Solvent Effects on Molecular and Ionic Spectra. 7. Modeling the Absorption and Electroabsorption Spectra of Pentaammineruthenium(II) Pyrazine and Its Conjugate Acid in Water

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Abstract: This work brings to a focus a series of papers concerning the modeling of solvent shifts in systems in which specific solute−solvent interactions such as hydrogen bonding occur: we consider the interpretation of the metal-to-ligand charge-transfer (MLCT) absorption and electroabsorption spectra of $Ru^{2+}(NH_3)_5$-pyrazine and its conjugate acid $Ru^{2+}(NH_3)_5$-pyrazine-H^+ in dilute aqueous solution. The electroabsorption spectra of these complexes (among the first to be observed for inorganic complexes) taken in S. G. Boxer's laboratory indicated that very small dipole moment changes occur on excitation from the ground to the excited state; it has been found necessary to develop and extensively test, in earlier parts of this series, a sophisticated model for solvent−solute interactions in order to interpret these experimental results. In our approach, first, *ab initio* MCSCF and INDO methods are used to estimate the gas-phase electronic excitation energies; second, Monte Carlo simulations are performed to determine the ground-state liquid structures; finally, the solvent shifts and excited-state dipole moments are evaluated on the basis of the gas-phase charge distributions and the explicit ground-state solvent structures. A variety of potential surfaces and boundary conditions are used in the simulations, and some variation in the liquid structures but little variation in the calculated solvent shifts and dipole moment changes result. The calculated solution frequencies agree quite well with those observed, and the anomalously low values observed for dipole moment change are reproduced; the Magnuson and Taube model for the electronic structure of $Ru^{2+}(NH_3)_5$-pyrazine-H^+ is verified.

I. Introduction

While most techniques for the prediction of electronic spectra apply to molecules in the gas phase, most experiments, and in particular those relating to inorganic complexes, are performed in solution or some other condensed phase. If a significant charge rearrangement is associated with the electronic transition, then in polar media sizeable electrostatic interactions between the solute and solvent molecules occur, and these can produce large solvent (solvatochromatic) shifts of electronic absorption bands. In this series (Parts I−VI), we have developed[1−3] a method for the evaluation of solvent shifts appropriate to environments in which specific solvent−solute interactions occur and tested it through the study of aqueous pyridine,[4] pyrimidine,[1−3] pyrazine,[5] $Fe^{2+}(H_2O)_6$,[6] and $Ru^{2+}(NH_3)_5$-pyridine;[7] here, we apply this method to study aqueous $Ru^{2+}(NH_3)_5$-pyrazine and its conjugate base $Ru^{2+}(NH_3)_5$-pyrazine-H^+.

This series of papers was inspired by the observation in 1991 by Oh, Sano, and Boxer[8] of the electroabsorption spectra of $Ru^{2+}(NH_3)_5$-pyrazine, $Ru^{2+}(NH_3)_5$-pyrazine-H^+, the Creutz−Taube ion, and other bis(ruthenium) complexes. From their spectra, it is possible to extract information such as the change in the dipole moment and the change in the polarizability of the complex as a result of the electronic transition, providing rare detailed information as to the nature of excited electronic states. Experiments of this type have been instrumental, for example, in determining the function of the bacterial photosynthetic reaction center,[9] and recently have also been applied to measure changes associated with purely vibrational excitations[10] for which we have developed an interpretive theory.[11,12] Other inorganic ruthenium complexes have recently been studied.[13] It has been our primary aim to develop a similar interpretive theory for the electronic electroabsorption spectra of inorganic complexes. Early results[14,15] indicated that interactions between the solvent and solute played a significant role in determining not only the absorption frequencies but also the electroabsorption responses. While we had previously[16,17] modeled successfully the absorption spectra of these and similar complexes using simplistic parameterized Hamiltonians, it became clear that a reliable method had to be developed for modeling the electronic structure of the solute *in solution* and, as specific solvent−solute interactions are involved, for modeling the structure of the liquid itself.

Our initial studies were applied[1−5] to azines in solution. These were chosen as their study was very important in the determination over 30 years ago of the basic properties of

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hydrogen bonding, a large amount of experimental data (including high-resolution gas-phase spectroscopy) is available, the molecules are small enough to treat with very accurate *ab initio* methods such as complete active space self-consistent-field theory followed by multireference configuration interaction (CASSCF-MRCI), the spectroscopy of many azine−water clusters is known, and the solvent shifts are relatively small (ca. 3000 cm^{-1}), so that these molecules pose difficult test cases. The results were very encouraging, showing that the solvent shift is sensitive to key qualitative aspects of the liquid structure such as the presence of hydrogen bonds, that fine details of the liquid structure are not important, and that reliable potential functions for use in the liquid simulations can be generated on the basis of the gas-phase electronic structure of the solute. Also, most of the originally deduced features of hydrogen bonding were confirmed, including the fraction of the solvent shift apportioned to dielectric and specific solvation effects, though significant changes to the perceived nature of excited states of the diazines and of the hydrogen bonding to such states were advanced.[3,5]

The next step[6] involved studies of aqueous $Fe^{2+}(H_2O)_6$. This system was chosen as some properties of the liquid structure are known experimentally, as the complex has been investigated thoroughly using accurate intermolecular potential functions, and as its absorption spectrum, known for over 60 years, has never been assigned. We showed that the (significant) technical problems associated with the reliable generation of an intermolecular potential function involving an inorganic complex, as well as those associated with the use of a charged sample, could be satisfactorily overcome, at least with regard to the evaluation of solvent shifts and the solute's electronic structure. The possibility that the observed absorption arises from a photodetachment process in which an electron transfers in a single step from the metal to a solvent cavity was considered, with the (extremely large) calculated solvent shift of −240 000 cm^{-1} being very well represented.

Subsequently,[7] we considered the electronic structure of aqueous $Ru^{2+}(NH_3)_5$-pyridine and, for reference, $Ru^{2+}(NH_3)_6$. They were considered before $Ru^{2+}(NH_3)_5$-pyrazine and Ru^{2+}-$(NH_3)_5$-pyrazine-H^+ as they are chemically simpler and more detailed experimental data are available, allowing our method to be more thoroughly tested. It was demonstrated that it is possible to generate intermolecular potential energy surfaces and perform simulations which produce qualitatively reasonable liquid structures and that the calculated aqueous metal-to-ligand charge-transfer (MLCT) energy is quite close (within 3000 cm^{-1}, which is smaller than the error range naively expected) to the experimental value.

Our method involves two independent stages which have been described in detail elsewhere.[1,3] In the first stage, an ensemble of configurations representing the structure of the solvent around the solute is generated. This can be done using any available technique; we use effective pair potentials derived[1] using the scheme of Kollman[18−21] and perform rigid-molecule Monte Carlo simulations (the geometry of the complex is taken to represent the geometry in solution as accurately as possible). Required intermolecular potential functions are generated by combining a standard set of Lennard-Jones potentials with intermolecular electrostatic interactions; to match the Lennard-Jones terms used, atomic charges for the solute should be determined at the *ab initio* Hartree−Fock self-consistent-field (SCF) level by fitting atomic charges to the molecular electrostatic potential (ESP) outside the molecular van der Waals shell. We have found that this approach gives reasonable results provided that the electronic structure of the solute is properly described at the SCF level. Use of potentials obtained using higher levels of theory, e.g., using multiconfigurational SCF (MCSCF), also produce qualitatively reasonable liquid structures but are quantitatively inferior; when the SCF electronic structure is qualitatively flawed, use of more accurate methods is essential, however.[5] We have not found a scheme which makes use of INDO charges to construct a realistic effective pair potential; potentials generated with this intent have been very useful, however, as they have allowed us to demonstrate that, when qualitatively poor liquid structures are used, our method predicts in general qualitatively poor solvent shifts.

In the second stage, sampled liquid configurations are processed in order to determine the solvent shift of the absorption band. It is assumed that a significant charge redistribution occurs as the result of the electronic transition and that the solvent shift arises from the changes in the electrostatic interactions between the solvent and solute (this method is thus clearly inappropriate for the study of d → d transitions as these involve essentially no macroscopic charge redistribution[22]). The effects of the solvent on the electronic structure of the solute, and *vice versa*, are included by treating each molecule as being individually polarizable. Charge transfer to solvent could easily be included, in principle; test *ab initio* calculations[3] indicated, however, that very little charge transfer is involved between azines in water and that the calculated solvent shift is very sensitive to its inclusion. We have found that charge transfer could only have a minor role in the systems considered and that, until a method is available that can reliably predict such charge transfer in solution, it is best to neglect this effect altogether. Finally, another important feature of our method is that spherical boundary conditions are used to treat very long range electrostatic interactions, and we truncate our liquid samples at some large radius (for the sample size we use, this is possibly as large as 11 Å; a value is chosen such that the solvent shift is independent of the value used) into a sphere embodied in a dielectric containing the solute and up to a maximum of typically 140 water molecules. In the appropriate limits, our method reduces to the well-known expressions for dielectric solvation,[23−28] with some small approximations introduced[3] through the use of Friedman imaging.[29]

While our method embodies a variety of options concerned primarily with choice of electronic structure method, the specification of the intermolecular potential functions, and the boundary conditions used, and while it requires the determination of a significant number of properties of the solvent and solute molecules in the gas phase, it contains no parameters which can *arbitrarily* be adjusted in order to fit experimental spectroscopic data.

There continues to be considerable interest in theoretical calculations of the electronic structure of ruthenium ammine complexes,[6,30−35] though often only in the gas phase. Over the

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past 5 years, a range of techniques for determining solution spectra and solvent shifts have been developed.[31,36−42] Many of these are based on self-consistent reaction-field (SCRF) models and have been successfully applied to a range of problems in which the solvent can be treated simply as a dielectric medium, having no specific interactions such as hydrogen bonding with the solvent. It is well-known[43−45] that because of specific interactions such models cannot be applied quantitatively to the systems of interest herein. They can provide a reasonable qualitative description, with the specific interactions being treated implicitly through choices concerning the solvent-cavity shape and size; however, these choices can be somewhat arbitrary. Recently,[31] Broo and Larsson have shown that such methods are broadly applicable to a variety of inorganic complexes including $Ru^{2+}(NH_3)_5$-pyrazine. Attempts have been made to adapt electronic structure methods, including SCRF methods, to include specific solvation effects through the inclusion of a small number of solvent molecules with the solute in the electronic structure calculation,[36,41] and indeed, approaches of this type have been applied to both azine solutions[38,39] and to $Ru^{2+}(NH_3)_5$-pyridine solutions.[35] Such *supermolecular* methods can again be useful in that they could highlight the key physical processes involved but are of limited applicability for quantitative work in that by necessity only at best a crude description of the solvent structure is possible. Methods[42,46] related to ours have also been introduced which overcome this limitation by performing a full liquid simulation; in particular, the method of DeBolt and Kollman[46] can be considered a simplification of our method, using more approximate expressions for the solvent shift, while that of Luzhkov and Warshell[42] can be considered an extension, being in fact a full supermolecular calculation for the entire liquid. Broo[47] has addressed questions concerning the minimum sample size required in supermolecular calculations, as indeed have we.[3,6,7]

An important feature of supermolecular calculations is that they should only be implemented at a level of *ab initio* theory sufficiently high to correctly describe intermolecular charge transfer. In particular, the semiempirical INDO method is inappropriate in this application as it predicts very short hydrogen-bond lengths and evokes large amounts of intermolecular charge transfer. An example of this is found in the application of INDO to azine solutions:[38,39] this method predicts a sizeable red shift for the (n,π^*) absorption in azine−water complexes, followed by a large blue shift associated with the solvation of this complex, whereas the observed spectra for azine−water complexes invariably show small blue shifts on cluster formation.[48−52] This observation also calls into question the conclusion drawn from a similar recent study[35] of $Ru^{2+}(NH_3)_5$-pyridine solution that charge transfer to solvent is essential in lowering the energy of MLCT transitions. According to our analysis, such transfer in fact plays a negligible role; a similar conclusion could also be drawn from the SCRF studies of Broo and Larsson.[31]

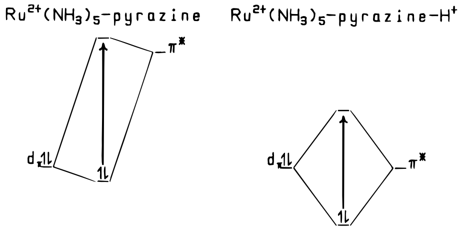

Figure 1. Key aspects of the Magnuson and Taube[53] model for $Ru^{2+}(NH_3)_5$-pyrazine-H^+ and their contrast to the (more usual) situation for $Ru^{2+}(NH_3)_5$-pyrazine showing the relative energies of the metal d_π orbital, the LUMO π^* orbital of the pyrazine ligand, the resulting molecular orbitals, and (arrow) the MLCT electronic transition.

Oh, Sano, and Boxer's electroabsorption experimental results[8] for $|\Delta\mu|$, the magnitude of the change in dipole moment upon MLCT absorption, measured for $Ru^{2+}(NH_3)_5$-pyrazine and $Ru^{2+}(NH_3)_5$-pyrazine-H^+ were suprizingly small, 4.8 ± 1.3 and 0 ± 0.3 D, respectively; the large uncertainty in the former case arises from the need to consider the local-field correction effect. Naively, the MLCT absorption would be expected to transfer an entire electron from the Ru atom to an average location corresponding to the center of the pyrazine ring, a distance of 3.5 Å, thus changing the dipole moment by 17 D. Using a crude analytical model for back-bonding and polarization effects, we showed[15] that the expected value for $Ru^{2+}(NH_3)_5$-pyrazine could be reduced to 8 D and thus that significant solvent effects could be involved. The very small dipole change for $Ru^{2+}(NH_3)_5$-pyrazine-H^+, however, is readily interpreted using the Magnuson and Taube model[53] for the electronic structure of this complex. While as shown in Figure 1 for $Ru^{2+}(NH_3)_5$-pyrazine and $Ru^{2+}(NH_3)_5$-pyridine the metal d_π orbital is far removed in energy from the ligand π^* LUMO orbital, protonation of pyrazine's other nitrogen atom lowers the LUMO energy, making it accidently degenerate with d_π. The result as shown in Figure 1 is the appearance of two delocalized molecular orbitals ψ_- and ψ_+, and the MLCT transition between these orbitals would be expected to have no dipole moment change associated with it. The challenge here is to first produce an electronic structure calculation which agrees qualitatively with the known electronic structures of the complexes and second to evaluate the aqueous transition energies and dipole moment changes. A possible complication is that the accidental degeneracy postulated in the Magnuson and Taube model may only manifest itself *in the presence* of the solvent. In this case, the solvent would introduce a highly nonlinear perturbation to the electronic structure of the solute, and schemes such as ours which treat the solvent−solute interaction perturbatively would be inappropriate so that use of either a supermolecular or SCRF

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Table 1. Atomic Coordinates (L = Pyrazine Long Axis, S = Pyrazine Short Axis, N = Pyrazine Normal Axis, See Figure 2) (Å) for $\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine (without $\mathrm{H_{17}}$) and $\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine-$\mathrm{H^+}$ (with $\mathrm{H_{17}}$), with Respect to the Center of Mass of $\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine, and ESP-Calculated Atomic Charges, q (e), from the *Ab Initio* MCSCF Calculations[a]

	coordinates			q ($\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine)		q ($\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine-$\mathrm{H^+}$)	
atom	L	S	N	MCSCF	MCSCF′	MCSCF	MCSCF′
$\mathrm{Ru_1}$	0.8760	0	0	0.9881	1.5487	1.1851	1.2530
$\mathrm{N_2}$	−1.1303	0	0	0.2498	0.1738	−0.0874	−0.1541
$\mathrm{C_3}$	−1.8749	−1.1492	0	−0.6728	−0.8714	−0.1745	−0.1333
$\mathrm{C_4}$	−3.2486	−1.1486	0	0.8385	0.8051	0.1399	0.0737
$\mathrm{N_5}$	−3.9711	0	0	−0.8242	−0.9355	−0.1777	−0.1477
$\mathrm{C_6}$	−3.2486	1.1486	0	0.8186	0.7833	0.1365	0.0688
$\mathrm{C_7}$	−1.8749	1.1492	0	−0.6693	−0.8635	−0.1854	−0.1414
$\mathrm{N_{A8}}$	3.0423	0	0	−0.9302	−0.9208	−0.9175	−0.9229
$\mathrm{N_{A9}}$,$\mathrm{N_{A10}}$	0.9276	−1.5146	±1.5273	−0.9463	−0.9274	−0.9028	−0.9145
$\mathrm{N_{A11}}$,$\mathrm{N_{A12}}$	0.9276	1.5146	±1.5273	−0.9362	−0.9249	−0.8925	−0.9053
$\mathrm{H_{13}}$	−1.2962	−2.0671	0	0.2014	0.2315	0.1775	0.1788
$\mathrm{H_{14}}$	−3.7160	−2.1278	0	0.0217	0.0345	0.2120	0.2202
$\mathrm{H_{15}}$	−3.7160	2.1278	0	0.0322	0.0457	0.2157	0.2238
$\mathrm{H_{16}}$	−1.2962	2.0671	0	0.2063	0.2332	0.1865	0.1866
$\mathrm{H_{A8}}$	3.3889	0.9805	0	0.3614	0.3594	0.3710	0.3721
	3.3889	−0.4903	±0.8492	0.3674	0.3664	0.3792	0.3784
$\mathrm{H_{A9}}$,$\mathrm{H_{A10}}$	0.9122	−1.0630	±2.4640	0.3631	0.3602	0.3671	0.3715
	0.0991	−2.1354	±1.4281	0.3810	0.3717	0.3513	0.3573
	1.7965	−2.0775	±1.4281	0.3615	0.3543	0.3747	0.3773
$\mathrm{H_{A11}}$,$\mathrm{H_{A12}}$	0.9122	1.0630	±2.4640	0.3643	0.3636	0.3686	0.3733
	0.0991	2.1354	±1.4281	0.3719	0.3663	0.3421	0.3488
	1.7965	2.0775	±1.4281	0.3624	0.3578	0.3750	0.3774
$\mathrm{H_{17}}$	−4.9511	0	0	−	−	0.3929	0.3911

[a] C_s symmetry (the π plane) is used; except for the axial ligand $\mathrm{A_8}$, the symmetry is C_{2v}.

calculation method would be essential. If, however, as reasoned above, the accidental degeneracy is induced primarily by protonation, then the electronic structure would be far less sensitive to the solvent and our method should produce reasonable results. The observed[8,54−56] insensitivity of this band to solvent effects suggests that this is indeed the case.

In this paper, we consider only complexes in dilute aqueous solution at 298 K. The electroabsorption results of Oh, Sano, and Boxer[8] with which we compare are obtained in 50% water−glycerol glass at 77 K. It is quite likely, however, that in these glasses the charged ions are preferentially solvated by water, and, as such, a qualitatively similar environment around the ions to that present in pure water would be expected. Hence, in these simulations, we expect to be able to model at least qualitatively the trends seen in the experimental data for $\Delta\mu$; the small solvent shift $\Delta\nu$ observed in the absorption spectrum between the room-temperature liquid and the low-temperature mixed-solvent glass, for a system involving significant charge-transfer and hence large solvent effects, supports this assumption. Computational methods are considered in section II, the gas-phase electronic structure in section III, calculated solution structures in section IV, and calculated solvent shifts and dipole moment changes in section V.

II. Calculation Details

(a) Gas-Phase Electronic Structure Calculations for the Complexes. All electronic structure calculations are performed at the observed[57] crystal geometry for $\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine. This structure has C_{2v} symmetry for the heavy atoms. Hydrogen atoms are added using standard bond lengths and angles, and the geometries used in these calculations are shown in Table 1 and Figure 2; these structures have C_s symmetry, maintaining pyrazine's π plane.

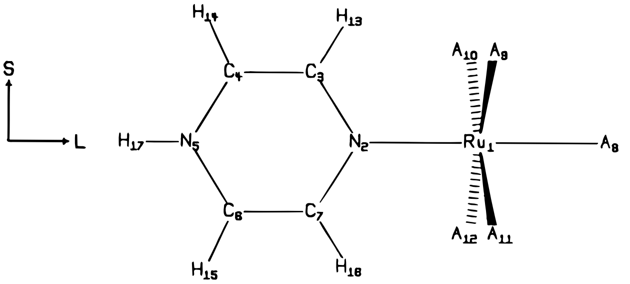

Figure 2. Geometry of $\mathrm{Ru^{2+}(NH_3)_5}$-pyrazine-$\mathrm{H^+}$, where A is for ammonia; see Table 1.

In all *ab initio* calculations, effective-core-potential basis sets are used for ruthenium,[58] nitrogen and carbon,[59] and a double-ζ basis set for hydrogen,[60] and the HONDO[61] suite of programs was utilized. Recent developments in hardware and computational methods have made *ab initio* calculations of the electronic spectra of coordination complexes feasible (see, e.g., refs 62−66). While self-consistent-field (SCF) and limited configuration interaction (CI) calculations have proven qualitatively inadequate for excited-state properties, the multiconfigurational SCF (MCSCF) method,[67] including the complete active space SCF (CASSCF) method,[68] is particularly appropriate for the description of the large near-degeneracy effects that occur in transition metal systems. Ideally, one would wish to perform a MCSCF calculation for each electronic state of interest, followed by individual large single- and double-excitation CI (SDCI) calculations; this approach has been shown to give excited state energies accurate to 2000 $\mathrm{cm^{-1}}$

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for gas-phase azines.[65,69] Unfortunately, a large CISD calculation cannot be performed for inorganic complexes such as this given the level of computer resources currently available. Also, while it is usually possible to converge a MCSCF calculation on the lowest-energy state of a given symmetry, it is difficult to force such a calculation to converge on some other state. Progress can be made, however, by forcing the MCSCF calculation to optimize the wave function so as to minimize the weighted average energy of a number of states, including the ground state and the MLCT state. In this fashion, one set of molecular orbitals is obtained which is optimized to provide simultaneously a reasonable description of both states. All states may need be included in this average whose energy is less than the $d_\pi \rightarrow \pi^*$ MLCT state at some stage of the MCSCF refinement process, though such states need not necessarily be assigned a large weight. For $Ru^{2+}(NH_3)_5$-pyrazine-H^+, we include the ground state and the MLCT state in the calculation, while for $Ru^{2+}(NH_3)_5$-pyrazine, we include low-lying ruthenium $d_\pi \rightarrow e_g$ and $d_\pi \rightarrow p_z$ states also; all states are assigned equal weight.

We also perform semiempirical INDO[70−74] calculations using Krogh-Jespersen's atomic parameters[75,76] utilizing our own program; these semiempirical parameters have been used successfully to study electronic spectra of many ruthenium complexes (see, e.g., ref 77 and references therein). The INDO calculations considered only the 400 lowest-energy singly excited configurations in the CI, a number sufficiently large so as to achieve convergence of the calculated energies (insignificant changes occur if this number is increased to 1000). Two types of calculations are performed. The first type involve single-excitation CI based on the SCF closed-shell ground-state reference determinant; this is a standard implementation of INDO and is termed INDO/S-CI. The second type involves the use of an initial MCSCF stage followed by a multireference CI calculation in which single excitations are taken from each determinant and used in the MCSCF. We choose a fixed-equal-weight MCSCF algorithm which includes all possible singlet states formed by placing two electrons in the metal d_π orbital and/or the ligand's lowest unoccupied π^* orbital. Such a calculation is easily implemented using standard restricted open-shell procedures.[71] This type of calculation is named INDO/MRCI; its advantages compared to the standard INDO/S-CI method are the same as the advantages of an *ab initio* MCSCF/MRCI calculation compared to an *ab initio* SCF/CIS calculation: basically, the spectator electrons not directly involved in the electron-transfer process are chosen in a manner which treats the ground and excited states on an equal footing. We have found its use to be essential to the reliable modeling of electron-transfer phenomena.[78,79]

From the INDO calculations, ground- and excited-state atomic point charges and point dipoles are obtained by simple partitioning of the density and dipole matrices for each desired state. For the *ab initio* electronic wave functions, Mulliken charge analysis is inadequate[1,2] and we determine atomic charges by fitting the resulting electrostatic potential (ESP) to that deduced directly from the wave function at data points evenly selected in the region from 1.4 to 2.5 times the van der Waals radii from the molecule. The values of the van der Waals radii for nitrogen, carbon, and hydrogen atoms are taken[80−82] to be 1.55, 1.7, and 1.2 Å, respectively, except for N_5 in $Ru^{2+}(NH_3)_5$-pyrazine for which hydrogen bonding requires use of 1.3 Å; as the central ruthenium ion is effectively shielded from the liquid by its inner coordination sphere, no van der Waals radius is required for this atom.

(b) Monte Carlo Simulations. Constant pressure, density, and temperature (NPT ensemble)[83] Monte Carlo simulations of a single ruthenium complex in a solution of 256 rigid water molecules were performed at a temperature of 298 K and a pressure of 1 atm with a periodic truncated octahedral boundary condition. To accelerate convergence of the simulations,[84] solute displacements and volume changes were performed every 10 and 100 moves, respectively. The magnitude of the Monte Carlo displacements were adjusted to maximize the diffusional and rotational motions (only about 25−30% of all moves are accepted), and solvent molecules were selected for displacement with a probability proportional to the solute−solvent separation.[84] Equilibration was performed for at least 10^7 moves, and in most cases, an ensemble of 5×10^6 equilibrium configurations was then generated. Every 1000th configuration was selected and its properties averaged in order to determine the radial distribution functions, and every 10 000th configuration was stored for subsequent solvent shift calculations.

The intermolecular potential surfaces used in these simulations have in common the interatomic Lennard-Jones potential functions specified by Kollman;[18−21] these have been described in detail elsewhere.[1,6,7] For each complex, two different ground-state potentials are generated by combining atomic charges with the Lennard-Jones interactions. These potentials are called (1) SCF- evaluated from an *ab initio* SCF calculation and (2) MCSCF-evaluated from an *ab initio* MCSCF calculation. In all simulations, the rigid-molecule TIP3P[85] water potential is used. In all but one simulation, the complex is also held rigid: we have shown that the flexibility of complexes such as these does effect fine details of the resulting liquid structure but does not effect its qualitative nature or calculated solvent shifts. One simulation is performed using a semiflexible potential to again test the applicability of this hypothesis; in this, the ammonia and pyrazine ligands are themselves held rigid but their connection to the central metal is allowed to relax using Broo's interligand potential.[47]

Technically, simulations of dilute ionic solutions are complicated by the long-range nature of the Coulomb potentials involved, and it is not feasible to use sample sizes of the order of that demanded by the range of these interactions. We have shown[6,7] that solvent shifts may be evaluated using a computationally efficient smoothing function[86] to dampen the long-range electrostatic interactions. This function has no effect at short range and is turned on only when the distance between the center of mass of the complex and the oxygen of a water molecule is within 2.0 Å of the distance from the solute center to the nearest (111) face of the periodic truncated octahedral unit cell.[1] It damps the electrostatic interactions to zero over this outer region of the sample. All but one simulation performed here employs these boundary conditions; in the other simulation, an Ewald summation[87] with neutralizing background[67,88,89] is used (in this case, only 1×10^6 liquid configurations are generated).

In total, six simulations are performed, four for $Ru^{2+}(NH_3)_5$-pyrazine and two for $Ru^{2+}(NH_3)_5$-pyrazine-H^+. For each molecule, one simulation is performed using each of the SCF and MCSCF potentials with rigid molecules using a smoothing function. The other simulations for $Ru^{2+}(NH_3)_5$-pyrazine use alternatively either flexible ligands or Ewald summations.

(c) MLCT Solvent-Shift Evaluation. The theory for the evaluation of the solvent shift is described in detail elsewhere.[6,90] In the MLCT

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Table 2. L and S Components of the Total Dipole Moments Determined from the Intermolecular Potential Functions, *V*, and the Electronic Wave Function, ψ, as Well as the Root Mean Square Error for Fitting the *Ab Initio* Electrostatic Potential (kcal mol^{-1} e^{-1})

	$Ru^{2+}(NH_3)_5$-pyrazine							$Ru^{2+}(NH_3)_5$-pyrazine-H^+						
	SCF	MCSCF	INDO/ S-CI	INDO/ MRCI	MCSCF′	INDO/ S-CI′	INDO/ MRCI′	SCF	MCSCF	INDO/ S-CI	INDO/ MRCI	MCSCF′	INDO/ S-CI′	INDO/ MRCI′
μ_L (*V*)	8.244	8.309	8.498	9.122	17.078	19.296	17.718	−6.364	−2.439	−5.691	−2.733	−1.441	4.136	−1.228
μ_S (*V*)	0.005	0.025	−0.004	−0.004	0.053	−0.015	−0.019	−0.004	−0.008	−0.005	0.035	−0.006	−0.022	−0.002
$\mu_L(\psi)$	8.243	8.312	8.498	9.122	17.074	19.296	17.718	−6.370	−2.443	−5.691	−2.733	−1.446	4.136	1.228
μ_S (ψ)			−0.004	−0.004	0.045	−0.015	−0.019	−0.006	−0.010	−0.005	0.035	−0.009	−0.022	−0.002
error	0.72	0.72			0.72			0.43	0.43			0.41		

solvent shift calculation presented here, the complex and every solvent water molecule whose oxygen atom lies within a radius *r* are enclosed within a small excluded volume of radius r_e and then inside a dielectric continuum of radius $a = r + r_e$. The dielectric continuum is treated using Friedman's image approximation.[29] The exclusion radius prevents unphysically large interactions across the boundary and must exceed 0.9572 Å, the O−H bond length in TIP3P water; we set it equal to 1.0 Å. It is possible to choose for *r* any value up to the inscribed radius of the unit cell used in the liquid simulation; it should be set sufficiently small to exclude effects arising from the damaged liquid structure near the simulation-unit-cell's boundary. This, as well as the use of spherical boundary conditions, minimizes errors (see, e.g., ref 89) in the evaluation of the solvent shift. On the basis of our simulations using a 2 Å wide smoothing function to dampen the potential, we set the maximum value of *r* to 9 Å, but the calculated solvent shifts appear[7] to have converged by $r = 6$ Å.

While the Monte Carlo liquid simulations are performed using computationally efficient effective pair potentials, the solvent shift is evaluated using an *n*-body polarizable potential.[3] For water, the dielectric constant, refractive index, and isotropic polarizability are taken to be $\epsilon = 78.5$, $n = 1.333$, and $\alpha = 9.6164$ au, respectively,[91] and the values of the oxygen and hydrogen charges are set to 0.33 and −0.66 e, respectively, so as to reproduce the observed gas-phase water dipole moment.[91] As the electroabsorption experiments which measure $\Delta\mu$ are recorded in a glass at 77 K, it is not obvious that this value of ϵ is appropriate. It can be shown to be so by considering the role that ϵ plays in the theory:[3] it models implicitly the reorientation of the solvent to solvate the solute. This solvation occurs in the room temperature liquid and, to a large extent, remains frozen-in in the glass.

For each solute, a total of seven sets of atomic point charges and possibly atomic point dipoles are used in the solvent-shift calculations; four of these are for the ground state while three are for the MLCT excited state. The ground-state models used are the SCF and MCSCF *ab initio* atomic point charges used previously in the liquid simulations and two new sets of atomic point charges and dipoles obtained from INDO/S-CI and INDO-MRCI calculations. For the excited state, analogous sets of charges and dipoles MCSCF′, INDO/S-CI′, and INDO/MRCI′ are also generated, but no set analogous to the SCF set is possible as one cannot force an *ab initio* SCF calculation to converge on an excited state whose symmetry is that of the ground state.

The effect of the solvent on the electronic structure of the solute is included perturbatively through the explicit inclusion of solute polarizability. For intense MLCT transitions, a significant contribution to the solvent shift $\Delta\nu$ arises[7] from this interaction and hence it is desirable to use the best-possible values for the ground- and excited-state electronic polarizabilities. We have found[7] that, for these transitions, hyperpolarizabilities are also important: the large relative change in the transition frequency modifies significantly the polarizability difference between the ground and excited states of the solute. In principle, this effect is most appropriately included through the explicit use of molecular polarizabilities and hyperpolarizabilities. Accurate values for such hyperpolarizabilities are very difficult to calculate, however, and we have found that a viable approach is to evaluate polarizabilities using INDO/MRCI by summing over all calculated absorption bands, but with the band frequencies corrected using a spherical-cavity solvent-shift model parameterized to reproduce the observed MLCT transition energy. This approach is contrary to our intent of introducing no arbitrary parameters, but its use has restricted impact as it describes only a correction to the polarizabilities which themselves provide only a correction to the calculated solvent shifts and dipole moment changes.

III. Electronic Structure of the Solute

The sets of point charges evaluated by the SCF, MCSCF, INDO/S-CI, and INDO/MRCI methods previously described for the ground state and by the corresponding MCSCF′, INDO/S-CI′, and INDO/MRCI′ methods for the MLCT excited state of $Ru^{2+}(NH_3)_5$-pyrazine and $Ru^{2+}(NH_3)_5$-pyrazine-H^+ along with the associated point dipoles for the INDO/S-CI, INDO/MRCI, INDO/S-CI′, and INDO/MRCI′ methods are provided in the supporting information; the MCSCF and MCSCF′ charges are also given in Table 1. It is difficult to attach absolute meaning to these values, especially if both point charges and dipoles are used. However, we see that the *ab initio* ESP results for $Ru^{2+}(NH_3)_5$-pyrazine predict a more negative charge on the exposed nitrogen, N_5, in the excited state than in the ground state, a result consistent with the observed basicity increase[56] of the excited state. Even in the ground state, the charge on N_5 is quite large, being −0.81 and −0.82 e from the SCF and MCSCF calculations, respectively, ca. 0.35 e more negative than the charges calculated via the same technique for free pyrazine; hence, significant basicity is implied for the ground state, and significant pro-hydrogen-bonding forces are expected. Qualitatively, this prediction is supported experimentally by the observation that pK_a for the complex is[54] 1.9 units higher than that of free pyrazine. Recent results obtained using the density-functional X-α method by Zhang and Ondrechen[33] attribute a large negative charge to N_2 and near zero charge to N_5, opposite to our results obtained *ab initio*. They justify the X-α results qualitatively through π-system polarization effects, but this argument neglects the large loss of electron density around N_2 associated with the Ru−N σ-bond formation. It is highly unlikely that their charge distribution could support hydrogen bonding to N_5, and this feature, along with the observed pK_a value, may serve to differentiate qualitatively between the different calculated charge distributions.

The total molecular dipole moments are shown in Table 2 as evaluated from the atomic charges and dipoles ($\mu(V)$) and from the electronic wave functions ($\mu(\psi)$); the root-mean-square error in fitting the *ab initio* electrostatic potential data is also shown in this table. These results indicate that the calculated atomic charge and dipole distributions do adequately reflect the properties of the full electronic wave functions. For $Ru^{2+}(NH_3)_5$-pyrazine, the total molecular dipole moments calculated at the geometry shown in Table 1 using the various electronic structure methods are qualitatively similar, ranging from 8 to 9 D for the ground state and 17 to 19 D for the MLCT excited state. The (origin-independent) dipole moment differences, which are shown in Table 3, range from 8 to 10 D; similar results from the *ab initio* and INDO calculations are expected as, crudely speaking, the dipole moment change is associated

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Table 3. Calculated Gas-Phase MLCT Transition Energies, ν_g (1000 cm^{-1}), and the Dipole Moment Change on Absorption, $|\Delta\mu_g|$ (D)

	$Ru^{2+}(NH_3)_5$-pyrazine		$Ru^{2+}(NH_3)_5$-pyrazine-H^+	
method	ν_g	$\lvert\Delta\mu_g\rvert$	ν_g	$\lvert\Delta\mu_g\rvert$
MCSCF	32.6	8.8	24.8	1.0
INDO/S-CI	32.3	10.8	24.3	9.8
INDO/MRCI	27.0	8.6	17.4	−1.2

with the electron-transfer process which is easily described at the semiempirical level. Also shown in this table are the calculated gas-phase transition energies ν_g which range from 27 000 to 33 000 cm^{-1}. We have also found agreement to this accuracy between *ab initio* and INDO methods in other similar systems.[6,7] Typically, an error limit of ±3000 cm^{-1} would be expected for an INDO calculation for gas-phase molecules such as azines, and a slightly larger error bar may apply to inorganic complexes; different INDO/CNDO methods predict transition energies within this range.[31] It is more difficult to estimate a similar error bar for the *ab initio* MCSCF calculation, given especially that this is the simplest *ab initio* method which describes the excited state in a manner which is qualitatively correct, but our experience[6,7] has been that the error range is comparable to that for INDO, and ±5000 cm^{-1} would appear reasonable. Results obtained recently[33] using X-α for $Ru^{2+}(NH_3)_5$-pyrazine predict a transition energy of 23 400 cm^{-1}, much lower than those obtained from our INDO or *ab initio* methods. This value leaves little scope for the observed[54] large solvent effects, however.

For $Ru^{2+}(NH_3)_5$-pyrazine-H^+, the single-reference SCF and INDO/S-CI calculations produce similar results, but these are quite different from the results from the multireference MCSCF and INDO/MRCI calculations. While the results from the multireference calculations reflect closely the electronic structure depicted in the Magnuson and Taube model[53] (see Figure 1), those from the single-reference calculations do not. From the single-reference calculations themselves, there is no evidence to suggest that the method has become inaccurate; while it is quite adequate in many (most) cases, care must always be taken in calculations of this type at both *ab initio* or semiempirical levels of theory.

Calculated polarizabilities (adjusted for the liquid environment) by the INDO/MRCI method for $Ru^{2+}(NH_3)_5$-pyrazine in its ground and excited states are (150, 80, 30) au and (40, 60, 30) au for the (L, S, N) components, respectively, while those for $Ru^{2+}(NH_3)_5$-pyrazine-H^+ are (180, 90, 40) au and (130, 90, 40) au, respectively.

IV. Ground-State Liquid Structure

Unfortunately, little experimental information is available for the structure of solutions around inorganic complexes in general and around these complexes in particular, and so it is difficult to determine the accuracy of the structures predicted in the simulations; hence, we seek to demonstrate that are qualitatively in accord with chemical intuition. We have found[6,7] that liquid structures obtained by analogous methods for $Fe^{2+}(H_2O)_6$, $Ru^{2+}(NH_3)_6$, and $Ru^{2+}(NH_3)_5$-pyridine are (at least) qualitatively reasonable and do reproduce quantitative experimental information when available. A total of six simulations are performed here, four for $Ru^{2+}(NH_3)_5$-pyrazine and two for $Ru^{2+}(NH_3)_5$-pyrazine-H^+, and a selection of resulting key radial distribution functions *g(r)* are shown in Figure 3. The ammonia-hydrogen to water-oxygen functions (H_A−O) show a distinct peak at ca. $r = 2$ Å arising from hydrogen bonding, as does the N_5 to water hydrogen function for $Ru^{2+}(NH_3)_5$-pyrazine and the H_{17} to water oxygen function for $Ru^{2+}(NH_3)_5$-pyrazine-H^+. This suggests that a reasonable definition of a hydrogen bond is that one exists whenever one of these distances is less than 2.6 Å, roughly the location of the center of the first trough in each case. Obtained using this definition, the numbers of hydrogen bonds per ammonia hydrogen and per pyrazine found in each simulation are shown in Table 4. Also shown in this table are the number of water molecules found hydrogen bonded to one or more ammonia ligands per complex. We see that 9−10 water molecules offer 13−16 hydrogen bonds to the 15 ammonia hydrogens. This result is very similar to that found for $Ru^{2+}(NH_3)_5$-pyridine using analogous simulations, and indeed, additional details of the hydrogen bonding not shown here are found to be very similar to those for $Ru^{2+}(NH_3)_5$-pyridine reported earlier.[7] The calculated Ru to water oxygen shell radius is 4.2 Å, slightly larger than the value of 3.9 ± 0.2 Å observed[92] for $Ru^{3+}(NH_3)_6$, but much smaller than the shell radius of 5 Å predicted in the simulations of Broo.[47] A total of 12 water

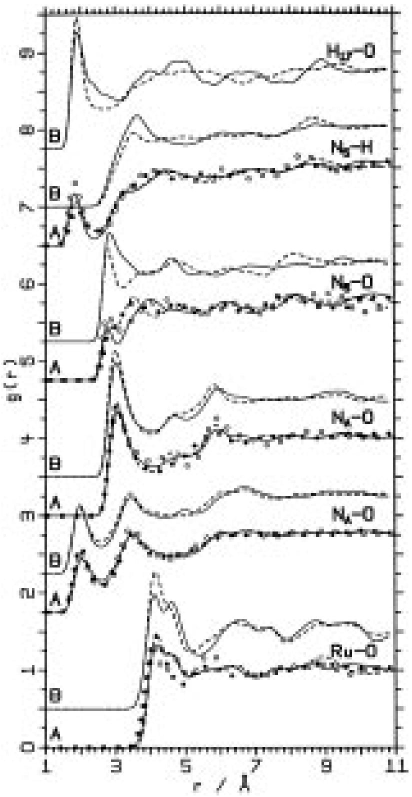

Figure 3. Radial distribution functions $g(r)$ between solute and solvent atoms (N_A and H_A are any ammonia nitrogen or hydrogen atom, respectively) for (A) $Ru^{2+}(NH_3)_5$-pyrazine and (B) $Ru^{2+}(NH_3)_5$-pyrazine-H^+ obtained using the potentials (—) SCF, (- - -) MCSCF, (●) SCF with flexible ligands, and (○) SCF with Ewald sums.

Table 4. Average Number of Hydrogen Bonds (HB) Obtained from Liquid Simulations Using the Ground-State SCF and MCSCF potentials by Integrating the Appropriate Radial Distribution Function (see Figure 3) up to $r = 2.6$ Å[a]

	$Ru^{2+}(NH_3)_5$-pyrazine				$Ru^{2+}(NH_3)_5$-pyrazine-H^+	
property	SCF	MCSCF	SCF/F	SCF/EW	SCF	MCSCF
no. of HB per ammonia H	0.9	0.9	0.9	0.8	1.0	1.0
no. of waters HB to ammonia	10	10	10	9	10	11
no. of HB to N_5 or H_{17}	1.0	1.2	1.0	1.5	1.8	1.5

[a] Rigid ligands and a smoothing function are used except for /F- flexible ligands and /EW- Ewald sum with neutralizing background.

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(92) Waysbort, D.; Navon, G. *J. Phys. Chem.* **1980**, *84*, 674.

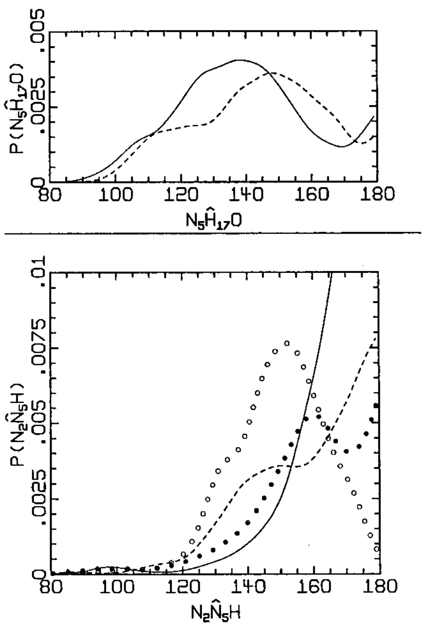

Figure 4. Angular probability functions $P(\theta)$ per degree with $\theta = \angle N_2N_5H$ for $Ru^{2+}(NH_3)_5$-pyrazine and $\theta = \angle N_5H_{17}O$for $Ru^{2+}(NH_3)_5$-pyrazine-H^+ for hydrogen bonds with water H and O atoms, respectively, normalized such that $\int_0^{180} P(\theta) \sin \theta \, d\theta$ equals the the number of hydrogen bonds present (see Table 4), obtained using the potentials (—) SCF, (- - -) MCSCF, (●) SCF with flexible ligands, and (○) SCF with Ewald sums.

molecules are found[6] to fill the shell at similar radius in Fe^{2+} solution, and indeed, this number of water molecules is known[93,94] to occupy the second coordination shell ($r = 4.5$ Å) in neat water itself. The first water shell is thus qualitatively similar to bulk water, a result consistent with the complete lack of experimental suggestion that the solute chemically or physically modifies the surrounding fluid.

For $Ru^{2+}(NH_3)_5$-pyrazine, one hydrogen bond is found attached to N_5 on the pyrazine ligand (none are found attached to N_2 whose environment is found to be similar to that calculated[7] for this atom in $Ru^{2+}(NH_3)_5$-pyridine). Angular distribution functions describing the probability of finding various $\angle N_2N_5H$ angles (with H on water) are shown in Figure 4, and this is the only structural property found to show significant differences between results for the four simulations performed. Varying simulation boundary conditions is known to have large effects on the liquid structure in the regions near the unit-cell boundary but is thought to have only a minor effect on the structure of the second coordination shell for samples of the size used herein.[6,7,95−98] The calculated differences may result as a consequence of the significant distance of the hydrogen-bonded water to the metal center (average $r_{Ru-O} = 7.6$ Å), or from a relative weakness in the strength of this hydrogen bond, or from shortcomings in the potential surfaces used as these, and in general, allow hydrogen bonds to be slightly too flexible. Simulations for this complex have also been performed by Broo[47] using a molecular mechanics potential, and these resulted in *no* hydrogen bonding to N_5; also, on the basis of the X-α charge distribution of Zhang and Ondrechen,[33] no hydrogen bond would be expected. It is difficult to obtain hard experimental evidence as to the possible existence of hydrogen bonds to N_5, and it would be beneficial if, e.g., ^{15}N-NMR experiments could be performed. We note that the observed difference in the enthalpies of the substitution of $Ru^{2+}(NH_3)_5$-(H_2O) for $Ru^{2+}(NH_3)_5$-pyrazine and $Ru^{2+}(NH_3)_5$-pyridine is -4.1 ± 1.1 kcal/mol, of the order of a hydrogen-bond energy.[99] Also, Broo's analogous potential for pyrazine itself in water also predicts no hydrogen bonds,[47] contrary to standard experimental interpretations (see e.g., refs 43 and 99), while potentials analogous to ours predict the expected result of two hydrogen bonds per pyrazine.[5] Intuitively, one would expect that the observed[54] increase in the basisity of Ru^{2+}-$(NH_3)_5$-pyrazine with respect to free pyrazine would be associated with an increased tendency to form hydrogen bonds to N_5. While molecular mechanics potentials are readily applicable to a very wide range of molecules, they do not allow for the individual tailoring possible in our approach; pyrazine, with its two large adjacent dipoles of opposite directionality, is possibly an exceptionally difficult structure for molecular mechanics to treat.

For $Ru^{2+}(NH_3)_5$-pyrazine-H^+, 1.5−2 hydrogen bonds are calculated from water-oxygen atoms to H_{17}. The associated $\angle N_5H_{17}O$ angular distribution functions are also shown in Figure 4 and again show significant differences between the two simulations run. For both simulations, one typical ("linear") hydrogen bond with $\angle N_5H_{17}O > 130°$ is found with $r_{HO} < 2.1$ Å at the end of the steep descent of the radial distribution function shown in Figure 3, and a large fraction of another hydrogen bond is found "under the trough" of the radial distribution functions up to their minimum at ca. 2.6 Å. If H_{17} were to bear the full formal charge of 1.0, then a large number of water molecules would be expected to be drawn near. The *ab initio* calculations (see Table 6 in the supporting information) predict a charge of only 0.4 e, however. Enhancement of one strong hydrogen bond by one weak bond is thus, in principle, possible.

V. Solvent Shifts of the MLCT Bands

On the basis of the liquid structures generated in the six simulations, it is possible to evaluate solvent shifts $\Delta\nu$, aqueous transition energies ν_s, and aqueous dipole moment changes $\Delta\mu_s$ using one of the appropriate pairs of charge/dipole distributions obtained using MCSCF, INDO/S-CI, or INDO/MRCI, and the results are given in Table 5.

For $Ru^{2+}(NH_3)_5$-pyrazine, varying the boundary conditions used or the flexibility of the complex had little effect on the results, as found previously for other systems.[6,7] Little variation was also seen depending on whether the SCF or MCSCF ground-state charges were used in the liquid simulations. Qualitatively similar results were obtained independent of whether charges and dipoles obtained using a single-reference calculation or multireference calculations were used in the solvent-shift evaluation, though quantitatively the calculated solvent shifts were -8000 cm^{-1} in the former case and $-10\,000$ cm^{-1} in the later, with the corresponding $|\Delta\mu_s|$ values being 7.7 and 5.5 D, respectively. The value of the dipole change observed by Oh, Sano, and Boxer[8] (in 50% water/glycerol glass) is 4.8 ± 1.3 D, and so it appears that the multireference calculations produce the best results. Calculated values for the solution absorption frequencies range from 19 000 to 24 000 cm^{-1}, all within just ± 3000 cm^{-1} of the observed[54] value, 21 000 cm^{-1}. These discrepancies are actually less than the errors that would be expected for the accuracy of the gas-phase

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Table 5. Calculated Aqueous Solvent Shifts, $\Delta\nu$ (1000 cm^{-1}), Solution Transition Energies, ν_s (1000 cm^{-1}), and Dipole Moment Changes, $|\Delta\mu_s|$ (D), Evaluated from Liquid Configurations with Either Rigid (R) or Flexible (F) Ligands Obtained Using Either a Smoothing Function (SM) or Ewald Summation with Neutralizing Background (EW), Using Different Pairs of Solute Potentials during the Solvent-Shift (SS) Evaluation[a]

simulation				$Ru^{2+}(NH_3)_5$-pyrazine			$Ru^{2+}(NH_3)_5$-pyrazine-H^+		
pot.	ligands	BC	SS pot.	$\Delta\nu$	ν_s	$\|\Delta\mu_s\|$	$\Delta\nu$	ν_s	$\|\Delta\mu_s\|$
SCF	R	SM	MCSCF	−8.3	24.3	5.7	−4.9	19.9	0.6
SCF	R	SM	INDO/S-CI	−10.0	22.3	7.8	−7.2	17.1	9.4
SCF	R	SM	INDO/MRCI	−8.0	19.0	5.7	−.3	17.1	1.4
SCF	R	SM	SCF[b]	−8.1		5.8			
SCF	F	SM	MCSCF	−8.6	24.0	5.5			
MCSCF	R	SM	MCSCF	−8.3	24.3	5.5	−0.5	24.3	0.3
MCSCF	R	SM	INDO/S-CI	−10.4	21.9	7.7	−4.8	19.5	9.5
MCSCF	R	SM	INDO/MRCI	−8.0	19.0	5.5	−0.6	16.8	0.8
MCSCF	R	EW	MCSCF	−8.8	23.8	5.7			
	obsd in water[54]				21.2			18.9	
	obsd in glass[8,15]				20.1	4.8 ± 1.3		18.8	0 ± 0.3

[a] The observed data are measured in aqueous solution at 298 K and in a 50% glycerol/water glass at 77 K. [b] SCF charges for the ground state and MCSCF′ charges for the excited state.

electronic structure calculations. Hence, it is possible that the reasonable final numbers arise as a fortunate cancellation between the errors of the gas-phase calculations and the solvent-shift calculations. This scenario is best tested by considering a much wider range of complexes; we feel that it is unlikely as the solvent-shift method has produced reliable results for a wide range of applications.[1,4−7]

For $Ru^{2+}(NH_3)_5$-pyrazine-H^+, results obtained using the single-reference determinate ground- and excited-state charges and dipoles INDO/S-CI are very poor, predicting $|\Delta\mu_s| = 9.5$ D as opposed to the experimental value[8] of 0 ± 0.3 D. Alternatively, using either of the MCSCF or INDO/MRCI pairs of charges and dipoles obtained from multireference calculations predicts values ranging from 0.3 to 0.8 D, in quite reasonable agreement with the experimental value. Similarly, the experimentally observed solvent independence[8,54,55] is only reproduced on the basis of the multireference wave functions. Use of a qualitatively correct electronic structure model is clearly paramount during the solvent-shift evaluation. Results obtained from the simulations using the SCF and MCSCF potentials are quite similar, however, despite the qualitative change in the electronic structure. This is an atypical result but comes about as the liquid structure was found to be insensitive to the delocalization of the electron from the ruthenium atom to the pyrazine ring. Evaluated using all methods, the calculated solution absorption frequencies range from 17 000 to 24 000 cm^{-1}, all within ±5000 cm^{-1} of the observed[54] value, 19 000 cm^{-1}. Finally, we note that the calculated solvent shift is insensitive to the variations in the H_{17} hydrogen bonding calculated using the SCF and MCSCF potentials. Hence, we conclude that this hydrogen bonding does not contribute significantly to the solvent shift; experimentally,[55] it is known that replacing H_{17} with CH_3 also has little effect.

VI. Conclusions

The observation by Oh, Sano, and Boxer[8] of the rather small value of $|\Delta\mu| = 4.8 \pm 1.3$ D for the MLCT transition on $Ru^{2+}(NH_3)_5$-pyrazine is interpreted using sophisticated *ab initio* and semiempirical calculations on this complex in the gas phase corrected for solvation effects. Naively, a value near 17 D is expected for this transition, representing the dipole change associated with the transport of an electron from the metal center to lie on average at the ring center. By considering processes operative within the complex itself such as π back-bonding, we were able to show[15] that this value in the gas phase could conceivably be halved, and this conclusion is verified here by both our *ab initio* MCSCF calculations and our INDO/MRCI calculations: calculations with a single-reference determinant reduce the value to 10.8 D while more accurate multireference calculations reduce this even further to ca. 8.7 D. The effect of the solvent on the electronic structure of the solute is then to reduce $|\Delta\mu|$ by another 3 D to ca. 5.6 D. This result is in excellent agreement with the observed quantity, given the difficulty of the calculations, likely uncertainties therein, and the fact that the calculations are for a room-temperature aqueous solution while the experimental measurements are performed on a low-temperature mixed-solvent glass.

In terms of the general perception of the process involved in inorganic charge-transfer transitions, the experimental results combined with our interpretation paint a very interesting picture. In simple systems such as $Ru^{2+}(NH_3)_5$-pyrazine, the simplest view is that a whole electron is transferred a macroscopic distance during the process. This would be thought to have a large impact on the electronic properties of the complex and on its interaction with its environment. We see, however, that the surrounding ligands and solvent molecules act to *minimize* this effect, with the entire system responding do create the illusion that only 30% of an electron is actually transferred. Electroabsorption spectroscopy thus provides not only a sensitive probe of molecular excited state properties but also much information concerning the interaction of these systems with their environment.

Taken on their own, our results might be questioned on several grounds, including the reliability of the solvent-shift model and the accuracy of the liquid structure to which the results are sensitive. We believe that the results are reliable, as our method has been tested by applying it to a large range of related problems. In all cases, qualitatively correct solute electronic structures are seen to lead to reasonable liquid structures and to calculated solution transition energies that are within the error limits expected for the electronic structure methods used when applied to simple gas-phase systems; conversely, incorrect solute electronic structures lead to poor liquid structures and poor transition energies. Problems considered include the azines,[1−5] which give rise to relatively small solvent shifts but for which a large range of detailed experimental data is available for comparison, including data for azine−water complexes. At the other extreme of very large solvent shifts, we have considered photodetachment processes[6] and have considered other MLCT bands in detail.[6,7] Finally, we have also considered $Ru^{2+}(NH_3)_5$-pyrazine-H^+, which provides a rather unusual situation in that the donor d_π orbital and acceptor ligand π^* orbital are accidently degenerate, providing a strong-coupling scenario in which the $\Delta\nu$ and $\Delta\mu$

both become very small, and our method is found to describe this situation quite well.

The solvent shift for these complexes is found to be significantly influenced by hydrogen bonding to the solvent. Results obtained earlier for $Ru^{2+}(NH_3)_5$-pyridine are found here to also apply to $Ru^{2+}(NH_3)_5$-pyrazine: beyond the second coordination shell ($r_{Ru-O} > 5$ Å in the vicinity of the ammonia ligands), the water molecules may be treated as a dielectric continuum, but it is important to include explicitly all of the first layer of water molecules around the solute. Similar conclusions have also been drawn from both experimental interpretations[100] and liquid simulations.[47] The scenario here is slightly different from that in the azines, however. For the azines, a small number of hydrogen bonds attached directly to the chromophore are paramount, with these hydrogen bonds being either broken or significantly weakened in the excited state. For the inorganic complexes considered, a large number of hydrogen bonds are attached at peripheral sites, and the qualitative nature of the hydrogen bonding is not effected by the electronic transition. The hydrogen bonds serve only to shape the interaction of the chromophore with the solvent.

On the basis of this and previous studies,[1−7] we believe that a reliable procedure for estimating solvent shifts for systems in which specific solvent−solute interactions occur is to construct liquid-simulation effective-pair potentials using *ab initio* ESP charges for the isolated ion in its ground state obtained at the SCF level (including electron correlation if this is essential to the provision of a qualitatively correct electronic structure) and then evaluating the solvent shift using INDO/MRCI charges for the ground and excited states of the isolated ion, evaluated using the required degree of (static) electron correlation. Errors obtained so far using this approach are 2000 cm^{-1} for $Ru^{2+}(NH_3)_5$-pyrazine, 1500 cm^{-1} for $Ru^{2+}(NH_3)_5$-pyrazine-H^+, and 2500 cm^{-1} for $Ru^{2+}(NH_3)_5$-pyridine[7]; using (expensive to obtain) *ab initio* MCSCF charges for the ground and excited states in the solvent-shift calculation appears[7] to have an error bar of ±4000 cm^{-1} associated with the choice of states used in the MCSCF, but the absolute errors obtained so far are 3000 cm^{-1} for $Ru^{2+}(NH_3)_5$-pyrazine, 5500 cm^{-1} for $Ru^{2+}(NH_3)_5$-pyrazine-H^+, and (estimated using a correction for solute geometry effects) 1500 cm^{-1} for $Ru^{2+}(NH_3)_5$-pyridine.[7] Last, we note that, although no experimental data are available with which to compare, similar calculations for a (possibly hypothetical high-energy) MLCT transition in $Fe^{2+}(H_2O)_6$ resulted in agreement to within 1000 cm^{-1} between the two theoretical methods.[6] To complete this series, our method will subsequently be applied to investigate the electronic and solution structures of pyridazine and, among others, the Creutz−Taube ion.

CAS Registry Numbers: $Ru^{2+}(NH_3)_5$-pyrazine, 19471-65-9; $Ru^{2+}(NH_3)_5$-pyrazine-H^+, 19441-21-5; $Ru^{2+}(NH_3)_5$-pyridine, 21360-09-8.

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Supporting Information Available: Tables of atomic charges and L, S, and N components of atomic point dipoles (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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