doublet lying low in energy. While in 1-imidazolyl radical the symmetry of the ground state is clearly predicted to be $^2B_1$, in the case of 1-pyrazolyl radical the calculated small (0.2 kcal/mol) energy difference between the two low-lying π-type states ($^2B_1$ and $^2A_2$) precludes a conclusive symmetry assignation. However, the calculated ^1H hyperfine coupling constant ratios for the latter states in 1-pyrazolyl radical suggest that its ESR spectrum should be conclusive in this concern.

(2) The single-configuration wave function of the two low-lying states $^2A_2$ and $^2B_2$ of both radicals is subject to Hartree–Fock "doublet instability". Due to this phenomenon, asymmetric planar structures (C_s) of lower energy than the symmetric structure (C_{2v}) are obtained at the ROHF level of theory for these states. The present CISD calculations suggest that an appropriate MCSCF treatment of the electron correlation effects should predict a symmetric (C_{2v}) equilibrium geometry.

(3) Although the σ-type doublet state ($^2B_2$) of 1-pyrazolyl radical is predicted to lie about 12 kcal/mol above the lowest π-type doublet ($^2B_1$), at the equilibrium geometry of the former state the latter is calculated to lie about 18 kcal/mol higher in energy. Therefore, on a chemical time scale 1-pyrazolyl can behave as a metastable σ-type radical if it is generated in the excited $^2B_2$ state.

(4) In 1-imidazolyl radical the σ-type doublet ($^2B_2$) is calculated to lie about 29 kcal/mol above the ground state ($^2B_1$). Although at the equilibrium geometry of the former state the latter is predicted to lie only about 6 kcal/mol above, it seems unlikely that if 1-imidazolyl radical is generated in the excited $^2B_2$ state, it would live long enough to behave chemically as a metastable σ-type radical before decaying to the ground state π-type radical.

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cyclo-Dodecaoxygen, O_{12}: Comparison with the Experimentally Characterized S_{12} Molecule

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Abstract: The O_{12} molecule has been examined by using ab initio quantum mechanical methods, specifically self-consistent-field (SCF) theory with basis sets as large as double-ζ plus polarization (DZ+P). The complete molecular structures for O_{12} and the 192-electron system S_{12} have been predicted, along with photoelectron, infrared, and Raman spectra. Comparisons between the two molecules are made throughout. Although O_{12} is predicted to lie energetically above six separated diatomic oxygen molecules, this energy difference is significantly less than suggested by simple bond energy arguments.

Elemental sulfur exists in the solid state as cyclic S_n molecules.[1-3] Although common elemental sulfur is largely S_8 rings, the compound now known to be *cyclo*-S_6 was first prepared[2] in 1891. Moreover, cyclic sulfur compounds as large as S_{20} have been synthesized and characterized.[1-3] Among the larger S_n molecules, the best understood is S_{12}, which was first prepared[4] in 1966. In fact, the stability of S_{12} approaches that of common S_8 rather closely.[5]

The structure of an isolated S_{12} molecule is expected from crystal structures[1-3,6,7] to be of D_{3d} symmetry. The S_{12}·CS_2 complex does indeed display D_{3d} symmetry within the S_{12} moiety, and this experimental structure[6] is shown in Figure 1. Given the stability of S_{12}, a reasonable question is: What about the existence of the valence isoelectronic O_{12} molecule?

In an earlier paper[8] on the smaller O_4 molecule, an extended explanation of the instability of *cyclo*-O_n molecules compared to *cyclo*-S_n molecules was given. To summarize briefly: (a) O–O single bonds are weaker than S–S single bonds, and (b) diatomic O_2 has a larger dissociation energy than diatomic S_2. The conjunction of these two effects means that the process

$$cyclo\text{-}S_n(g) \rightarrow \frac{n}{2}S_2(g) \qquad (1)$$

is usually (e.g., for S_6, S_8, and S_{12}) endothermic while that for

$$cyclo\text{-}O_n(g) \rightarrow \frac{n}{2}O_2(g) \qquad (2)$$

is predicted to be significantly exothermic.

From an experimental perspective, this analysis[8] means that O_{12} will be much more difficult to prepare in the laboratory than S_{12}. However, if makeable, O_{12} would be a very interesting molecule due to its extremely high energy content. Specifically, for the O_{12} system, the fragmentation reaction (2) is crudely estimated[8] to be 300 kcal/mol exothermic. The goal of the present research is to characterize the unknown molecule O_{12} structurally

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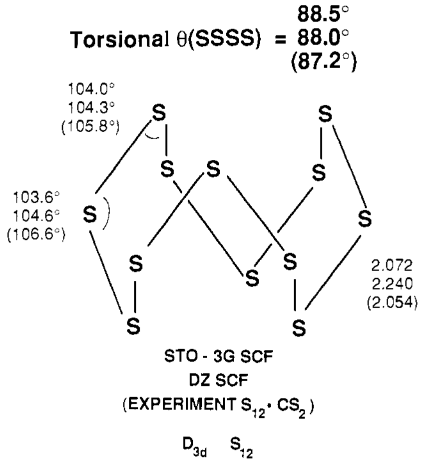

Figure 1. Comparison between self-consistent-field (SCF) theory and experiment for the equilibrium geometry of S_{12}. For each geometrical parameter the minimum basis set prediction is the upper entry, the double-ζ (DZ) prediction the middle entry, and the experimental[6] $S_{12}\cdot CS_2$ structure (in parentheses) the lower entry. The S–S bond distance is given in angstroms.

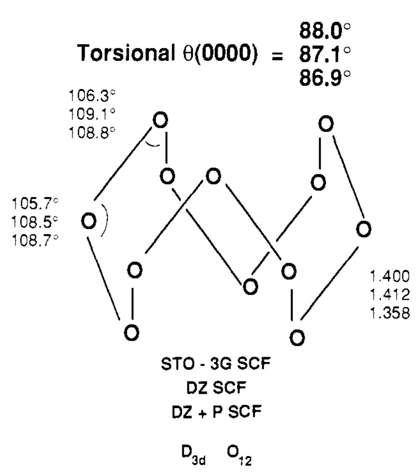

Figure 2. The molecular structure (D_{3d}) of O_{12} predicted by using self-consistent-field theory in conjunction with three distinct basis sets. Note that the bottom entry (DZ+P SCF) for each predicted geometrical parameter represents a larger basis set than was used for the experimentally known, valence isoelectronic S_{12} molecule. The O–O bond distance is given in angstroms.

and to make some comparisons with the well-described S_{12} molecule.

Theoretical Details

All results reported here were obtained from ab initio self-consistent-field (SCF) theory. For O_{12} three distinct basis sets were employed: minimum basis set (MBS), double-ζ (DZ), and double-ζ plus polarization (DZ+P). The minimum basis set includes 60 contracted Gaussian functions and is the standard STO-3G basis of Hehre, Stewart, and Pople.[9] The double-ζ basis is Huzinaga's (9s5p) primitive Gaussian set[10] contracted to (4s2p) following Dunning[11] and includes 120 contracted functions. Finally, the double-ζ plus polarization set adds a set of five d functions (orbital exponent $\alpha = 0.85$) to the DZ set to give a total of 180 contracted Gaussian functions.

For S_{12}, the minimum basis set includes 108 contracted Gaussian functions and is the standard STO-3G basis of Hehre, Ditchfield, Stewart, and Pople.[12] The double-ζ basis includes 216 contracted Gaussian functions and is Dunning and Hay's (6s4p) contraction[13] of Huzinaga's (11s7p) primitive set.[14] The DZ+P basis for S_{12} includes 276 contracted Gaussians and was slightly out of reach of our current computational capabilities.

At each level of theory, the structures of O_{12} and S_{12} were optimized in D_{3d} symmetry with respect to all geometrical parameters. This was accomplished by using the analytica derivative methods incorporated in the GAUSSIAN 86 suite of computer programs.[15] Harmonic vibrational frequencies were also evaluated to characterize all of the stationary points.

Equilibrium Geometries for S_{12} and O_{12}

The theoretical predictions for the D_{3d} structure of S_{12} are shown in Figure 1. The agreement with experiment[6] cannot be expected to be exact because (a) the theoretical result is for one gas-phase S_{12} molecule, while all experimental data refer to solid S_{12} and (b) what is apparently the best crystal structure for S_{12} is a crystal structure[6] for the weakly bound complex $S^{12}\cdot CS_2$. In the present author's opinion, the crystal structure for $S_{12}\cdot CS_2$ should not be expected to be closer than ±0.01 Å in bond distances and ±0.5° in bond angles to the gas-phase r_e structure for S_{12}.

For S_{12} the ab initio bond angles from either the MBS SCF or DZ SCF method are in reasonable accord with experiment. The errors in the DZ SCF bond angles (SSS) are somewhat less, namely, 2.0 and 1.5°. However, the ordering of the two SSS angles differs from the experimental structure for $S_{12}\cdot CS_2$. The two SSS angles (Figure 1) may be distinguished by their central S atoms. The three topmost S atoms in Figure 1 form an equilateral triangle, and for $S_{12}\cdot CS_2$ experiment suggests that the angle about each of these three S atoms is the smaller by (106.6 − 105.8) = 0.8°. However, theory predicts that the three equivalent angles about these upper S atoms should be *larger* by 0.37° (MBS) or 0.21° (DZ). It would be desirable to eventually carry out the full 276-function DZ+P SCF structural computations to see if the MBS/DZ ordering of gas-phase equilibrium angles hold up. The O_{12} results suggest that a reversal of bond angles could occur with the DZ+P basis set. The SSSS torsional angles differ by only 1.3° (MBS) and 0.8° (DZ) from the experimental crystal structure.[6]

For D_{3d} S_{12} all 12 S–S bond distances are identical. With the minimum basis set, SCF theory does quite well, being 0.018 Å longer than experiment.[6] However, the DZ SCF level of theory overshoots the experimental distance by 0.186 Å, a major error. Nevertheless, one should be quick to point out that an error of this magnitude is to be expected for DZ SCF sulfur–sulfur bond distances. Most notably, for the cyclic D_{3h} isomer of S_3 the DZ SCF[16] and DZ+P SCF[17] bond distances r_e(S–S) are 2.297 and 2.083 Å, respectively. Thus the comparable DZ/DZ+P difference for cyclic S_3 is even larger, namely, 0.214 Å. Fortunately, for the smaller O_{12} system, it is possible to use the larger DZ+P basis set.

Figure 2 shows the three theoretical predictions for the D_{3d} equilibrium geometry of *cyclo*-dodecaoxygen. Of these, the DZ+P SCF structure is expected to be the most reliable and, in fact, quite reliable. Inspection of the O–O–O bond angles suggests that the potential energy surface as a function of the two distinct angles is rather flat. All three theoretical methods agree that the angle Θ_1 about each of the upper three O atoms is larger than the angle Θ_2 about each of the six atoms that form a central regular hexagon.[2] However, the difference in bond angles Θ_1(OOO) − Θ_2(OOO) varies from 0.6° (MBS and DZ) to only 0.1° (DZ+P).

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The theoretical ordering of OOO bond angles is the opposite of that determined experimentally for S_{12}.

The theoretical bond angles about oxygen are unusual in that they are not significantly decreased by the addition of polarization functions to the basis set. As emphasized by Boggs and Cordell,[18] this X–O–Y oxygen atom d function effect is widespread.

Theory predicts the O–O–O bond angles for O_{12} to be consistently larger than the analogous angles for S_{12}. With the MBS the top O–O–O angle is 2.3° wider than the analogous S–S–S angle for S_{12}, while the central O–O–O angles are 2.1° larger. With the DZ basis set the top angle is 4.8° larger for O_{12} than S_{12} and the central angle is 3.9° larger for O_{12}. It seems safe to conclude that the bond angles in O_{12} are much closer to tetrahedral than those for S_{12}. The latter conclusion, taken in vacuo, might falsely lead one to conclude that O_{12} is more stable than S_{12}.

The predicted O_{12} torsional angles decrease with increasing basis set size. The final prediction, $\Phi(\mathrm{OOOO}) = 86.9°$ (DZ+P SCF), is very close to the experimental value[6] of 87.2° for S_{12}. In fact, we expect the equilibrium torsional angle to be slightly less for O_{12} than for S_{12}. With the MBS the O_{12} torsional angle is 0.5° less than for S_{12} and with DZ SCF, the O_{12} torsional angle is 0.9° less. Again it would be helpful to have the 276 basis function DZ+P S_{12} equilibrium geometry to better calibrate the final DZ+P estimates for O_{12}.

The MBS, DZ, and DZ+P O–O bond distances for O_{12} are 1.400, 1.412, and 1.358 Å, respectively. The same three distances for the smaller cyclic O_4 molecule[8] are 1.424, 1.464, and 1.392 Å. For O_4 we also have the DZ+P single- and double-excitation configuration interaction (CISD) bond distance, namely, 1.433 Å. It is clear that the O–O distance in O_{12} is significantly less (by 0.034 Å with DZ+P SCF) than for O_4. We take this as one measure of the greater stability of the O_{12} molecule compared to O_4. For O_{12} a final estimate of the bond distance may be obtained by adding 0.04 Å (the correlation effect for O_4) to the DZ+P SCF prediction, i.e., $1.358 + 0.04 \approx 1.40$ Å. This estimate is of course a significantly shorter bond distance than the 1.475 Å observed[19] in the laboratory for HOOH, hydrogen peroxide. Structurally, then, the O–O bonds in O_{12} would appear to be rather normal single bonds.

The D_{3d} structure observed experimentally[6] for S_{12} is not the only conceivable equilibrium geometry for O_{12}. One possibility explicitly considered in this research was the higher symmetry D_{6d} geometry for O_{12}. The optimized D_{6d} total energies for O_{12} were −885.68763 (MBS) and −896.97683 (DZ) hartrees. These energies are 26.6 kcal (MBS) and 31.6 kcal (DZ) above the comparable D_{3d} total energies for O_{12}. Furthermore, the vibrational analysis of this stationary point shows that it has *six* imaginary vibrational frequencies. Thus the D_{6d} structure is not a candidate for the conformational minimum among various O_{12} structures.

Energetics

Total energies for O_{12} and S_{12} at the higher levels of theory are given in Table I. The comparable total energy for S_2 is −794.93007 hartrees (DZ SCF) and for O_2 −149.57130 (DZ SCF) and −149.63605 (DZ+P SCF). The diatomic total energies refer to the restricted Hartree–Fock method for these ground-state triplets. Thus S_{12} at the DZ SCF level of theory is predicted to lie 21.9 kcal/mol below six S_2 molecules. This result may readily be translated into the prediction that S_{12} lies $21.9/12 = 1.8$ kcal/mol below separated S_2 molecules on a *per-atom* basis. The analogous experimental value[20] for gaseous S_8 is 12.2 kcal/mol per S atom. It is of course anticipated[21] that DZ SCF theory will do a better job for 6 S_2 than for S_{12}, and an error of ~10 (kcal/mol)/atom seems to us to be perhaps less than might have been expected.

Table I. Orbital Energies (hartrees) for the Valence Molecular Orbitals of O_{12} and S_{12}

	DZ O_{12}	DZ+P O_{12}	DZ S_{12}
total energies	−897.02725	−897.40376	−4769.61541
symmetry			
a_{1g}	−1.7450	−1.7571	−1.1247
e_u	−1.7087	−1.7172	−1.1077
e_g	−1.6107	−1.6115	−1.0609
a_{2u}	−1.4722	−1.4662	−0.9936
a_{1u}	−1.4694	−1.4599	−0.9919
e_g	−1.3087	−1.2925	−0.9131
e_u	−1.1544	−1.1267	−0.8412
a_{1g}	−1.0877	−1.0530	−0.8119
a_{2g}	−0.8501	−0.8736	−0.5610
e_u	−0.8497	−0.8640	−0.5606
a_{2u}	−0.8495	−0.8639	−0.5505
e_g	−0.8018	−0.8094	−0.5289
a_{1g}	−0.8016	−0.8048	−0.5261
e_g	−0.7693	−0.7705	−0.5180
e_u	−0.7243	−0.7321	−0.4936
a_{1u}	−0.6845	−0.6872	−0.4804
e_u	−0.6809	−0.6547	−0.4539
a_{2u}	−0.6691	−0.6421	−0.4512
a_{1g}	−0.6113	−0.5974	−0.4253
e_g	−0.5980	−0.5770	−0.4176
a_{2g}	−0.6047	−0.5723	−0.4083
e_g	−0.5826	−0.5560	−0.4082
a_{2u}	−0.5505	−0.5276	−0.3907
e_u	−0.5473	−0.5181	−0.3842

At the DZ SCF level O_{12} lies 20.9 kcal/mol *above* six O_2 on a per-atom basis. With the DZ+P SCF method O_{12} lies 21.6 (kcal/mol)/atom above six separated diatomic oxygen molecules. Thus the addition of polarization function (d functions on each oxygen atom) lowers the energy of 6 O_2 somewhat more than that of O_{12}.

Analogous to S_{12}, one certainly expects that higher levels of theory (larger basis sets, and especially explicit treatment of electron correlation) will lower the energy of O_{12} relative to 6 O_2. However, at present such an assumption remains open, although second-order perturbation theory appears to support this view. With the DZ basis set, the MP2 energy difference between O_{12} and 6 O_2 is 16.1 kcal/mol on a per O atom standard. These results suggest that O_{12} may be significantly more stable than our earlier back-of-the-envelope calculation[8] (based on standard bond energies), which indicated that generic cyclic O_n molecules might store 24 kcal/mol of oxygen atoms relative to the separated O_2 molecules.

Also shown in Table I are orbital energies for the valence electrons of O_{12} and S_{12}. O_{12} has 96 electrons, S_{12} has 192 electrons, and both molecules have 72 valence electrons. Table I shows that with one exception, the DZ SCF and DZ+P SCF orbital energies are ordered identically. The one exception is the (e_g, a_{2g}) pair near −0.6 hartree. The DZ+P orbital energies for O_{12} fall in precisely the order of the DZ S_{12} orbital energies, confirming that the electronic structures of the two molecules are similar. Of course, all of the S_{12} valence molecular orbitals lie higher energetically than the analogous O_{12} MOs.

An interesting observation is that the 24 distinct orbital energies for O_{12} span a smaller energy range (−1.757 to −0.518 hartrees) than do the 9 distinct orbitals of the much smaller cyclic O_4 molecule[8] (−1.760 to −0.464 hartrees). Of course, the fact that the HOMO (b_1) of O_4 is higher than the HOMO (e_u) of O_{12} may simply reflect the instability of O_4. For both O_{12} and S_{12} there is a sharp distinction in orbital energies between s- and p-derived valence electrons. For O_{12} with the DZ+P basis, this 2s–2p gap is $(1.0530 - 0.8736) = 0.1794$ hartree = 4.9 eV.

Infrared and Raman Spectra

Table II collects the DZ SCF theoretical predictions of the vibrational frequencies for S_{12} and O_{12}. With one exception the ordering by symmetry of the vibrations is identical between S_{12}

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Table II. Ab Initio Predictions of the Infrared and Raman Spectra of S_{12} and O_{12}

	S_{12} DZ SCF			O_{12} DZ SCF			O_{12} DZ+P SCF		
symmetry	ω,[a] cm^{-1}	IR intens, km/mol	Raman intens, Å^4/amu	ω, cm^{-1}	IR intens, km/mol	Raman intens, Å^4/amu	ω, cm^{-1}	IR intens, km/mol	Raman intens, Å^4/amu
e_u	456 (465)	0.2	0	1046	1.7	0	1119	0.2	0
a_{2g}	455	0	0	1038	0	0	1100	0	0
e_g	452 (459)	0	114	1037	0	54	1130	0	19
a_{2u}	441 (465)	0.3	0	1017	0.4	0	1129	3.8	0
a_{1u}	440	0	0	1018	0	0	1122	0	0
e_g	429 (447)	0	13	1003	0	23	1121	0	20
e_u	416 (425)	1.1	0	979	0.3	0	1101	1.2	0
a_{1g}	409 (459)	0	280	972	0	160	1092	0	81
a_{1g}	251 (288)	0	21	745	0	13	848	0	7
a_{2u}	235 (266)	1.7	0	704	22.7	0	802	20.0	0
e_u	223 (253)	2.6	0	679	21.4	0	772	16.0	0
e_g	210 (243)	0	6	642	0	2	730	0	1
e_g	156 (177)	0	26	471	0	12	529	0	7
e_u	136 (165)	0.2	0	404	1.0	0	457	1.8	0
a_{1u}	122	0	0	395	0	0	436	0	0
a_{1g}	99 (128)	0	29	308	0	13	348	0	8
a_{2u}	66 (72)	0.2	0	204	0.8	0	242	0.3	0
a_{2g}	53	0	0	148	0	0	162	0	0
e_g	39 (51)	0	10	122	0	3	144	0	2
e_u	36 (62)	0.0	0	106	0.0	0	122	0.0	0

[a] For S_{12} the experimental fundamental frequencies[22] ν are given in parentheses.

and O_{12}. The one exception is the (a_{2u}, a_{1u}) pair, which is (441, 440 cm^{-1}) for S_{12} and (1017, 1018 cm^{-1}) for O_{12}—for both molecules the two fundamentals are nearly coincident.

The IR intensities for S_{12} are not large, the strongest being 2.6 km/mol for the e_u vibration predicted at 223 cm^{-1}. The analogous IR intensities of two of the fundamentals of O_{12} are much stronger. Specifically the a_{2u} mode of O_{12} predicted at 704 cm^{-1} (DZ SCF) and the e_u mode predicted at 679 cm^{-1} (DZ SCF) have intensities 23 and 21 km/mol, respectively. Not all of the O_{12} IR intensities are greater than their S_{12} counterparts; the S_{12} e_u mode (an S–S stretch) predicted at 416 cm^{-1} is stronger than the analogous O_{12} e_u mode at 979 cm^{-1}.

With one exception (the second e_g mode) the DZ SCF Raman intensities of S_{12} are greater than those of O_{12}. The totally symmetric S–S stretching vibration predicted at 409 cm^{-1} is very intense (280 Å^4/amu), while that for O_{12} is also expected to produce a strong Raman signal (160 Å^4/amu). The first e_g mode of both molecules (452 cm^{-1} for S_{12}; 1037 cm^{-1} for O_{12}), another bond stretching vibration, should also give rise to strong Raman bands (114 Å^4/amu for S_{12}; 54 Å^4/amu for O_{12}).

For O_{12} only it was also possible to predict the vibrational frequencies with the larger DZ+P basis set. We note first that the DZ+P SCF method provides a more reliable ordering of the O–O stretching frequencies. In fact, the relative changes in going from DZ to DZ+P are a bit surprising. For example the e_u O–O stretch from DZ SCF is 29 cm^{-1} above the a_{2u} O–O stretch. With the more reliable DZ+P basis set the order is reversed, with the a_{2u} frequency lying 10 cm^{-1} higher than e_u. Instead of being the highest (DZ) of the eight distinct O–O stretching vibrations, the e_u mode with the DZ+P basis becomes fifth highest. All of the O–O stretching vibrational frequencies are shifted upward by the addition of polarization functions to the basis set, typically by ~100 cm^{-1}.

Table II shows that the remaining DZ SCF vibrational frequencies are also increased by the addition of d functions on the oxygen atoms. The largest increase is 122 cm^{-1} (e_u, 979 → 1011 cm^{-1}) and the smallest 14 cm^{-1} (a_{2g}, 148 → 162 cm^{-1}). However, it should be emphasized that some of the DZ SCF predictions may be closer in *absolute* value to the exact (unknown) fundamentals. This is because the effects of both electron correlation and anharmonicity will be to reduce the DZ+P SCF harmonic vibrational frequencies. Nevertheless, we expect the DZ+P frequencies to lie in a more *uniform* relationship to the true fundamentals.

For S_{12} there exist experimental IR and Raman spectra[22] and these allow us to get a rough idea of the reliability of the present O_{12} predictions. The DZ SCF predictions for S_{12} are particularly interesting in that the harmonic vibrational frequencies all fall *below* the observed fundamentals. Typical DZ SCF harmonic frequencies lie well above the experimental anharmonic frequencies.[23] The S_{12} results combined with the finding that the DZ+P ω values for O_{12} uniformly lie above the analogous DZ results suggest that the DZ SCF results for O_{12} may likewise fall below the exact (unknown) fundamentals. The absolute agreement between DZ SCF theory and experiment is rather good, the differences ranging from 7 cm^{-1} (e_g, expt 459 cm^{-1}) to 50 cm^{-1} (a_{1g}, expt 459 cm^{-1}). Thus we are encouraged that the DZ+P SCF frequencies for the unknown O_{12} molecule may be quite reasonable.

Concluding Remarks

In many respects O_{12} is predicted here to be a normal molecule, that is, normal in comparison with the well-characterized, stable S_{12} species. From the O_{12} theoretical molecular structure, photoelectron spectrum, infrared spectrum, and Raman spectrum, this molecule does not appear extraordinary—there is little hint of instability.

The qualitative reasons for the fact that O_{12} lies energetically well above 6 O_2 (while the opposite is true for the analogous sulfur species) have been discussed earlier.[8] However, the present ab initio quantum mechanical study suggests that O_{12} may lie significantly lower in energy than expected from simple bond energy considerations.[8] Should it be possible to synthesize O_{12} (or other cyclic oxygen molecules O_n) this molecule could nevertheless be capable of storing a great deal of energy per mass.

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