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Prediction of Vibrational Frequencies of UO_2^{2+} at the CCSD(T) Level

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Electronic structure calculations at the coupled cluster (CCSD(T)) and density functional theory levels with relativistic effective core potentials and large basis sets were used to predict the isolated uranyl ion frequencies. The effects of anharmonicity and spin−orbit corrections on the harmonic frequencies were calculated. The anharmonic effects are larger than the spin−orbit corrections, but both are small. The anharmonic effects decreased all the frequencies, whereas the spin−orbit corrections increased the stretches and decreased the bend. Overall, these two corrections decreased the harmonic asymmetric stretch frequency by 6 cm^{-1}, the symmetric stretch by 3 cm^{-1}, and the bend by 3 cm^{-1}. The best calculated values for UO_2^{2+} for the asymmetric stretch, symmetric stretch, and bend were 1113, 1032, and 174 cm^{-1}, respectively. The separation between the asymmetric and the symmetric stretch band origins was predicted to be 81 cm^{-1}, which is consistent with experimental trends for substituted uranyls in solution and in the solid state. The anharmonic vibrational frequencies of the isoelectronic ThO_2 molecule also were calculated and compared to experiment to calibrate the UO_2^{2+} results.

Introduction

There is substantial interest in the behavior of the uranyl dication due to the role that it plays in many different technological regimes from energy production to waste storage. Vibrational spectroscopy of uranyl has been used to determine the types of ligands bonded to uranyl as well as the effect of the ligand on the uranyl frequencies. One issue is that there are no direct measurements of the vibrational spectra of the isolated ion. There have been many measurements, however, of the spectra of the ion in solution when complexed to different ligands.[1−11] More recently, the spectra of complexes of uranyl with different ligands were observed in the gas phase through a combination of electrospray ionization, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), and infrared multiphoton dissociation using the FELIX free electron laser. The combination of these techniques has enabled the spectra of uranyl complexed to acetone and acetontrile as well as other ligands to be measured.[12]

At the same time as the advances in experimental techniques, there was a comparable advance in electronic structure methods for the treatment of actinides. Until recently, computational studies of heavy elements, particularly actinides, were challenging because of the large number of electrons and the importance of relativistic effects. However, with the development of density functional methods and relativistic effective core potentials, the treatment of actinide-containing complexes has become more routine and the results more reliable.[13−17] There have been numerous studies of uranyl complexation with ubiquitous ligands such as H_2O, NO_3^-, CO_3^{2-}, and the halides.[13−16,18,19]

An important issue for understanding as to how ligands affect the vibrational spectrum of the ion is the value of each of the three vibrational frequencies that describes isolated uranyl. The critical frequencies for comparison with experiment are the symmetric and asymmetric stretches, and improved values are needed for the harmonic value and the fundamental including the role of anharmonicity. Although a number of computational studies previously were performed, we focused on three studies with the results summarized in Table 1. de Jong and co-workers[20] performed benchmark calculations on UO_2^{2+} at a variety of levels. The largest calculations were performed at the Dirac−Hartree−Fock plus coupled cluster single and double excitations plus a perturbative correction for triples (CCSD(T)) level[21−24] with the U(6s, 6p, 6d, 5f) electrons correlated as well as the O(2s, 2p) electrons. In addition, these workers studied the use of density functional theory (DFT) with the local and B3LYP exchange-correlation functionals in combination with different effective core potentials (ECP) and basis sets. Gagliardi and Roos[25] performed complete active space plus second-order perturbation theory (CASPT2) calculations on the frequencies of UO_2^{2+}. The CAS was a (12/12) calculation. They used the Stuttgart ECP and basis set for U without *g* functions[26,27] and the ANO-s (4s3p2d)[28] and ANO-L (4s3p2d1f) basis functions on O.[29] They also reported results for the B3LYP functional with the 6-311G** basis set on O. Clavaguéra-Sarrio et al.[30] studied the use of different exchange-correlation functionals in combination with the small core Stuttgart pseudo-potential for

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TABLE 1: Calculated Bond Distances (Å) and Harmonic Frequencies (cm^{-1})

method	R_e	asymmetric stretch	symmetric stretch	$\Delta(A-S)^a$	bend	ref
CASPT2/ANO-s	1.714	1153	1043	110		25
CASPT2/ANO-L	1.705	1066	959	107		25
DHF + CCSD/VTZ + cc-pVTZ	1.697	1186	1041	145	180	20
DHF + CCSD(T)/VTZ + cc-pVTZ	1.715	1121	974	147	164	20
CCSD/aVTZ(1)	1.6800	1175.7	1093.3	83	198.7	this work
CCSD(T)/aVTZ(1)	1.6984	1108.5	1019.4	89	176.7	this work
CCSD(T)/aVTZ(2)	1.6941	1119.9	1027.6	92	184.4	this work
CCSD(T)/aVQZ(1)	1.6924	1123.6	1030.8	93	180.9	this work
CCSD(T)/aVQZ(2)	1.6898	1120.0	1035.3	85	178.4	this work
B3LYP/ECP + DZP + diff	1.705	1140	1041	99	161	30
B3LYP/ECP + TZVP	1.696	1142	1049	93	163	20
B3LYP/aVTZ(1)	1.6935	1137.3	1046.2	91	165.6	this work
B3LYP/SO/aVTZ(1)	1.6950	1138.9	1049.7	89	162.7	this work

[a] Difference between asymmetric and symmetric stretching frequencies in cm^{-1}.

TABLE 2: Calculated Anharmonic Fundamental Frequencies (cm^{-1}) for UO_2^{2+}

mode	asymmetric stretch	symmetric stretch	$\Delta(A-S)^a$	bend
CCSD/aVTZ(1)	1168.8	1087.2	81.6	197.9
CCSD(T)/aVTZ(1)	1100.7	1012.8	87.9	175.8
CCSD(T)/aVTZ(2)	1111.6	1020.5	91.1	183.2
CCSD(T)/aVQZ(1)	1115.4	1023.9	91.5	179.7
CCSD(T)/aVQZ(2)	1111.4	1028.1	83.3	177.4
CCSD(T)/SO/aVQZ(2)[b]	1113.0	1031.6	81.4	174.5
B3LYP/SO (ref 30)	1132.7	1033.9	98.8	169.5

[a] Difference between asymmetric and symmetric stretching frequencies in cm^{-1}. [b] Obtained by adding correction from spin−orbit DFT calculations to CCSD(T)/aVQZ(2) anharmonic frequencies.

TABLE 3: UO_2^{2+} Vibrational Anharmonicity Constants[a]

method	X_{11}	X_{22}	X_{33}	X_{12}	X_{13}	X_{23}
CCSD/aVTZ(1)	−1.35	−0.12	−1.58	−0.63	−5.59	−0.94
CCSD(T)/aVTZ(1)	−1.35	−0.11	−1.83	−0.73	−6.23	−1.11
CCSD(T)/aVTZ(2)	−1.45	−0.15	−1.93	−0.89	−6.52	−1.19
CCSD(T)/aVQZ(1)	−1.43	−0.18	−1.90	−0.82	−6.43	−1.22
CCSD(T)/aVQZ(2)	−1.54	−0.02	−1.89	−0.85	−6.66	−1.51

[a] X_{ij}: 1 is symmetric stretch, 2 is bend, and 3 is asymmetric stretch) in cm^{-1}. For definition of X_{ii}, see ref 50.

uranium and a polarized double-ζ plus diffuse function basis set for oxygen with the 1s electrons treated by a pseudopotential.[31] Of interest to our study is the fact that they predicted the anharmonic contributions to UO_2^{2+} with the B3LYP functional.

The vibrational spectrum of the isoelectronic neutral ThO_2 molecule was observed in both Ar[32,33] and Ne[34] matrices, and two stretches were observed, confirming that the molecule was bent. Thus, ThO_2 can serve as an additional benchmark of the computational approach.

Calculations

The current CCSD(T) calculations were performed with the program system MOLPRO 2006.1[35] on the University of Alabama Opteron-based Parallel Quantum Solutions Linux cluster computer. As in the previous calculations by de Jong et al., we correlated 24 valence electrons in the CCSD(T) calculations. We used the small core RECP and spin−orbit potential from the Stuttgart group with the associated basis set on U augmented by 2 *g* functions [8s,7p,6d,4f,2g][14,19,26,36] (*g* exponents = 0.42 and 1.18) and the aug-cc-pVTZ [5s,4p,3d,2f] on O.[37] We labeled this basis set as aVTZ(1). We calculated the CCSD(T) energies (30 symmetry-unique points) on a three-dimensional grid in terms of the bond lengths and bond angles. These energies were fit to polynomials in displacement coordinates, and the resulting full quartic force field (with selected quintic contributions) was used in the program SURFIT[38] to calculate the harmonic frequencies and anharmonic corrections from the usual second-order perturbation theory expressions.[39] Additional CCSD(T) calculations on this same three-dimensional grid also were carried out with the newer segmented basis set for U of the form (14s,13p,10d,8f,6g)/[10s,9p,5d,4f,3g] and the aVTZ basis on O.[26,27] We labeled this basis set as aVTZ(2). Two additional grids were calculated by adding a set of two optimized *h* functions (exponents = 1.7696 and 0.7134) and a set of *i* functions (exponent = 1.2525) to the U basis set (optimized for the ^5I $5f^4$ state of U in averaged coupled pair functional calculations), both for our original [8s,7p,6d,4f,2g] set and the newer [10s,9p,5d,4f,3g] basis set, with the aVQZ basis set on O. These basis sets were labeled as aVQZ(1) and aVQZ(2), respectively. To calibrate the uranyl ion calculations, analogous calculations on ThO_2 also were carried out at the CCSD(T) level with the aVTZ(2) basis set. These latter calculations involved a grid with a total of 47 symmetry-unique geometries.

DFT calculations also were carried out with the previous basis set with the B3LYP exchange-correlation functional[40,41] with the programs Gaussian03[42] and NWChem.[43,44] Two-component spin−orbit relativistic ECP DFT calculations,[45] with the appropriate Stuttgart one-electron spin−orbit potentials included variationally, were performed with NWChem.

Results and Discussion

The calculated harmonic frequencies are given in Table 1, and the anharmonic fundamentals are shown in Table 2. The anharmonicity constants are explicitly shown in Table 3.

The harmonic frequencies exhibited interesting behavior. Our calculated asymmetric stretch was predicted to be 1108 cm^{-1} at the CCSD(T)/aVTZ(1) level. This can be compared to the value of 1121 cm^{-1} calculated at the DHF + CCSD(T) level of theory. The difference of 13 cm^{-1} is within the differences expected due to the use of different basis sets and the different

TABLE 4: ThO_2 Harmonic and Anharmonic Fundamental Vibrational Frequencies in cm^{-1}

method	R_e[a]	θ_e[b]	asymmetric stretch	symmetric stretch	bend
CCSD(T)/aVTZ(2) Harmonic	1.9054	116.47	809.9	755.4	165.1
CCSD(T)/aVTZ(2) Anharmonic			805.1	751.6	164.1
CCSD(T)/SO/aVTZ(2)[c]			807.7	756.0	165.3
B3LYP/SO/aVTZ(2)	1.8992	119.23	822.5	770.4	156.1
experiment[d,e] (Ar)		122.5 ± 2[c]	787.4	735.3	
experiment[f] (Ne)			808.3	756.8	

[a] Bond distance in angstroms. [b] Bond angle in degrees. [c] Obtained by adding correction from spin−orbit DFT calculations to CCSD(T)/aVTZ(2) anharmonic frequencies. [d] Ref 32. [e] Ref 33. [f] Ref 34.

treatment of the relativity. What is of interest is that the bond distance does not correlate exactly with the harmonic frequency. The longer bond distance obtained at the DHF + CCSD(T) level has a higher asymmetric stretching frequency than the calculation with the shorter bond distance at the CCSD(T)/aVTZ(1) level. The symmetric stretch is, however, smaller in the former case. A similar result was found by Gagliardi and Roos,[25] who added *f* functions to the O atom and obtained a shorter bond distance by 0.009 Å and a surprising decrease in the asymmetric stretch frequency of 87 cm^{-1}. The effect of the (T) correction is essentially the same for the DHF-CCSD(T) and ECP-CCSD(T) calculations, a lowering of 65 cm^{-1} in the former and of 67 cm^{-1} in the latter.

The behavior of the symmetric stretching frequency, which lies below the asymmetric stretch, shows a larger variation on the electronic structure method than does the asymmetric stretch. In particular, the difference between the symmetric and the asymmetric stretch varies depending on the method. At the CASPT2 level, the difference is ~110 cm^{-1} and is not strongly dependent on the basis set, even though the individual frequencies are very sensitive. At the DHF level, the difference is ~145 cm^{-1} at the CCSD and CCSD(T) levels. With the aVTZ(1) basis set, we found a difference of 83 cm^{-1} at the CCSD level and 89 cm^{-1} at the CCSD(T) level. The different B3LYP values ranged from 90 to 100 cm^{-1}. Thus, all of the differences obtained with an ECP-based approach fell in the range of 80−110 cm^{-1}. Within a given approach, the symmetric stretch does depend on the U═O bond distance, but different methods can give quite different symmetric stretches at the same bond distance. For example, the CASPT2/ANO-s calculation predicts a bond distance of 1.714 Å and a symmetric stretch of 1043 cm^{-1} as compared to the DHF-CCSD(T) value of 974 cm^{-1} at a bond distance of 1.715 Å. Similarly, the CASPT2/ANO-L calculation predicts a bond distance of 1.705 Å and a frequency of 959 cm^{-1}, whereas the B3LYP value of the frequency at the same bond distance is 1041 cm^{-1}.

The bending frequency ranges from 160 to 200 cm^{-1}, and all of the methods where the bends are reported predict a linear structure. We note that the CCSD(T)/aVTZ(1) results predict a bending frequency that is 13 cm^{-1} higher than the DHF + CCSD(T) value.

We next estimated the spin−orbit correction for the harmonic frequency at the spin−orbit DFT level. The calculations were performed with the B3LYP exchange-correlation functional and the same basis set and ECP as used for the CCSD(T)/aVTZ(1) calculations. The bending frequency was very sensitive to both the geometry and the energy convergence in these calculations since it was calculated numerically. Hence, very tight convergence thresholds were required for all of the computational parameters including the integrals. The effect of the spin−orbit was to increase the asymmetric stretch by 1.6 cm^{-1} and to increase the symmetric stretch by more than double this amount, 3.5 cm^{-1}. The effect of the spin−orbit on the bend was to decrease the frequency by just 2.9 cm^{-1}. Thus, spin−orbit effects on the harmonic frequencies were small. Rösch and coworkers[46] reported that the spin−orbit correction at the DFT level[47] with gradient corrected functionals is small, −3 cm^{-1}, and opposite to the direction we found.

The calculated fundamental frequencies (i.e., including anharmonic effects) are shown in Table 2, and the associated anharmonicity constants X_{ij} are given in Table 3. The latter are all relatively small and negative, indicating only small overall effects due to vibrational anharmonicity. The asymmetric stretch was calculated to decrease by just 7.8 cm^{-1} on incorporation of anharmonic effects at the CCSD(T)/aVTZ(1) level. The symmetric stretch has a slightly smaller change of 6.6 cm^{-1} at the same level of theory. The bend is predicted to decrease by only 0.9 cm^{-1} at the CCSD(T)/aVTZ(1) level. Essentially the same changes were predicted at the CCSD/aVTZ(1) level of theory, and these small effects were borne out by the small calculated anharmonicity constants. The anharmonic effects at the B3LYP level[30] for the two stretches are comparable to the CCSD(T)/aVTZ(1) and CCSD/aVTZ(1) values. The B3LYP functional[30] surprisingly predicts the bend to increase by 8−9 cm^{-1} upon inclusion of anharmonic effects. This could, perhaps, be due to the sensitivity of the bending frequency to the computational convergence parameters in the DFT calculations. Overall, the anharmonic effects on the two UO_2^{2+} stretching modes were less than 10 cm^{-1}, so the comparison of calculated harmonic values to experimental fundamentals would be expected to produce agreement to within about 10 cm^{-1} if the harmonic values were predicted exactly.

We next improved the quality of the basis set to aVTZ(2). The asymmetric stretching fundamental increased by ~11 cm^{-1}, and the symmetric stretching fundamental increased by ~8 cm^{-1}, both consistent with the bond distance slightly decreasing. The fundamental bend also was predicted to increase. The addition of the 2*h* and *i* functions to aVTZ(1) led to a shortening of the U−O bond distance as expected and an increase in the fundamental stretching frequencies by 14.7 cm^{-1} for the asymmetric stretch and 11.1 cm^{-1} for the symmetric stretch. The bend only increased slightly. Addition of the 2*h* and *i* basis functions to the aVTZ(2) basis set to give the AVQZ(2) basis set led to no change in the asymmetric stretch, an increase of 7.6 cm^{-1} in the symmetric stretch, and a decrease of 5.8 cm^{-1} in the bend. As a consequence, the difference in the symmetric and asymmetric stretch was reduced to 81.4 cm^{-1} from 91.1 cm^{-1} with the aVTZ(2) basis set. Our best estimated values for the fundamental frequencies were at the CCSD(T)/SO/aVQZ(2) level, where the spin−orbit correction was taken from the SO-DFT calculations and are given in Table 2. The effects of anharmonicity are small: 8.6 cm^{-1} for the asymmetric stretch, 7.2 cm^{-1} for the symmetric stretch, and 1 cm^{-1} for the bend.

The spin−orbit correction is even smaller and in the opposite direction, leading to an increase in the stretches.

To test our approach, we also calculated the fundamental frequencies for ThO_2. ThO_2 was predicted to be bent with a bond distance of 1.9054 Å and a bond angle of 116.47° at the CCSD(T)/aVTZ(2) level. This is in agreement with the experimental observation of two stretching fundamentals in an infrared study of matrix-isolated ThO_2.[32−34] The calculated frequencies at the CCSD(T)/aVTZ(2) level are given in Table 4 and compared to the experimental values from the Ar[32,33] and Ne[34] matrices. The anharmonic correction is even smaller for ThO_2 than for UO_2^{2+} with the asymmetric stretch reduced by 4.8 cm^{-1}, the symmetric stretch by 3.8 cm^{-1}, and the bend by 1 cm^{-1} as compared to the respective harmonic values. The spin−orbit DFT corrections are small and in the opposite direction to the anharmonic corrections, increasing the asymmetric stretch by 2.6 cm^{-1}, the symmetric stretch by 4.4 cm^{-1}, and the bend by 1.2 cm^{-1}. As in UO_2^{2+}, the spin−orbit correction for the asymmetric stretch is smaller than for the symmetric stretch. The agreement with the Ne matrix values[34] is excellent, with the two stretching frequencies predicted to within 1 cm^{-1} of the experimental values. The addition of higher angular momentum basis functions probably would raise the symmetric stretch by a few cm^{-1} on the basis of the UO_2^{2+} results. The comparison of our results with the Ne matrix values indicate that there is likely to be only a small matrix effect due to Ne and an Ar matrix effect of about 20 cm^{-1}, reducing the stretching frequencies. The results for ThO_2 support the quality of the UO_2^{2+} results and demonstrate that our results at the CCSD(T)/SO/aVQZ(2) level for UO_2^{2+} should be good to ±5 cm^{-1}.

From the previous results, it is clear that the harmonic stretching frequencies for UO_2^{2+} are sensitive to the correlation treatment, the basis set, and the treatment of relativistic effects. Comparison of the results at the CCSD(T)/aVTZ(1) level shows that the CCSD method overestimates the values by a substantial amount. The CCSD(T) values for the asymmetric stretch are in the range of 1100−1120 cm^{-1} and do not show much dependence on whether an ECP is used or if the relativistic effects are included at the DHF level. Once a reasonable size basis set is reached (aVTZ(1)), the frequencies are not strongly dependent on the quality of the basis set. The CASPT2 values show that there can be a substantial underlying basis set dependence for the asymmetric stretch. Although it is difficult to draw a definitive conclusion due to the use of different basis sets, it appears that the CASPT2 method underestimates the harmonic stretching frequencies. The DFT B3LYP values, however, show little dependence on the basis set for this stretch and are about 20 cm^{-1} above the CCSD(T)/aVQZ(2) value. The difference between the asymmetric and the symmetric stretch is very dependent on the method. Essentially, all of the calculations with an ECP predicted a separation of 80−100 cm^{-1}. The CASPT2 calculations predicted a value of around 110 cm^{-1}, whereas the DHF+CCSD(T) results predicted a separation of close to 150 cm^{-1}. This latter value seems to be too high and may be due to the somewhat smaller basis set that was used in that case. Experimental results for mono-, di-, and triacetate binding to uranyl in solution and the solid state showed a decrease in the band origin separation from 93 to 87 to 75−78 cm^{-1} as the charge changed from +1 to 0 to −1.[6,8−10,48] The splitting for UO_2^{2+} in aqueous solution with four to five bound H_2O molecules was ∼90−95 cm^{-1}.[49] Calculations at the B3LYP/ECP level[19] on UO_2^{2+} embedded in up to 15 H_2O molecules predicted a value of ∼95 cm^{-1}, consistent with the experimental results. Our best results (CCSD(T)/SO/aVQZ(2)) predicted a splitting of 81.4 cm^{-1}. Thus, we suggest that the splitting for the symmetric and asymmetric stretches in the bare ion UO_2^{2+} should be 80−85 cm^{-1}. We also note that the bending frequency is sensitive to the method and to the actual criteria used in the calculations. We found that the accuracy criteria can cause variations in the bending frequency by up to 30 cm^{-1} in DFT calculations. This can present issues when one is looking at the deviation of uranyl from linearity in the presence of different ligands, so one should be careful in such calculations to ensure that there are no artifacts being introduced by the grid or the convergence criteria.

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