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Ab initio spectroscopy of Van der Waals molecules: a comparison of three different theoretical methods applied to NeHF and NeDF

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Abstract

Three ab initio methods, namely MP2, CCSD(T) and SIMPER-1K, are used to calculate the intermolecular potential between neon and a rigid HF molecule. The energies of Van der Waals rovibrational bound states are calculated from the potential energy surfaces, and compared with previously published high-resolution spectra. The MP2 method does not predict all the observed bound states, but the SIMPER-1K and CCSD(T) methods both give good agreement with the experimental results. Using the SIMPER-1K method, rotational constants differ from experiment by less than 10%, stretching and bending frequencies by less than 3% and centrifugal distortion constants by less than 4%.
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1. Introduction

The thermodynamic, spectroscopic and structural properties of Van der Waals molecules depend mainly on their intermolecular interactions, and obtaining the intermolecular potential energy surfaces to sufficient accuracy is an important and difficult scientific problem. Van der Waals molecules are usually weakly bound and highly non-rigid, so it is necessary to know the potential energy at a wide range of different bond lengths and angles, not just around the Van der Waals minimum. This means that hundreds or thousands of data points (either points on the potential energy surface, or experimental data related to it) are often required to characterise the potential energy surface satisfactorily.

High-resolution spectroscopy of cold gas-phase Van der Waals molecules provides the most precise information on intermolecular potential energy surfaces. Transition wavenumbers involving rotation, bending and stretching of Van der Waals bonds can be measured to a precision of better than 0.1%. However, the small number of bound vibrational states of most Van der Waals molecules limits the number of spectral transitions which can be measured, and it is seldom possible to deduce the complete multidimensional potential energy surface (or even simple features such as the position of the potential energy minimum) from experimental data.

Theoretical methods have therefore been used extensively alongside experiments in attempting to obtain intermolecular potential energy surfaces. In principle, quantum chemistry gives the intermolecular potential exactly, as the difference between the dimer and isolated monomer energies. However, methods which have been developed mainly for covalent molecules do not work well for Van der Waals molecules. Self-consistent-field and density-functional theories predict no Van der Waals bonding, and the missing electron correlation is only recovered as a slowly converging function of order in many-body perturbation theory, or of excitation level in coupled-cluster theory. The additional need to use large, polarised basis sets with diffuse functions makes calculations of individual interaction energies expensive, and accurate calculation of a complete surface is a very demanding, often impossible, task. Spectroscopic accuracy is not achieved with computationally feasible calculations. Therefore, it is common practice to adjust the

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results of quantum chemical calculations to obtain better agreement with experimental data [1–6]. This may involve changing the depth of the calculated potential, or the equilibrium separation, or both. The advantage of these partly-empirical 'morphing' methods is that a complete potential energy surface is obtained, even with limited experimental data. The disadvantage is that some fitting to experimental data is required, which reduces the applicability of the method to systems already studied experimentally, and the fitting method is inevitably arbitrary, and would generally be difficult to apply to larger molecules.

The main purpose of this Letter is to compare three methods for direct (non-empirical) quantum-mechanical calculation of intermolecular potentials, and assess their accuracy compared with 'morphed' potentials and with experiment. The NeHF and NeDF dimers are chosen for this comparison. They are Van der Waals molecules for which high-resolution experimental data and a high-quality 'morphed' potential energy surface are available [6], and bound-state calculations can be performed to high precision, such that discrepancies with experiment can be ascribed entirely to the potential energy surface. The Van der Waals binding in these dimers depends on a delicate balance between dispersion, induction and exchange-repulsion, and the dimers are small enough to allow correlated ab initio methods to be used, with large basis sets.

2. Calculations and results

Potential energy surfaces are calculated using MP2 and CCSD(T) supermolecule methods with the MOL-PRO package [7], applying the full counterpoise correction [8], with the SP-aug-cc-pV5Z basis set [9,10], giving a total of 334 basis functions for the complex. This basis set is believed to be close enough to the complete basis set limit that the different methods can be fairly compared (see below). A polar co-ordinate system is used, in which R is the Ne–F distance, and θ is the angle between the $H \rightarrow F$ and $Ne \rightarrow F$ vectors. The H–F distance is fixed at its equilibrium value, $1.73291\ a_0$; the effect on the potential energy surface of changing the H–F bond length is considered below. Calculations are performed at nine distances, $(R/a_0) = 4\ (1)\ 10$, 5.5 and 6.5, and seven angles, $\theta = 0\ (30)\ 180°$.

The SIMPER-1K method (Systematic InterMolecular Potential Extrapolation Routine, version 1K) is used to extrapolate the MP2 supermolecule calculations. The same basis set is used for SIMPER-1K as for the other calculations. The method has already been described [11], so only a brief summary is given here. The first-order Coulomb interaction energy at the MP2 supermolecule level is removed from the MP2 supermolecule energy and replaced by a first-order Coulomb energy

calculated from CCSD monomer charge densities. The dispersion energy at the MP2 supermolecule level is replaced by a higher-level dispersion energy, which is calculated using long-range coefficients C_n, obtained from TD-CISD frequency-dependent polarizabilities, and short-range damping functions, obtained by scaling the length co-ordinate in the damping functions by the ratio $(C_6/C_8)^{1/2}$. The exchange-repulsion energy at the MP2 supermolecule level is scaled by the ratio of the charge density overlap at the CCSD monomer level and the MP2 supermolecule level. Finally, the remaining Coulomb energy in the MP2 supermolecule calculation is retained without any scaling; this includes the induction energy. Adding the first-order CCSD Coulomb energy, the higher-level dispersion energy, the scaled exchange-repulsion energy, and the remaining MP2 Coulomb energy, gives the SIMPER-1K potential energy surface.

Much of the difference between the MP2 and SIMPER-1K potentials can be ascribed to the different treatment of the dispersion interaction. For example, the C_6 dispersion energy coefficient is given in atomic units by $C_6 = 9.27 + 0.80\ P_2(\cos\theta)$ in the supermolecule MP2 calculation, and by $C_6 = 10.72 + 0.70\ P_2(\cos\theta)$ in the SIMPER-1K calculation. Consequently, at the equilibrium Ne–H–F geometry the SIMPER-1K dispersion energy is about $22\ \mathrm{cm}^{-1}$ more negative than the MP2 dispersion energy.

To obtain a full two-dimensional potential energy surface, which is suitable for calculating bound states, the dependence of the interaction energy on the angle θ is expanded as a series of Legendre polynomials

$$E(R, \theta) = \sum_{l=0}^{l_{\max}} E_l(R) P_l(\cos\theta), \tag{1}$$

with $l_{\max} = 6$. Each Legendre component of the potential, $E_l(R)$, is then fitted using

$$E_l(R) = A\exp(-BR) - C(R+X)^{-n} - D(R+X)^{-n-2}. \tag{2}$$

The value $n = 6$ is used for $l = 0$ and $l = 2$, $n = 7$ for $l = 1$ and $l = 3$, $n = 8$ for $l = 4$, $n = 9$ for $l = 5$, and $n = 10$ for $l = 6$. The errors in this fit are usually about $0.1\ \mathrm{cm}^{-1}$ at the potential minimum, and are insignificant compared to the differences between the potentials. Unique values of the non-linear parameters B and X are always found in the fits, and the values of all the fitted parameters are physically reasonable.

The three fitted potential energy surfaces are plotted in Fig. 1. This shows that the qualitative shape of the potential energy surfaces is the same, with the deepest well in the Ne–H–F linear geometry, a secondary minimum in the Ne–F–H geometry, and a transition state in a roughly T-shaped geometry. The repulsive wall deviates from spherical symmetry about the F nucleus by
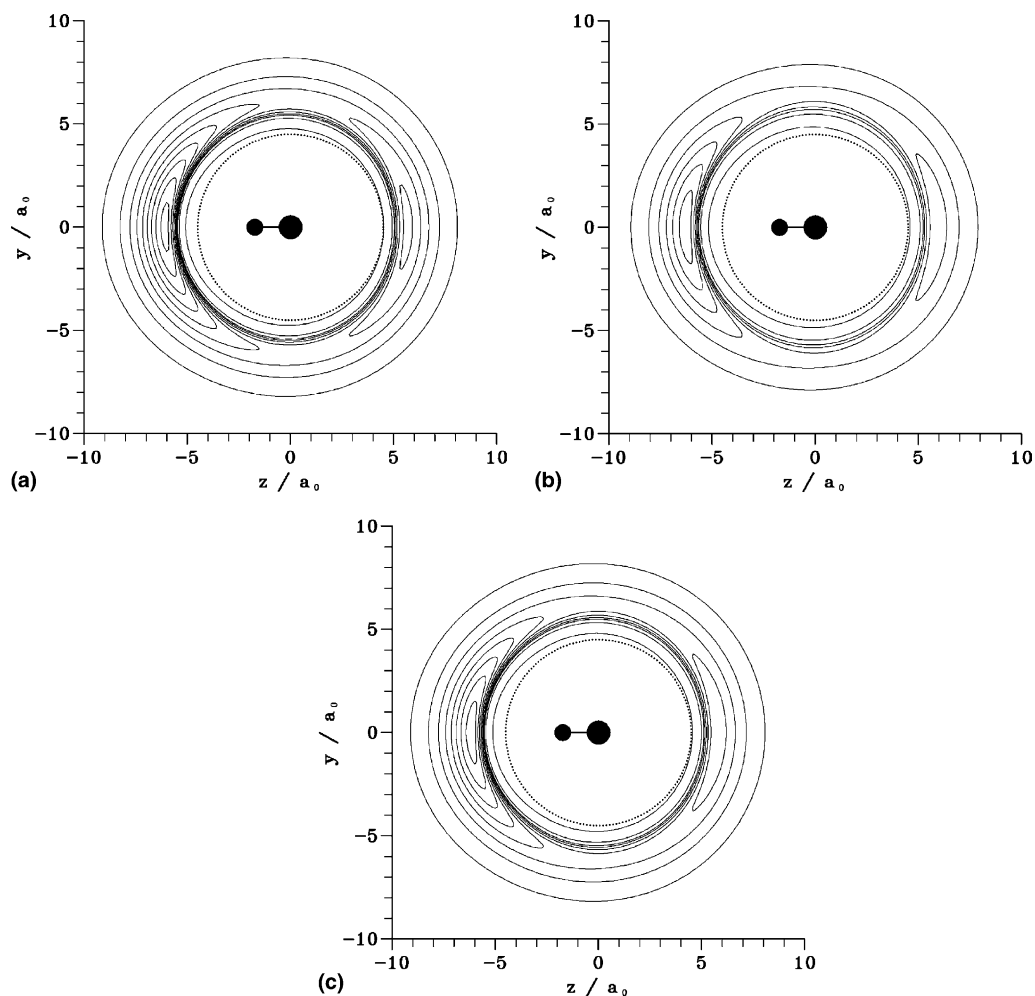
Fig. 1. Contour plots of the Ne–HF potential energy surface, calculated using the three different methods described in the text: (a) SIMPER-1K; (b) MP2; (c) CCSD(T). Contours are drawn at 300, 30 cm^{-1}, zero, and intervals of 10 cm^{-1} below zero. Distances are in atomic units. The dotted circle has a radius of 4.5 a_0 and is centred on the F nucleus.

about 0.6 a_0 in each case, with the largest repulsion being in the direction of the H nucleus. Significant quantitative differences between the potential energy surfaces are apparent from the figures, with the MP2 potential well being by far the most shallow, and the CCSD(T) potential well being slightly more shallow than the SIMPER-1K potential. The well depths and equilibrium separations at the linear Ne–H–F minimum and Ne–F–H secondary minimum are compared with the best 'morphed' potential of Meuwly and Hutson [6]

(MH) in Table 1. The positions and depths of the SIMPER-1K and CCSD(T) potential energy minima agree about equally well with the MH potential, although the SIMPER-1K potential is slightly deeper, and the CCSD(T) potential is slightly shallower. The tendency of SIMPER-1K to overestimate the well depth may be partly explained by the fact that the second-order induction energy is not corrected in the SIMPER method [11]. The results for the equilibrium distance in the Ne–H–F geometry appear to be anomalous, as even

Table 1
Comparison of potential well parameters calculated for Ne–H–F in two linear geometries, using three ab initio potentials and the morphed MH potential [6]

	MH	SIMPER-1K	MP2	CCSD(T)
$-\varepsilon$ (Ne–H–F)	88.5	93.7	66.1	85.1
$-\varepsilon$ (Ne–F–H)	50.0	53.0	35.7	46.6
R_e (Ne–H–F)	6.19	6.08	6.26	6.15
R_e (Ne–F–H)	5.70	5.67	5.88	5.75

Interaction energy minima ε are in cm^{-1}, equilibrium distances R_e are in atomic units (a_0) and refer to the Ne–F distance.

the CCSD(T) potential underestimates this quantity. This is probably because the MH potential surfaces were fitted to the experimental data for HF in its $v = 1$ vibrational state, which increases the average HF bond length, and therefore increases the anisotropy of the repulsive wall.

Bound states for the MP2, CCSD(T) and SIMPER-1K potentials are calculated using the program BOUND [12,13]. Nine rotational functions, from $J = 0$ to $J = 8$, are included in the angular expansion of the rovibrational wavefunctions, with rotational constants of 19.787478 cm^{-1} for Ne–HF and 10.564179 cm^{-1} for Ne–DF. The reduced masses are 9.999665 u for Ne–HF and 10.24489 u for Ne–DF. The radial wavefunctions are propagated between 4 and 20 a_0, and the step size used in the calculations is 10^{-4} a_0, with a convergence limit tolerance of 10^{-4} cm^{-1}.

The calculated transition wavenumbers are compared in Table 2 with experimental values and with the MH potential energy surface giving the smallest overall deviation from experiment. Ne–HF has one excited Van der Waals vibrational state, the π bend. Ne–DF also has a Σ stretch and a Σ bend. The ground state and π bend rotational constants (roughly equal to half the $E_1 - E_0$ transition wavenumbers) mostly contain information about the radial minimum between $\theta = 0$ and $\theta = 90°$, whereas the Σ bend rotational constant is a measure of the location of the radial minimum at around $\theta = 180°$. The parameter Δ, which is approximately equal to the

centrifugal distortion constant, is sensitive to the radial curvature of the potential around the minimum. The difference between the $J = 1f$ and $J = 1e$ levels of the π bend represents the Coriolis splitting.

The overall accuracy of the potential energy surfaces, relative to experiment, is assessed by the weighted RMS deviation σ_1, given by

$$\sigma_1^2 = \frac{1}{n} \sum_{i=1}^{n} [(P_{i,\text{calc}} - P_{i,\text{expt}})/\delta_{i,\text{expt}}]^2 \qquad (3)$$

and by the RMS percentage deviation σ_2, given by

$$\sigma_2^2 = \frac{1}{n} \sum_{i=1}^{n} [100(P_{i,\text{calc}} - P_{i,\text{expt}})/P_{i,\text{expt}}]^2, \qquad (4)$$

where n is the number of experimental values used in the comparison, the ith experimental value is $P_{i,\text{expt}}$ with experimental uncertainty $\delta_{i,\text{expt}}$ [6,14–16], and the corresponding calculated value is $P_{i,\text{calc}}$. The quantity σ_1 is similar to that used by MH [6], and gives a guide to the average accuracy of the theoretical calculations, compared to the resolution of the experimental measurements. The value of n is 14 for the CCSD(T) and SIMPER-1K results, and 8 for the MP2 results. This is because the MP2 potential energy surface is too shallow to predict all of the bound states. Even disregarding this fact, it is clearly seen that the CCSD(T) and SIMPER-1K surfaces are superior in overall fit of the data, by a factor of 4–6 in the weighted RMS deviation. Since the MP2 surface also does not produce all the bound states,

Table 2
Comparison of transition wavenumbers for Ne–HF and Ne–DF, calculated using three ab initio potentials and the morphed MH potential [6], with experimental values and uncertainties δ [14–16]

Transition	Experiment	δ	MH	SIMPER-1K	MP2	CCSD(T)
Ne–HF						
Binding energy D_0[a]			32.830	32.683	18.409	28.898
$v = 0$: $E_1 - E_0$	0.2989	0.0002	0.2997	0.3003	0.2706	0.2916
$(-E_2 + 3E_1 - 2E_0)/24 = \Delta$	1.970×10^{-5}	1.7×10^{-7}	1.954×10^{-5}	2.023×10^{-5}	2.972×10^{-5}	2.160×10^{-5}
π bend: $E_{1f} - E_0$ ($v = 0$)	44.0340	0.01	44.0716	44.4898	[b]	43.9214
$E_{2f} - E_{1f}$	0.5938	0.0004	0.5936	0.5974	[b]	0.5795
$E_{1e} - E_{1f}$	0.0205800	0.0002	0.0194762	0.0285614	[b]	0.0171194
Ne–DF						
Binding energy D_0[a]	35.1	0.76	35.009	35.018	19.523	30.911
$v = 0$: $E_1 - E_0$	0.2961	0.0002	0.2959	0.2907	0.2642	0.2829
$(-E_2 + 3E_1 - 2E_0)/24 = \Delta$	1.608×10^{-5}	1.7×10^{-7}	1.660×10^{-5}	1.647×10^{-5}	$2.551 \times 10{-5}$	1.782×10^{-5}
Σ bend: $E_0 - E_0$ ($v = 0$)	19.5295	0.01	19.5380	19.2978	15.0181	19.2291
$E_{J=1} - E_{J=0}$	0.2689	0.0002	0.2689	0.2949	0.1896	0.2844
Σ stretch: $E_0 - E_0$ ($v = 0$)	23.3811	0.01	23.3809	23.4722	17.9296	21.3463
$E_1 - E_0$	0.2382	0.0002	0.2377	0.2262	0.2575	0.2155
π bend: $E_{1f} - E_0$ ($v = 0$)	27.2791	0.01	27.2533	27.9340	[b]	27.0403
$E_{2f} - E_{1f}$	0.5830	0.0004	0.5823	0.5836	[b]	0.5662
$E_{1e} - E_{1f}$	0.0229800	0.0002	0.0232908	0.0189720	[b]	0.0194825
Weighted RMS, σ_1			2.55	43.60	268.18	66.80
% RMS, σ_2			1.73	11.81	32.10	8.31

All transition wavenumbers and uncertainties are in cm^{-1}. The dimensionless RMS deviations are defined in Eqs. (3) and (4).
[a] not used in the RMS deviations.
[b] missing bound states; not used in the RMS deviations.

it can be seen that MP2 is not an adequate method to describe this system theoretically.

CCSD(T) and SIMPER-1K perform at roughly the same level. Depending on whether the weighted RMS deviation or RMS percentage deviation is taken as the measure of performance, either could be said to be 'better'. The SIMPER-1K surface gives a weighted RMS deviation which is about 1.5 times less than that of the CCSD(T) surface. However, the performance of the CCSD(T) surface is better by about a factor of 1.4 when the RMS percentage deviation is considered. The weighted RMS deviation penalises a prediction if it is not accurate compared to the experimental uncertainty. It is larger for the CCSD(T) surface, because this is less accurate in some areas which are precisely known experimentally, such as rotational constants. On the other hand, the SIMPER-1K surface is less accurate in areas where the experimental precision is lower, particularly the Coriolis splitting. The binding energies D_0, which are not included in the RMS deviations, are reproduced more closely by SIMPER-1K. The SIMPER-1K well depth is larger than the MH well depth by about 5 cm^{-1}, but this is cancelled almost exactly by the greater zero-point energy obtained from the SIMPER-1K potential. It should be emphasised that the SIMPER-1K surface is produced without doing supermolecule calculations at a higher level of theory than MP2. It thus takes an order of magnitude less computer time than the CCSD(T) surface.

In order to check that the results are sufficiently converged with respect to the value of l_{max} chosen in Eq. (1), calculations are performed using different values of l_{max}, and the results are shown in Table 3. It can be seen that the error estimates converge as the number of expansion functions increases, and that using a higher value of l_{max} is unlikely to change the relative performance of the different methods. Generally, the agreement with experiment improves or remains approximately constant when l_{max} is increased, although the RMS percentage deviation of the CCSD(T) surface is lowest when $l_{max} = 2$. This rather erratic convergence behaviour is not particularly surprising, since the RMS deviations tend to be dominated by one or two values.

All the ab initio potential energy surfaces are considerably less accurate than the morphed MH surface, where experimental data are used to adjust the potential energy surface and minimise the weighted RMS deviation. The weighted RMS deviation of the MH surface is a factor of between 18 and 28 better than the SIMPER-1K and CCSD(T) surfaces. The RMS deviation (not directly optimised by MH) is better by a factor of between 5 and 7. Using 'morphing' is possible when a system is experimentally well characterised, like Ne–HF, but it is limited in its applicability.

3. Conclusions

Differences between experiment and ab initio theory are the result of basis set incompleteness, approximations made in calculating the electron correlation, the assumption that the HF molecule is rigid, the neglect of relativity, approximations made in calculating the bound states, and errors in the experimental measurements. In this work, different approximate methods for calculating the electron correlation are compared, and for this comparison to be valid, it is important that the other errors are relatively small. It is reasonable to assume that this is the case for any errors arising from experiment, from neglecting relativity, and from the bound-state calculations, but the effects of basis set incompleteness and intramolecular non-rigidity may be more significant.

Based on previous CCSD(T) calculations on Ne–H_2O [17] it is estimated that the use of a complete basis set would reduce the equilibrium separation by less than 1%, and make the potential well deeper by about 1 cm^{-1}. Vibrational averaging of the potential over the intramolecular stretch co-ordinate is expected to increase the equilibrium Ne–HF separation and the well depth. Additional CCSD(T) calculations, with an HF bond length of 1.79 a_0 (which is approximately equal to $\langle r^{-2} \rangle^{-1/2}$ for HF in its $v = 1$ state) indicate that the increase in equilibrium Ne–HF separation is about 0.05 a_0, and the increase in well depth is about 1.5 cm^{-1}. The effect is less for Ne–DF than for Ne–HF. Overall, basis

Table 3
Convergence of the differences between ab initio predictions and experimental measurements of the Van der Waals transition wavenumbers of Ne–HF and Ne–DF, as a function of the maximum angular momentum l_{max} of the Legendre polynomials used in the expansion of the potential energy

l_{max}	SIMPER-1K		MP2		CCSD(T)	
	σ_1	σ_2	σ_1	σ_2	σ_1	σ_2
2	43.42	21.69	269.26	33.27	74.64	7.31
3	42.23	13.01	267.91	32.22	67.85	8.10
4	43.36	11.91	268.14	32.02	66.91	8.29
5	43.59	11.82	268.18	32.12	65.97	8.42
6	43.60	11.81	268.18	32.10	66.80	8.31

The dimensionless RMS deviations σ_1 and σ_2 are defined in Eqs. (3) and (4).

set incompleteness and vibrational averaging have similar but opposing effects on the equilibrium separation, and the total effect is small, relative to the difference between the calculated potential energy surfaces. The estimated total increase in the potential well depth of about 2.5 cm^{-1} is more significant. However, it is less than the difference of 8.6 cm^{-1} between the CCSD(T) and SIMPER-1K potentials, and is only about 10% of the difference between these potentials and the MP2 potential. Scaling the CCSD(T) potential energy by a factor of 1.03, which increases the well depth by 2.5 cm^{-1}, is found to improve the deviations from experiment to $\sigma_1 = 57.7$ and $\sigma_2 = 6.5$, but the value of σ_1 is still larger than the SIMPER-1K value. The effect of 'morphing' the SIMPER-1K potential has not been investigated.

The SIMPER-1K method is therefore competitive with the accuracy of the CCSD(T) method for weak intermolecular interactions, and SIMPER-1K is faster to use. The formal scaling of the computer time with system size is N^5 for MP2 and SIMPER-1K, and N^7 for CCSD(T). The MP2 method requires a similar amount of computer time to SIMPER-1K, but the MP2 method is inadequate for predicting spectroscopic constants and bound states. The MP2 binding is too small, the π-bend bound states are missing, and the vibrational frequencies and rotational constants are both too low.

The high computational cost of using the CCSD(T) method with a one-electron basis set near the complete basis set (CBS) limit can be reduced by performing calculations with two or more smaller basis sets and attempting to extrapolate their results to the CBS limit. The CBS extrapolation makes the results less reliable than those obtained using a larger basis set, but is generally considered to give an improvement over the non-extrapolated results obtained using the smaller basis sets in a case where the use of a large basis set is infeasible. The cost of the SIMPER calculations could also be reduced, by the same fraction as the cost of the CCSD(T) calculations, using CBS extrapolation. There are several plausible ways in which CBS extrapolation could be applied within the SIMPER methodology, but we have not yet pursued this line of investigation further.

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