Interaction Energy of the Radon−Water ($Rn\cdot H_2O$) Complex

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The radon−water complex ($Rn\cdot H_2O$) is studied using ab initio methods employing effective core potentials combined with various valence basis sets. The minimum energy geometry and harmonic vibrational frequencies are calculated using levels of theory up to QCISD; the interaction energy is calculated using levels of theory up to the CCSD(T) level. The minimum energy geometry corresponds to a C_s hydrogen-bonded structure, with a near-linear Rn···H−O bond, with a Rn···H bond length of 3.0 Å. A lower bound for the binding energy is obtained as $D_e = 0.52$ kcal mol^{-1} (180 cm^{-1}), which may be used to derive a ΔH_f^{298} of −57.9 kcal mol^{-1}.

1. Introduction

The presence of radon in water has long been postulated as a health hazard, since it may lead to the formation of cancer. In particular, investigations have been carried out into the risks posed by the presence of radon in well water[1] and private water supplies[2] (more specifically, showering with radon-containing water[3] and using toilets that employ radon-containing water[4]). Very recent studies have, however, concluded that the risks from radon in water are small.[5,6] Rn has been shown to have a role to play in the production of OH and HO_2 in indoor air,[7] and so it is possible that in areas where Rn concentrations are significant, the $Rn\cdot H_2O$ complex may have a role to play in OH production. Ding and Hopke[8] have studied the production of OH and HO_2 caused by radon: presumably the closer proximity of the Rn to H_2O in a complex would enhance the possibility of OH formation.

There do not appear to have been any ab initio molecular orbital studies of the interaction of a radon atom with water—no doubt this is due to the prohibitive number of electrons contained within a radon atom. On the other hand, there have been some detailed studies of other members of the $Rg\cdot H_2O$ (Rg = rare gas) family of complexes, with $Ar\cdot H_2O$ being the most studied[9] by spectroscopic and theoretical methods, and $He\cdot H_2O$ only apparently being studied by theory, with the most recent reports on $He\cdot H_2O$[10] and $Ar\cdot H_2O$[9] being by ab initio methods. It is the aim of the present work to calculate the minimum energy geometry of the $Rn\cdot H_2O$ molecular complex, and its interaction energy using ab initio methods. Clearly, with Rn expected to be very polarizable, and water having a significant dipole moment, this interaction is expected to be reasonable.

One immediate question that arises is what orientations of the radon atom with respect to the water molecule are possible. The obvious ones are along the C_2 axis of water, interacting with either the O atom, or the two hydrogen atoms, each of C_{2v} symmetry. The former might be favored, owing to the larger partial charge on O, but will be disfavored by the repulsion of the electrons; the latter might be favored as the repulsion is lower, but the radon will have to interact with two hydrogen atoms, each of which has only half the charge of O. The other possibilities are, first, that the radon becomes hydrogen bonded, i.e., it is positioned on one of the hydrogen atoms so that there is a close-to-linear O−H···Rn bond; and second, a nonplanar geometry. Of course, a structure between these limiting cases is possible. For $Ar\cdot H_2O$ the minimum energy structure appears to have the Ar atom lying in the H_2O plane at an angle of 100° to the C_2 axis on the O side of H_2O;[9] for $He\cdot H_2O$,[10] the structure is very similar, with the equivalent angle being 75°. The bond length (He to center of mass of H_2O) for $He\cdot H_2O$ (3.15 Å) is much shorter than that for $Ar\cdot H_2O$ (3.75 Å), which is contrary to the weaker $He\cdot H_2O$ binding energy ($D_e = 32$ cm^{-1} for $He\cdot H_2O$; $D_e = 108$ cm^{-1} for $Ar\cdot H_2O$), but consistent with the larger size of the Ar atom. If these trends are carried forward to $Rn\cdot H_2O$, then it is to be expected that a coplanar geometry will be obtained, with the Rn atom positioned more in a hydrogen-bonded orientation, with an interaction energy greater than the 108 cm^{-1} of Ar, and a longer bond length.

Each of the above geometries was optimized, and characterized by calculating second derivatives to obtain the harmonic vibrational frequencies. Note that nonplanar structures that were not of C_s symmetry were not considered as these seemed unlikely; in addition, Chalasinski et al.[9] considered these geometries for $Ar\cdot H_2O$ and found that they were higher in energy than the C_s ones.

2. Calculational Details

Owing to the large number of electrons in the radon atom and the fact that relativistic effects are certainly important for such a heavy atom, appropriate effective core potentials (ECPs) were employed to overcome these difficulties. In addition, owing to the rapid oscillation of the high-n atomic orbitals of Rn, and because the $Rn\cdot H_2O$ molecular complex is expected to be only weakly bound, and so have a long intermolecular bond, it is necessary to ensure that the valence basis set used is flexible

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TABLE 1: Optimized Geometry of the Single-Hydrogen-Bonded Rn·H_2O Minimum

	basis set						
method	H_2O	Rn	R_{Rn-H}/Å	R_{O-H1}/Å	R_{O-H2}/Å	∠HOH/deg	∠RnHO/deg
MP2	6-311++G(2d,2p)	RCEP-411+G(2d)	3.243	0.959	0.958	104.3	173.3
QCISD	6-311++G(2d,2p)	RCEP-411+G(2d)	3.317	0.957	0.956	104.5	179.4
MP2	6-311++G(2d,2p)	ECP78MWB-311+G(2d)	3.327	0.959	0.958	104.2	179.6
MP2	6-311++G(3df,3pd)	ECP78MWB-3111+G(3df)	3.143	0.959	0.959	104.0	176.2
MP2	6-311++G(3df,3pd)	RCEP-411++′G(3df)	2.997	0.960	0.959	104.1	173.4
QCISD	6-311++G(3df,3pd)	RCEP-411++′G(3df)	3.026	0.957	0.957	104.4	174.1

and is diffuse enough to cover the region between the two moieties. Also, polarization functions are required to describe the distortion of the electron distribution.

Two ECPs were used. The first was the full relativistic compact effective potential (RCEP) of Stevens et al., which has a core potential, plus a standard -41G set of valence basis functions.[11] This was augmented with extra sets of two sp (exponents 0.2, 0.02) and two d (exponents 0.25, 0.0625) functions, to give a 411+G(2d) basis set overall. The second was the ECP reported by Stoll, Preuss, and co-workers,[12] which was used in its quasirelativistic form, with 78 electrons described by the core (leaving the 6s and 6p orbitals as valence)—denoted ECP78MWB, where the M indicates that the neutral atom is used in the derivation of the ECP and WB implies the use of the quasirelativistic approach described by Wood and Boring,[13] which was used in ref 12 in order to derive the ECP. In its standard form,[12] the latter ECP is augmented by four s, four p, and a d function, giving a (4s4p1d)/[2s2p1d] valence space. This was augmented in the present work with extra sets of two s (exponents 0.445 76, 0.036 388 5), two p (exponents 0.361 27, 0.029 491 4) and one d (exponent 0.074 285) functions, to give an ECP78MWB-311+G(2d) basis set overall, i.e., similar in quality to the RCEP-411+G(2d). Next, the polarization space was increased to 3df quality in both cases (where the three d functions replace the former two in the case of the RCEP-basis set), and an extra set of diffuse sp orbitals were added to the RCEP basis set (in an even-tempered way), and this new basis set is denoted RCEP-411++′G(3df). (Note that the ++′ notation implies two diffuse functions on Rn; when ++ is used in the description of basis sets for H_2O, below, the first + implies the addition of a diffuse function on O, whereas the second refers to H.) The functions added were as follows: RCEP-411++′G-(3df): sp (exponent 0.006); d (exponents 0.3, 0.085, 0.024); and f(0.07).

For the ECP78MWB-based basis set, the valence region was redesigned (vide infra for the reason this was done) and this is denoted ECP78MWB-3111+G(3df). The functions added to the standard 31(d) valence basis set were as follows: s (exponents 0.75, 0.3, 0.042 453 3); p (exponents 0.7, 0.28, 0.034 406 6); d (0.78, 0.086 667); and f (0.1).

Finally, the ECP78MWB potential of ref 11 was used with a set of even-tempered valence orbitals derived in-house—these were obtained in a step-by-step process, where the exponents and the geometrical ratio were varied to give the lowest Hartree−Fock energy. In more detail, a single contracted s and a single contracted p function (each of which will correspond to the 6s and 6p orbital in Rn) were obtained by performing an atomic calculation on Rn with an even-tempered set of uncontracted s and p functions. A sufficient number of these was used such that the most diffuse exponent was less than 0.01. The contraction was then formed using the tightest Gaussian functions and those whose contraction coefficients were >0.02; the more diffuse primitives, which had contraction coefficients <0.02, were then discarded. Once these s and p contracted functions were obtained, these were augmented with sets of uncontracted s and p functions, obtained in an even-tempered way, with the exponent of the tightest function chosen to correspond to the region where the oscillation of the coefficients of the primitives forming the contracted function became significant. In this way, a good coverage of the whole valence region was obtained; d and f functions were then added. Thus, a $[8,1,1,1,1,1,1/7,1,1,1,1,1,1/5 \times 1/ 3 \times 1]$[14] valence basis set was derived; this is denoted ECP78MWB-[7s7p5d3f]. In a similar fashion, a larger $[8,1,1,1,1,1,1,1,1,1/7,1,1,1,1,1,1,1,1/7 \times 1/ 4 \times 1/2 \times 1]$[15] valence basis set was derived, which contains up to g functions; this is denoted ECP78MWB-[10s9p7d4f2g]. These last two basis sets were used to calculate the interaction energy at the QCISD/RCEP-411++′G(3df)-optimized geometry.

Note that for H_2O, the basis sets used were as follows: for the radon RCEP-411+G(2d) and ECPMWB-311+G(2d) basis sets, the 6-311++G(2d, 2p) basis set was used; for the radon RCEP-411++′G(3df) and ECPMWB-311++′G(3df) basis sets, the 6-311++G(3df, 3pd) basis set was used; for the radon ECP78MWB-[7s7p5d3f] basis set, the aug-cc-pVQZ basis sets were used, where the g functions of O and the f functions of H were excluded; and for the radon ECP78MWB-[10s9p7d4f2g] basis set, the full aug-cc-pVQZ basis sets were used.

All MP2, B3LYP, and QCISD geometry optimizations and harmonic frequency calculations were performed using Gaussian98,[16] whereas the CCSD(T) single-point energy calculations were performed using MOLPRO.[17]

3. Results and Discussion

Geometry And Harmonic Vibrational Frequencies. The initial set of geometry optimizations were performed using the MP2 and B3LYP methods, with a C_{2v} symmetry constraint, with the radon atom on the O side of the water, or bridging the two hydrogens. When the Rn RCEP-411+G(2d) basis was used in conjunction with the O and H 6-311++G(2d,2p) basis sets, then the O-bonded structure was found to be a second-order transition state at the MP2 level of theory. The H-bridged structure was higher in energy (but by only 10 cm^{-1}), and was a saddle point at the MP2 level, and a second-order transition state using the B3LYP method. An unconstrained optimization was then performed with the radon moved off of the C_{2v} axis, which yielded a minimum at the MP2 and the QCISD levels. As may be seen from Table 1, this single hydrogen-bonded structure has an almost linear O−H···Rn bond. Reoptimization of this structure using larger basis sets led to the results collected in Tables 1 and 2. Note that an optimization which started with a nonplanar C_s geometry, with the Rn above the H_2O in the σ_v plane, went back to a C_{2v} planar geometry.

Interestingly, the MP2 and QCISD methods lead to very similar results using the larger basis sets. Our best results for the complex indicate that the Rn···H−O bond is almost linear, and the Rn···H bond distance is 3.0 Å. From Table 1, it is clear that as the basis set quality increases, the Rn···H bond decreases, and the hydrogen bond moves slightly away from linear. As

TABLE 2: Harmonic Vibrational Frequencies for the Single-Hydrogen-Bonded Rn•H_2O Minimum (cm^{-1})

	basis set		intermolecular			H_2O		
$MeH_{10}Cl$	H_2O	Rn	a′	a′	a″	a′	a′	a″
MP2	6-311++G(2d,2p)	RCEP-411+G(2d)	40	96	162	1663	3856	3975
QCISD	6-311++G(2d,2p)	RCEP-411+G(2d)	38	95	160	1689	3877	3979
MP2	6-311++G(2d,2p)	ECP78MWB-311+G(2d)	40	53	95	1662	3857	3977
MP2	6-311++G(3df,3pd)	ECP78MWB-3111+G(3df)	48	78	128	1623	3862	3980
MP2	6-311++G(3df,3pd)	RCEP-411++′G(3df)	60	139	231	1626	3860	3978
QCISD	6-311++G(3df,3pd)	RCEP-411++′G(3df)	57	140	232	1656	3884	3984

far as the MP2 and QCISD methods are concerned, when using the RCEP ECP with the largest basis set used for the optimization, the two results are very similar.

As well as the basis sets noted in Table 1, we also attempted an optimization with an ECP78MWB-311++′G(3df) basis set, which was designed in the same way as the RCEP-411++′G(3df) basis set, which we hoped would allow a comparison of the two ECPs; however, it was found that the surface was very flat using this basis set (this was indicated by a convergence of the gradient, but still with a large predicted displacement), and this prompted us to redesign the valence space and use a 3111+G(3df) basis set instead, which emphasizes the valence region further. The extra valence s and p functions were chosen to fill a gap in the standard contracted s and p functions, thus making the 3111G region of the ECP78MWB basis set closer to the 411G region of the RCEP one. Consequently, we are unable to comment in detail about the relative performance of the two ECPs, but it would be expected that the RCEP, which takes a more complete account of relativistic effects, would be the more accurate—indeed, the energy obtained using the RCEP is lower than that using the ECP78MWB one, which only uses a quasirelativistic approach. Our feeling is, however, that as far as the geometry and calculation of the vibrational frequencies of the complex is concerned, it is the quality of the valence region of the basis set which is the more important. We note also that increasing the valence region of the ECP78MWB-3111+G(3df) basis set leads to results that are not too different from those obtained using the RCEP-411++′G(3df) one, and so we are confident that the results obtained below for the interaction energy, employing the RCEP-4111++′G(3df)-optimized geometry, should be reliable.

We did attempt to use the B3LYP density functional method, but found that it led to very long Rn•••H bond lengths, and so we discounted it as a viable method to study this complex.

The calculated geometry for Rn•H_2O falls into the general trend expected, based upon the calculated (and in the case of Ar•H_2O, measured) minimum energy geometries for the Rg•H_2O series. For He•H_2O, the He atom is situated closer to the O atom, whereas for Ar•H_2O, the Ar atom has moved more toward the H atoms. This may be rationalized by a competition between a dipole/induced-dipole interaction, which would favor the oxygen atom and the Pauli repulsion between the electrons of O and the rare gas atom, where the H atoms are favored. The small number of electrons on He allows it to remain on the O atom, whereas the larger number on Ar causes it to move toward the hydrogens. Clearly, the Pauli repulsion will be much larger for Rn, and so it moves such that it is positioned almost straight along an O−H bond, forming what looks like a nominal hydrogen bond.

With regard to the harmonic vibrational frequencies, first it is noted that the water vibrational frequencies are in very good agreement with experiment and high-level ab initio harmonic values.[18] Second, it may be seen that the intermolecular values are sensitive to the quality of the valence basis set, as expected. The most reliable values are expected to be those obtained with the RCEP-411++′G(3df) basis. It is notable that the presence of the extra diffuse and polarization functions in this basis set is having a dramatic effect. Interestingly, the values obtained using both the MP2 and the QCISD methods are extremely close, for the same basis set.

In conclusion, it is clear that the standard valence basis sets which are associated with the Rn ECPs are not adequate for the description of Rn•H_2O. Increasing the quality of the valence basis set increases the interaction, as illustrated by the shorter intermolecular bond and the higher vibrational frequencies. The vibrational frequencies are expected to be more sensitive to the basis set than the geometry of the complex, and this is borne out. The interaction energy is expected to be even more sensitive to the valence basis set, and for this, larger ones are anticipated as being necessary.

Interaction Energy. Once the minimum energy geometry had been obtained, the more demanding interaction energy was calculated via single-point energies. For these calculations, much higher quality redesigned valence basis sets, described in the Calculational Details section, were employed at the geometry obtained at the QCISD/RCEP-411++′G(3df) level of theory (see last row of Table 1); the interaction energy was obtained at the MP2, CCSD, and CCSD(T) levels of theory. The use of these large basis sets at the CCSD(T) level necessitated the use of the MOLPRO program, which is much faster than Gaussian98 for CCSD(T) calculations. Unfortunately, only the ECP78MWB ECP for radon is available in the version we have access to; however, use of this program allowed the use of a much larger valence basis set than would have been possible otherwise. This allowed the use of a smaller ratio for the production of the even-tempered exponents, and so a better description of the oscillatory behavior of the high-n orbitals of radon. Since the core region of Rn is not expected to affect the complexation to a large extent, the interaction energy should not be too sensitive to the actual form of the ECP.

With the smaller of the two valence basis sets, it may be seen from Table 3 that the basis set superposition error (BSSE), calculated using the full counterpoise correction of Boys and Bernardi,[19] is >60% of the uncorrected interaction energy, with the vast majority of the BSSE being localized on the Rn atom. Thus, the valence basis set was increased further, with a corresponding increase in the O and H basis sets to retain balance. This led to a large lowering of the BSSE on the Rn atom, with the final result being ∼36% of the uncorrected interaction energy. Note that the BSSE on the H_2O moiety is basically the same with each of these two basis sets, suggesting saturation. The BSSE on the Rn atom is still significant with respect to the interaction energy (although we note that the magnitude is actually quite small). This may possibly be reduced by a further increase in the valence space, but we feel it would not be prudent to invest computer time doing this, as there are almost certainly unaddressed inadequacies in the Rn ECP, which are not so straightforward to study, a comment we have made in a recent paper when using ECPs in a study of Kr•NO^+ and Xe•NO^+ (ref 20).

TABLE 3: Interaction Energy (ΔE_e) for the Rn·H_2O Complex[a]

	BSSE/kcal mol^{-1}			$-\Delta E_e$/kcal mol^{-1}	
method[b]	Rn	H_2O	total	no CP correction	with CP correction
MP2/A	0.77	0.04	0.81	1.26	0.46
CCSD/A	0.81	0.03	0.84	1.11	0.27
CCSD(T)/A	0.87	0.03	0.90	1.36	0.46
MP2/B	0.32	0.03	0.34	0.88	0.54
CCSD/B	0.26	0.04	0.30	0.60	0.30
CCSD(T)/B	0.28	0.02	0.30	0.83	0.52

[a] Single-point calculations at the optimized geometry as given in the final row of Table 1. [b] Basis set A = ECP78MWB-[7s7p5d3f][14] for radon and aug-cc-pVQZ for H, O, where the f functions were excluded for H, and the g functions were excluded for O; basis set B = ECP78MWB-[10s9p7d4f2g][15] for radon and aug-cc-pVQZ for H, O. Basis set A has 200 valence basis functions, whereas basis set B has 290.

As an additional test of our basis set, we computed the equilibrium bond length of the Rn_2 dimer, and the interaction energy, to compare with the recent results of Runeberg and Pyykko.[21] These workers also used the ECP of ref 12 and augmented with their own basis sets. Their best results at the MP2 level (CP corrected) with one of their largest basis sets, [7s7p6d6f2g], were $r_e = 4.452$ Å and $D_e = 250$ cm^{-1}, whereas at the CCSD(T) level (CP corrected) with a slightly different basis set, [9s8p7d7f], the results were $r_e = 4.588$ Å and $D_e = 184$ cm^{-1}. Using our largest basis set, [10s9p7d4f2g], (basis B, see footnote to Table 3) at the CCSD(T) level values, of $r_e = 4.508$ Å and $D_e = 205$ cm^{-1} were obtained. Certainly the basis sets designed in the present work are at least comparable to those used in ref 21.

Thus, at present, our best value for the interaction energy of Rn·H_2O is 0.52 kcal mol^{-1} (180 cm^{-1}). It is notable that the interaction energy calculated using the MP2 method is almost identical to that obtained using the CCSD(T) method, with the triples correction moving the lower CCSD result back to the MP2 value.

With regard to how reliable the value of 180 cm^{-1} is for the interaction energy, it is necessary to consider the size of the BSSE. As mentioned above, it is clear that going from basis set A to basis set B, a large decrease in the BSSE is obtained. The BSSE is still ~36% of the CP-uncorrected interaction energy, however, with basis set B. Considering that there are 18 electrons active in the system, the BSSE per electron is only 6 cm^{-1}, which compares favorably with results obtained for Rg·NO^+ complexes using basis sets of a similar quality.[20] What is clear from the results in Table 3 is that the value of 180 cm^{-1} is a lower bound for the true interaction energy of the Rn·H_2O complex. This conclusion is supported by two points: first, the increase in size and/or quality of basis set is leading to a slightly larger interaction energy; and second, *if* the full counterpoise correction is an overcorrection, then the true value would also be larger.

Thermodynamics. The interaction energy may be converted to a ΔH_R^{298} value of -0.14 kcal mol^{-1} for the association reaction, Rn + H_2O → Rn·H_2O, using standard statistical mechanical methods, under the assumption of an ideal gas, and a rigid rotor, harmonic oscillator model. (The interaction energy used is that calculated at the CCSD(T) level, using the largest basis set (see last row of Table 3), with the harmonic vibrational frequencies and geometry being used from the QCISD calculations reported in the last rows of Tables 1 and 2.) The loss in entropy conspires to give a ΔG_R^{298} value of $+4.2$ kcal mol^{-1}, which can be converted to a K_p value of 9×10^{-4}.

In addition, using standard values for $\Delta H_f^{298}(H_2O) = -57.798$ kcal mol^{-1} (ref 22), since $\Delta H_f^{298}(Rn) = 0$ by definition, $\Delta H_f^{298}(Rn \cdot H_2O)$ may be calculated to be -57.9 kcal mol^{-1}.

4. Conclusions

The Rn·H_2O molecular complex has been studied using effective core potentials augmented with sets of valence basis functions. The geometry has been found to be of a near-hydrogen-bonded structure, with a Rn···H distance of ~3.0 Å. As always with such weakly bound complexes, the equilibrium geometry will not be that observed experimentally, and the magnitude of the zero-point vibrational energy, compared to the dissociation energy, D_e, suggests that the complex will be very floppy, exhibiting large-amplitude motion.

The interaction energy has been found to be quite demanding to calculate accurately, owing to the large amount of basis functions required to describe the valence region of Rn, and the intermolecular region adequately. We have found that it is the basis set, rather than the level of theory, that is the most important factor in describing the Rn·H_2O complex; in particular, we conclude that the standard valence basis sets (which are of only double-ζ quality, with four or five primitives) associated with the two ECPs are inadequate, and that a much more flexible one is needed to describe the Rn·H_2O complex adequately, owing to the need to describe the oscillatory nature of the valence orbitals of Rn, and the intermolecular region. The MP2 and QCISD results for the geometry and harmonic vibrational frequencies were very similar for the same basis set. We offer a best value of 0.52 kcal mol^{-1} (180 cm^{-1}) for the interaction energy of Rn·H_2O. Note that this is D_e, and that D_0 will be significantly less, owing to zero-point vibrational energy.

The low value of K_p suggests that the concentrations of the complex should be small at room temperature, but will become significant at low temperatures, such as higher in the atmosphere or other cold environments. Whether the complex has an important role in processes involving radon, such as the production of OH and HO_2 mentioned in the Introduction, will depend on the increased efficiency of the radical production caused by the closer proximity of the Rn and H_2O in the complex.

Note Added in Proof. The Ne·H_2O potential energy surface has recently been studied by Bagno.[23]

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(14) The contracted s function consists of eight Gaussians with exponents ranging from 2.8 to 0.021 875, with a even-tempered ratio of 2.0; the uncontracted s basis functions have exponents ranging from 1.1 to 0.006 994, with an even tempered ratio of 2.75. The contracted p function consists of seven Gaussians with exponents ranging from 2.2 to 0.034 375, with an even-tempered ratio of 2.0; the uncontracted p basis functions have the same exponents as those of the uncontracted s ones. The uncontracted d basis functions range from 0.4 to 0.004938, with an even-tempered ratio of 3.0. The uncontracted f exponents are 0.25, 0.071 43 and 0.020 41.

(15) The contracted s and p functions are the same as those described in ref 14. The uncontracted s basis functions range from 2.0 to 0.001 310 72, with an even-tempered ratio of 2.5. The uncontracted p basis functions range from 1.5 to 0.002 457 6, with an even-tempered ratio of 2.5. The d basis functions range from 1.25 to 0.002 898 0, with an even-tempered ratio of 2.75. The f basis functions range from 0.5 to 0.018 52, with an even-tempered ratio of 3.0. The g basis functions have exponents 0.3 and 0.075.

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