for amino ruthenium(II) complexes[6−14] belonging to the $[Ru(NH_3)_xL_{6−x}]^{2+}$

family of compounds, Figure 1. The major thrust of the theoretical work done by Zeng et al.[8] was to predict the absorption spectra of the ruthenium(II) pentaaminopyridine ion and its conjugate acid in aqueous solution. While they were able to reproduce the experimental spectra within 3000 cm^{-1} using several different quantum mechanics methods, they did not provide any insight into the origin of this phenomenon. The theoretical work by Stavrev, Zerner, and Meyer[7] reproduced the experimental spectra for the ruthenium(II) pentaaminopyridine complex and noted that considerable charge transfer occurred between the solute and the solvent. The work by Stavrev et al.[7] was controversial in that the geometry used for these spectroscopic calculations possessed some very short N−H···O hydrogen bonds (2.3 Å). The short hydrogen bond distances coupled with some questions pertaining to the accuracy of the semiempirical INDO/S Hamiltonian[15,16] in predicting spectra have left unanswered questions concerning the validity of the nearly one electron predicted to transfer from the solvent to the solute.

This work examines the significance of the solvent−solute charge transfer predicted by Stavrev et al.[7] for modeling the condensed phase absorption spectroscopy of the $[Ru(NH_3)_xL_{6−x}]^{2+}$ class of compounds. The validity of the INDO/S method is also examined by comparing the predicted charge on the ruthenium complex by performing ab initio Hartree−Fock calculation

* Address correspondence to this author.

(1) (a) Karelson, M. M.; Katritzky, A. R.; Zerner, M. C. *Int. J. Quantum Chem.* **1986,** *S20,* 521. (b) Karelson, M. M.; Zerner, M. C. *J. Phys. Chem.* **1992,** *96,* 6949. (c) Rösch, N.; Zerner, M. C. *J. Phys. Chem.* **1994,** *98,* 5817.

(2) Mennucci, B.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1995,** *102,* 6837.

(3) Stavrev, K. K.; Tamm, T.; Zerner, M. C. *Int. J. Quantum Chem.* **1996,** *30,* 1585.

(4) Coutinho, K.; Canuto, S.; Zerner, M. C. *Int. J. Quantum Chem.* **1997,** *65,* 885.

(5) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990,** *112,* 4768.

(6) Ford, P.; Rudd, De F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968,** *90,* 1187.

(7) Stavrev, K. K.; Zerner, M. C.; Meyer, T. J. *J. Am. Chem. Soc.* **1995,** *117,* 8684.

(8) Zeng, J.; Hush, N. S.; Reimers, J. R. *J. Am. Chem. Soc.* **1996,** *118,* 2059.

(9) Curtis, J. C.; Meyer, T. J. *J. Inorg. Chem.* **1982,** *21,* 1562.

(10) Meyer, T. J. *Pure Appl. Chem.* **1986.** *58,* 1193.

(11) Woitellier, S.; Launay, J. P.; Joachim, C. *Chem. Phys.* **1989,** *131,* 481.

(12) Jurus, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988,** *84,* 85.

(13) Ondrechen, M. J.; Ratner, M. A.; Ellis, D. E. *J. Am. Chem. Soc.* **1981,** *103,* 1656.

(14) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983,** *105,* 40.

(15) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973,** *32,* 111−134.

(16) (a) Zerner, M. C. In *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishing: New York, 1991; Vol. 2, pp 313−366. (b) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.
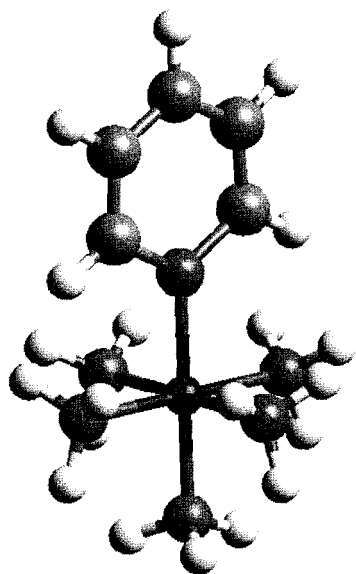
Figure 1. Ruthenium(II) pentaaminopyridine.

utilizing several different basis sets. The significance of the solvent−solute charge transfer is examined not only for aqueous solutions but also for several other solvents where there are experimental studies for comparison.

II. Method

1. Structural Considerations. The structural configurations used to calculate the spectra were obtained with a hybrid quantum mechanics-molecular mechanics (QM/MM) model.[17−23] The QM/MM method decomposes the system into two regions: one region is treated with quantum mechanics, the other with molecular mechanics. The partitioning of the two regions for the systems being studied was done in such a manner that whole molecules were treated as either classical or quantum, therefore avoiding problems associated with "link" atoms.[22] The quantum mechanics region always contained the chromophore and up to all solvent molecules within the first solvent shell. The molecular mechanics region was then responsible for modeling the remainder of the explicit solvent molecules. The QM/MM method as implemented in the ZINDO program package[24] was used: the specifications of this QM/MM method can be found in ref 23. The QM/MM simulations all used the INDO/1 semiempirical model for the quantum mechanics regions[16] and either SPC,[25] CFF,[26] or AMBER[27] force fields for modeling the molecular mechanics regions.

Due to the complex nature of the potential energy surface of a large molecular system, stochastic methods were employed. These methods

provide many energetically equivalent structures, instead of locating a single local minimum energy structure, simulating finite temperature. Both Monte Carlo (MC) and molecular dynamics (MD) techniques have been used for determining the conformations that were used in the subsequent spectroscopic calculations. The specific details of the MC and MD methods as implemented within ZINDO are also discussed in ref 23.

The ab initio calculations were performed with either the Gaussian 94[28] or GAMESS[29] programs. These calculations were carried out at the Hartree−Fock level of theory and used a variety of basis sets, which are specified along with the results. The ab initio calculations were performed with use of the structures obtained from the QM/MM simulation to verify that the amount of charge transfer from the solvent to the complex as predicted by the INDO/S Hamiltonian is not an artifact of the semiempirical procedure. This charge transfer seems to be required to reproduce the experimentally observed spectra.

2. Spectroscopic Considerations. To investigate the solvent dependence of the MLCT band, the INDO/S-CIS method as parametrized in the ZINDO program package[24] was chosen along with the ruthenium parameter defined by Broo and Lincoln (β(s,p) = −5.0.0 eV; β(d) = −15.0 eV).[30] Uncorrelated structures were taken from the QM/MM simulations. Uncorrelated structures were defined by structures that had a time correlation function less than 0.2 referenced to the last structure used for the quantum mechanics. On average this required 50 000 conformations per accepted geometry. Typically the solute and the first solvent shell, as determined by the nitrogen−oxygen (or nitrogen−nitrogen) radial distribution function, were included in the SCF/CIS quantum mechanical calculation. The remainder of the solvent molecules within the 15−20 Å cutoff were modeled as point charges; the charges were the same as those used in the molecular mechanics force field, rather than those obtained from the quantum mechanics. The reason for this is that the dipole moment of water is poorly reproduced by the quantum chemistry charges, as the lone-pair hybrid contributions are sizable, but the classical charges are fit to reproduce these moments. The long-range interactions were then incorporated into the quantum calculation by using a self-consistent reaction field (SCRF) with the radius equal to the cutoff. The C1 SCRF model was chosen by calculating the dipole and quadrapole interactions.[1b,31]

III. Results

To investigate the importance of the solvent−solute charge-transfer model for describing the solvent dependence of the MLCT band in pentaamineruthenium complexes, the INDO/S method is used to calculate the spectra for hexaaminoruthenium-(II) and -(III) and pentaaminopyridineruthenium(II) and -(III) along with pyridine. These calculations are then compared to the work published by Ford et al.[6] In general, the MLCT band appears to be predicted at higher energies with the more positive Mulliken charges, of either the ruthenium ion or the entire complex, as might be expected, and as already suggested in Table 1.

Although there are reaction field models that can include the effects of hydrogen bonding directly into the parameters,[33−37]

(17) Warshel, A.; Levitt, M. *J. Mol. Biol.* **1976**, *103*, 227.

(18) Gao, J. *Reviews In Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers Inc.: New York, 1996; Vol. 7, Chapter 3.

(19) Field, M. J.; Bash, P. A.; Karplus, M. *J. Comput. Chem.* **1990**, *11*, 700.

(20) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1986**, *7*, 718.

(21) Thompson, M. A. *J. Phys. Chem.* **1995**, *99*, 4794.

(22) Eurenius, K. P.; Chatfield, D. C.; Brooks, B. R. *Int. J. Quantum Chem.* **1996**, *60*, 1189.

(23) Broo, A.; Pearl, G.; Zerner, M. C. *J. Phys. Chem. A* **1997**, *101*, 2478.

(24) ZINDO-97, a semiempirical program package. M. C. Zerner, C. Warren, J. E. Ridley, A. D. Bacon, R. F. Kirchner, W. D. Edwards, J. McKelvey, J. C. Culberson, J. D. Head, B. Weimer, A. D. Cameron, M. Kotzian, N. Rösch, B. Parkinson, J. Yu, R. Pitzer, M. Cory, T. Tamm, M. Karelson, and G. Pearl; University of Florida, Gainesville, FL 32611.

(25) Berendsen, H. J. C.; Postma, J. P. M.; von Gunstarin, W. F.; Hermans, J. *Intermolecular Forces*; Pullman, B., Ed.; Reidel: Dordrecht, Holland, 1981.

(26) Niketic, S. R.; Rasmussen; K. *The Consistent Force Field*; Springer: New York, 1977.

(27) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, S.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*, 765.

(28) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Peterson, J. A. Montogomery, K. Raghavachari, M. A. Allaham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Reploge, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Detrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. Pople; *Gaussian*; Gaussian Inc.: Pittsburgh, PA.

(29) GAMESS; M. W. Schmidt, K. K. Baldridge, J. J. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nugyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Motgomery, Jr.: Distributed by M. Schmidt, Department of Chemistry, Iowa State University, Ames, Iowa.

(30) Broo, A.; Lincoln, P. *Inorg. Chem.* **1997**, *36*, 2544.

(31) Tamm, T.; Zerner, M. C. In preparation.

(32) Zerner, M. C. *Navel Research Reviews*, Four 1993−One 1994.

(33) Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 8305, 8552.

(34) Cramer, C. J.; Truhlar, D. G. *J. Comput. Chem.* **1992**, *13*, 1089.

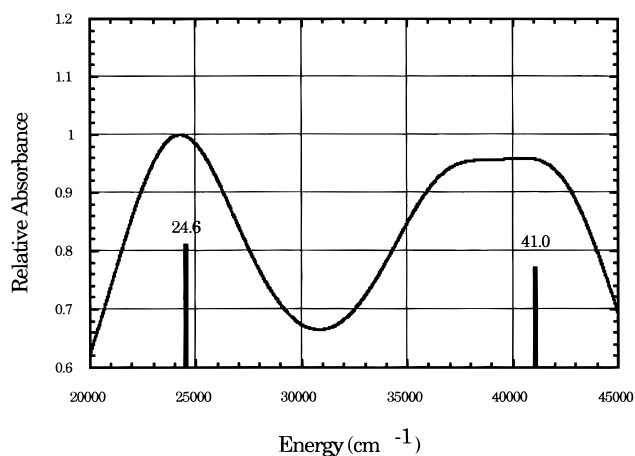**Table 1.** Calculated Aqueous Spectra for Pentaammine Ruthenium Complexes[a]

complex	ν_{max}[b]	exp[c]	ν_{max}[b]	exp[c]	$Q(Ru)$[d]
$(NH_3)_6Ru^{2+}$	25.0	25.0	34.6	36.4	0.089
	(1.0×10^{-5})	(1.48)	(1.0×10^{-6})	(2.80)	
$(NH_3)_6Ru^{3+}$	33.9	31.3	35.2	36.4	0.673
	(1.6×10^{-19})	(2.00)	(2.4×10^{-18})	(2.68)	
$(NH_3)_5Ru(pyr)^{2+}$	27.7	24.6	41.5	41.0	0.431
	(0.231)	(3.89)	(0.140)	(3.66)	
$(NH_3)_5Ru(pyr)^{3+}$	37.2	38.2	38.2	39.5	0.926
	(0.063)	(3.66)	(0.180)	(3.66)	
pyridine			38.8	39.5	
			(0.073)	(3.55)	

[a] All transitions in 1000 cm^{-1}, calculated numbers in parentheses are oscillator strengths, experimental numbers in parantheses are molar extinction coefficients. [b] INDO/S-CIS using SCRF to model solvent. [c] Reference 6. [d] Mulliken population on the Ru Atom.

it is known that the INDO model we use here must include hydrogen bonding solvent molecules explicitly for the best accuracy.[38] The INDO/1 method is also known to predict short intermolecular hydrogen bonds. This has been corrected by using the hybrid quantum mechanics−molecular mechanics (QM/MM) method. The QM/MM method was therefore used to obtain the supermolecule structures needed to properly model the chromophore in an aqueous solution. The pentaaminopyridineruthenium(II) ion was equilibrated to 300 K in the presence of 218 water molecules. The equilibration process was accomplished with geometry optimization techniques, constrained Monte Carlo simulations, and high-friction temperature scaling molecular dynamics simulations.[23] The production run for this system then consisted of a Monte Carlo simulation to obtain 500 uncorrelated structures. The spectra for each of these configurations were then calculated by including the first solvent shell, as determined by the nitrogen−oxygen radial distribution function, in the quantum mechanics region. The remainder of the simulation solvent molecules within the 20 Å cutoff were modeled as point charges with use of the SPC water charges unless otherwise noted. The long-range interactions were then modeled with use of a spherical SCRF at the cutoff of 20 Å. The C1-SCRF model was chosen and the electrostatic expansion was calculated up to the quadrapole. The results obtained from the QM/MM simulation were then fitted to a Lorenzian shape by using a width at half-height of 250 cm^{-1}, Figure 2. The numerical values from this simulation are presented in Table 2.

To approximate the effect of including the solvent molecules explicitly in the Ru(III) complex, the Ru(II) QM/MM uncorrelated structures were used for the Ru(III) complex. While this method introduces an error in the calculated spectra, it should capture the effect of solvent polarization and solvent−solute charge transfer on the 3+ ruthenium complexes through the self-consistent quantum chemical procedure. This approximate model was used since the open-shell formalism required for the open-shell Ru(III) complex requires 3−5 times longer than the closed shell Ru(II) calculations.

Both of the ruthenium complexes receive approximately 1 electron from the surrounding solvent (15−20 water molecules). The solvent−solute charge transfer agrees with the results published by Stavrev et al.[7] The QM/MM calculations have an

(35) Cramer, C. J.; Truhlar, D. G. *Science* **1992**, *256*, 213.
(36) Cramer, C. J.; Truhlar, D. G. *Review in Computational Chemistry*; Lipkowitz, K., Boyd, D. B., Eds.; VCH Publishers: New York, Vol 6.
(37) See also the review by: Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.
(38) Karelson, M.; Tamm, T.; Zerner, M. C. *J. Phys. Chem.* **1993**, *97*, 11901.

Figure 2. INDO/S-CIS predicted spectra for the ruthenium(II) pentaaminopyridine−water supermolecule complex fitted to Lorenzians. The observed spectrum occurs as sticks with height proportional to extinction coefficient, from ref 6.

Table 2. QM/MM Predicted Aqueous Solution Spectra from Monte Carlo Simulation[a]

	Ru(II)	Ru(III)
MLCT	24.2	
$\pi-\pi^*$	41.66	41.15
Q[b]	1.1 ± 0.3	1.9 ± 0.4

[a] All energies in 1000 cm^{-1}. [b] Sum of the net Mulliken charge on the ruthenium ion, 5 ammonias, and the pyridine ring.

average intermolecular bond distance of 2.75 Å, as calculated from the nitrogen−oxygen radial distribution function. The nitrogen−oxygen intermolecular bond distance used by Stavrev et al.[7] was only 2.3 Å, as previously mentioned, and considered too short. The solvent−solute charge-transfer mechanism is still valid at these short intermolecular distances, although perhaps exaggerated, since placing dichloromethane or ethane at 2.3 Å does not predict any significant solvent−solute charge transfer.

In Tables 3 and 4 we report a detailed population analysis of the $[Ru^{II}(NH_3)_5py]^{2+}$ complex using the same geometry for both tables from one of the INDO calculations. Table 3 reports the details from a calculation on the isolated complex, Table 4, the details of this complex with 19 waters treated quantum mechanically, 241 water molecules treated as point charges, and the entire complex embedded in a cavity of 15 Å using self-consistent reaction field theory. The first line in these tables, MULL, refers to the Mulliken population of the ground state, STATE 1. All the other entries in these tables are from a Löwdin population analysis. The calculated populations on the metal are very different with these two population schemes, but the net charge to the water and the trends are very similar. About 70% of the 0.84 e donated from the water to the complex is on the five NH$_3$ ligands with either population analysis, although the net population on the Ru is also increased by about 0.15 e when compared with the gas-phase structure. In these tables are also reported a population analysis of the excited states in both the gas phase and solution. In both simulations, approximately 0.7 e is transferred from Ru to pyridine in the states that are labeled MLCT (d→π^*) (STATE 7 in the gas-phase simulation, STATES 4 and 5 in the solution simulation; i.e., the charge transfer states with calculated oscillator strength). There is considerable mixing between the MLCT states and some of the d→d states. Were there not this mixing there would be only 6 d→d transitions and two MLCT. We observe essentially four d→π^* states, rather than two, as the simulation has split the occupied d orbital energies, nearly degenerate in

a

b

2.7 - 3.0 Å

2.8 Å

Idealized axial hydrogen bonding geometry between the ruthenium complex and the nearest neighboring water moleules.

Idealized facial hydrogen bonding between the ruthenium complex and the nearest neighboring water molecules.

c

Ruthenium (II) pentaaminopyridine in the presence of the 24 nearest water molecules from the QM/MM simulation.
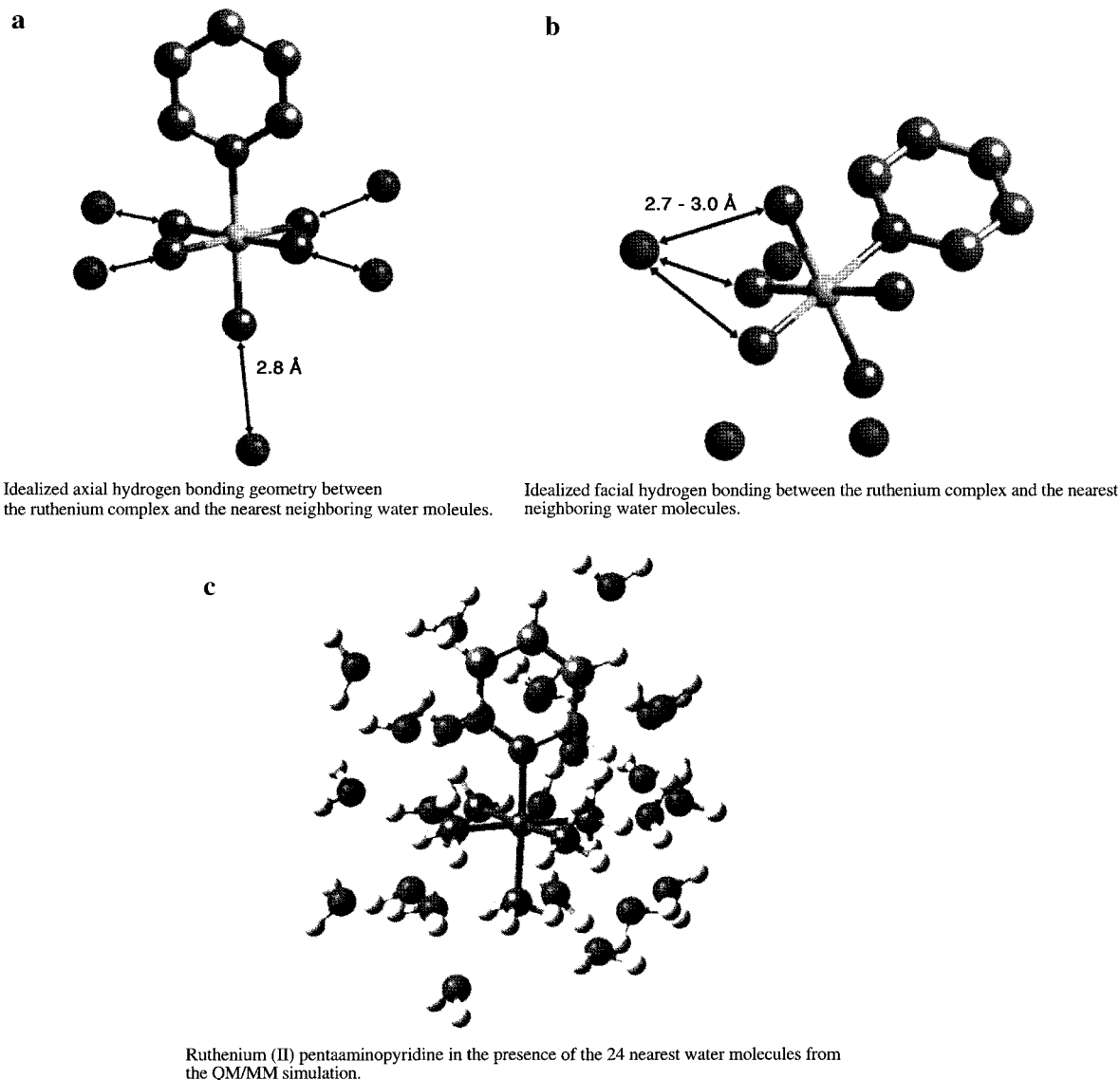
Figure 3. Structural dependency of solvent−solute charge transfer for ruthenium(II) complexes.

the unperturbed gas-phase structure, by about 1000 cm.$^{-1}$. In this particular simulation the geometry (mostly a decreased Ru−N$_{py}$ distance) has depressed the MLCT transition from that of the unperturbed gas-phase structure by about 4000 cm^{-1} (29 900 vs 34 000 cm^{-1}) and the solution another 5000 cm^{-1} (from 29 900 to 24 500 and 25 400 cm^{-1}, compare Tables 3 and 4). The observation that most of the charge transfer is between the amino groups and water is particularly interesting in light of the fact that amines are difficult to model with use of classical models.[39]

Further investigations were performed upon the ruthenium-(II) and -(III) complexes in the presence of 4−10 explicit water molecules in conjunction with the SCRF for modeling the "bulk" solvent. There are two different "model" hydrogen bonding configurations that were investigated: The first, places the water molecules in a hydrogen-bonding conformation (2.7−2.9 Å) along the axis, Figure 3a. The second configuration places the water molecules in a hydrogen-bonding conformation with three neighboring ammonia groups along the face of the octahedron, Figure 3b. While neither of these ideal hydrogen-bonding conformations were obtained consistently from the QM/MM

(39) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. *J. Phys. Chem.* **1996**, *100*, 11775.

Table 3. Population Study of the [Ru(NH$_3$)$_5$py]$^{2+}$ Complex in the Gas Phase, but with the Geometry from One of the Simulations in Water^a

	Q-(RU)	Q-(PYR)	Q-(5NH3)	Q-(NET)	nature	energy (Osc)
MULL 1	0.565	0.188	1.247	2.000		
STATE: 1	−0.577	0.436	2.142	2.000	ground state	
STATE: 2	−0.251	0.386	1.866	2.000	d−d	25.5 (0.00)
STATE: 3	−0.234	0.329	1.906	2.000	d−d	26.7 (0.00)
STATE: 4	0.129	−0.230	2.100	2.000	d−d	27.7 (0.00)
STATE: 5	0.037	−0.093	2.056	2.000	d−d, MLCT	28.3 (0.01)
STATE: 6	0.021	−0.074	2.053	2.000	d−d, MLCT	29.1 (0.00)
STATE: 7	0.131	−0.286	2.155	2.000	MLCT	29.9 (0.30)
STATE: 8	−0.065	−0.059	2.124	2.000	d−d, MLCT	32.0 (0.00)
STATE: 9	−0.254	0.337	1.917	2.000	d−d	33.3 (0.00)
STATE: 10	−0.271	0.415	1.856	2.000	d−d	34.4 (0.01)
STATE: 11	0.290	−0.472	2.182	2.000	MLCT	37.0 (0.00)
STATE: 12	−0.120	0.140	1.978	2.000	MLCT, d−d	37.2 (0.01)
STATE: 13	0.259	−0.420	2.161	2.000	MLCT	38.3 (0.01)
STATE: 14	−0.342	0.185	2.157	2.000	p−p*	42.7 (0.26)
STATE: 15	− 0.318	0.496	1.822	2.000	p−p*	43.8 (0.00)
STATE: 16	−0.237	0.417	1.820	2.000	mixed	44.9 (0.00)
STATE: 17	−0.239	0.420	1.819	2.000	mixed	45.4 (0.00)
STATE: 18	−0.558	0.409	2.148	2.000	p−p*	48.3 (0.15)

^{a} The Ru−N$_{py}$ distance is 1.99 Å, and the average Ru−N$_{amino}$ distance is 2.08 Å. The Ru−N$_{amino}$ distances range from 2.06 to 2.12 Å. The energies given are in 1000 cm^{-1}. Q is the charge in electrons.

Table 4. Population Study of the $[Ru(NH3)5py]^{2+}$ Complex with 19 Quantum Waters and 241 Classical Waters with SCRF, Using a Cavity Radius of 15 Å[a]

	Q-(RU)	Q-(PYR)	Q-(5NH3)	Q-(NET)	nature	energy (Osc)
MULL	0.511	−0.012	0.660	1.159	ground state	
STATE: 1	−0.653	0.286	1.562	1.195	ground state	
STATE: 2	0.149	−0.577	1.621	1.194	d−d	20.7 (0.00)
STATE: 3	0.170	−0.597	1.622	1.196	d−d	21.0 (0.00)
STATE: 4	−0.008	−0.394	1.579	1.177	MLCT	24.5 (0.19)
STATE: 5	−0.009	−0.393	1.587	1.184	MLCT	25.4(0.19)
STATE: 6	−0.338	0.228	1.308	1.198	d−d	26.4 (0.01)
STATE: 7	−0.302	0.131	1.366	1.194	d−d	27.5 (0.00)
STATE: 8	0.096	−0.480	1.573	1.189	MLCT	28.9 (0.00)
STATE: 9	−0.294	0.135	1.356	1.197	$\pi-\pi^*$, MLCT	29.0 (0.00)
STATE: 10	0.219	−0.656	1.626	1.189	MLCT	29.5 (0.01)
STATE: 11	−0.415	0.307	1.302	1.194	d−d	33.6 (0.00)
STATE: 12	−0.383	0.283	1.299	1.198	d−d	35.4 (0.00)
STATE: 13	−0.306	0.120	1.380	1.193	d−d	36.1 (0.00)
STATE: 14	−0.561	0.098	1.571	1.108	$\pi-\pi^*$	37.6 (0.23)
STATE: 15	−0.297	−0.150	1.582	1.135	$\pi-\pi^*$	43.2 (0.15)
STATE: 16	−0.204	−0.222	1.571	1.145	$\pi-\pi^*$	43.8 (0.08)
STATE: 17	−0.093	−0.332	1.578	1.156	$\pi-\pi^*$	45.5 (0.02)

[a] This is the same geometry as given in Table 3 for the isolated complex in the gas phase. The Ru−Npy distance is 1.99 Å, and the average Ru−Namino distance is 2.08 Å. The energies given are in 1000 cm^{-1}. Q is the charge in electrons.

Table 5. Measurements of the Solvent−Solute Charge Transfer in Aqueous Solution[a]

			Q			
conf[b]	no. of waters	MLCT[c]	INDO/S[d]	3-21G[e]	3-21G(p)[f]	3-21G-(d,p)[g]	6-31G**/3-21G[h]
3a	5	27.58	1.965	1.834	1.843	1.843	1.905
3b	4	25.82	1.602	1.634	1.635	1.625	1.820
3b	6	25.77	1.227	1.524	1.525	1.517	1.740
QM/MM	12	23.80	1.345	1.378	1.347	1.302	1.726
QM/MM	18	23.63	1.212				
QM/MM[i]	24	24.68	1.134	1.034	0.995	0.911	1.633
QM/MM	75	23.35	1.098				
Q(Ru)	24		+0.71	+0.78	+0.81	+0.48	+1.26

[a] All the charges are the sum of the Mulliken charges for the ruthenium ion, 5 ammonias, and the pyridine ring. The last row refers only to the charge on the Ru atom. [b] The conformation refers to the ideal structures in Figure 3 or the QM/MM simulation. [c] The MLCT is measured in 1000 cm^{-1}, using the INDO/S method as implemented in ZINDO.[24] [d] INDO/S semiempirical method as parametrized in ZINDO.[24] [e] 3-21G basis set for everything, Hartree−Fock level of theory, GAMESS.[29] [f] 3-21G** basis set for everything, Hartree−Fock level of theory, Gaussian 94.[28] [g] 3-21G** basis set for everything, added d orbitals to the C, N, O, used the d orbitals from 6-31G** basis set, Hartree−Fock level of theory, Gaussian 94.[29] [h] 6-31G** basis set for C, N, O, H and 3-21G basis set for the Ru, Hartree−Fock level of theory; Gaussian 94.[28] [i] Using a different configuration from the QM/MM simulation.

Table 6. Ruthenium(II) Pentaaminopyridine Predicted Spectra for Several Solvents[a]

solvent	MLCT	exp	Q
gas phase	35.91		2.000
water	26.11	24.57	1.610
acetonitrile (3a)	35.87	24.51	1.931
acetonitrile (3b)	24.90	24.51	1.482
methanol (3b)	25.77	24.10	1.622
ethanol (3b)	25.71	23.99	1.617
ethane (3b)	35.89		1.996

[a] Note that only model 3b seems to be able to reproduce the observed spectra systematically, see text.

simulation, the simulation was comprised of a combination of these two conformations, Figure 3c. In the work of Stavrev et al.,[7] negative point charges placed along the axis (Figure 3a) could be used to mimic the inductive effect of the actual charge transfer, and led to spectroscopic predictions that were similar to those obtained from the simulation.

Both of the "model" hydrogen-bonding configurations show some solvent−solute electron transfer, with the 3b conformation showing significantly larger charge transfer. The magnitude of the electron transfer is less than that originally reported by Stavrev et al.,[7] although reducing the nitrogen−oxygen distance to 2.3 Å does increase the amount of charge transfer from the solvent to the solvent by as much as 0.6 e. The QM/MM simulation produces a net charge on the ruthenium complex of +1.1 ± 0.3, which is significantly greater than the charge transfer obtained from the ideal systems of Figures 3a and 3b. The additional charge transfer is most likely due to the water molecules interacting with each other to disperse the positive charge over a greater number of water molecules. Since this charge transfer might be due to using the INDO/S semiempirical method, rather than a real phenomenon, the solvent−solute charge transfer was checked by using ab initio methods. The 3-21G(d,p) calculations give results very similar to those obtained with the INDO/S model, in general, indicating, if anything, a greater degree of electron transfer in the actual QM/MM calculations. The 6-31G** calculations use a 3-21G basis on the ruthenium. They yield considerably less electron transfer, but this we associate with an imbalance in the basis set, as indicated by the inability of the smaller Ru basis to compete for electrons with the better treated chelating atoms, as indicated by the Ru charge in the table. These results are summarized in Table 5. The charges in this table are calculated by using the Mulliken population procedure. Although there are shortcomings in this method of assigning regions of space to various atoms in a molecule for electron count, since the complexed water molecules are well separated spatially from the complex we do not think this a problem, except, perhaps, for the estimate of the charge on the Ru atom, the last row of this table (see Tables 3 and 4). Calculations with the LANL2DZ were also examined, and are not reported in the table. These results were somewhat

erratic, and did not agree with the results of any of the other calculations. The reasons for this are not clear, although this was the only calculation that employed an effective core potential.

The structural dependence of the charge transfer was also tested with acetonitrile as the solvent. The solvent−solute charge transfer and MLCT absorption band were calculated for the two different model acetonitrile conformations. The hydrogen bonds of the first solvation shell of the first conformation resembled that of Figure 3a, while the second conformation had a hydrogen-bonding pattern in the first solvation shell resembling that of Figure 3b. The calculation reported in Table 3 for both of these conformers contained the solute and 15 solvent molecules with use of the multi-cavity SCRF dielectric continuum model.[38] These conformations maintained all of the nitrogen−nitrogen (solute−solvent) hydrogen bonds between 2.65 and 3.2 Å. Table 6 presents the solvent−solute charge transfer for several solvents along with the calculated and experimental MLCT bands. Structure 3a clearly does not reproduce the observed spectrum for acetonitrile: model 3b is better in all cases.

The QM/MM supermolecule method for predicting the spectra of the amino ruthenium complexes has been quite successful at determining the relative ordering of the solvents, as noted in Table 6. The next step is to show that this method is also capable of obtaining the proper relative ordering for the pyridine derivatives. There are several ruthenium (II) pentaaminopyridine for which the aqueous solution spectroscopy is available.[6] While

Table 7.   Ruthenium Complex Derivatives in Aqueous Solution

compd	exp	calc	Q
pyridine	24.57 (3.89)	26.11 (0.41)	1.610
pyrazene	21.19 (4.03)	22.25 (0.58)	1.335
pyrimidine	22.47 (3.78)	22.96 (0.18)	1.143
p-CHO	18.35 (3.97)	19.64 (0.71)	1.056
p-CH$_3$	25.13	25.64 (0.38)	1.423
m-CH$_3$	24.75	25.22 (0.51)	1.369

only a few of these compounds were investigated by us, the QM/MM supermolecule method was successful at predicting the relative ordering of these compounds by using a model containing 15−30 solvent molecules in the quantum mechanics and the multi-cavity reaction field. The predicted spectra for these derivatives are given in Table 7.

Although the results obtained for our solvent and different related complexes with model 3b are not as accurate as the full QM/MM MC simulation, they are accurate enough to show that this simpler method is capable of predicting the proper ordering for these systems. In addition, comparing the "crude" water solvent model to the complete QM/MM simulation indicates about a 1500 cm^{-1} difference, an error that appears systematic, and results in relative errors of between 100 and 500 cm^{-1} in the spectra predictions.

IV. Conclusions

The solvent−solute charge transfer originally reported by Stavrev et al.[7] is significant for determining electronic absorption spectra of ruthenium(II) pentaaminopyridine. The solvent contributes approximately 1 electron to the ruthenium complex, regardless of the quantum mechanical method used. The solvent−solute charge transfer improves the accuracy of the predicted MLCT. Using the INDO/s model the predicted peak maximum is within 500 cm^{-1} of that observed. Simulations indicate that, although the first solvation shell contributes most of the electron transfer, more than the nearest neighboring solvent molecules are necessary for accurately modeling this system. In addition, the results from the larger systems were less dependent upon the method or the basis set chosen. The amount of electron transferred from solvent to solute depends on the nature of the solvent, and the predictions that we make based upon the structures obtained from the QM/MM model seem to reproduce the observed trends quite well.

It is important here to remark that the donation of charge from water to the complex must be shared by the solvent. No single water molecule donates an electron to the complex, but rather this is shared by many. Table 5 seems to suggest that the calculation of the spectroscopy stabilizes after about 12 waters, suggesting, in turn, that no single water loses more than 0.083 e. The addition of more water molecules to the quantum chemistry further dilutes the charge that each water molecule must bare.