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Muoniated radical states in the group 16 elements: Computational studies

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ABSTRACT

Recent experimental studies on positive muon implantation in silicon, selenium, and tellurium have been interpreted on the basis that the primary paramagnetic species observed is XMu ($X = S, Se, \text{ or } Te$), the muonium-substituted analog of the appropriate diatomic chalcogen monohydride radical. However, temperature-dependent signal visibility, broadening, and hyperfine shift effects remain puzzling. The interplay of degeneracy, spin–orbit coupling, and vibrational averaging in these species makes them computationally challenging despite their small size. In this work computational studies are carried out on all hydrogen isotopomers of the series OH, SH, SeH, and TeH. Several different methodological approaches are compared, and the effects of wavefunction symmetry, spin–orbit coupling, and zero-point vibrational corrections on the isotropic and anisotropic components of the hyperfine interaction are examined. Additionally, some models of the Mu site in rhombic sulfur are briefly considered.

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1. Introduction

Experimental μ SR studies on the chalcogens began exactly 50 years ago with the work of Swanson [1], who observed a loss of 95% of the incident muon polarization on implantation into sulfur, but it was not until 1997 that Reid [2] made a definitive observation of a paramagnetic state in that material utilizing ALC- μ SR. Subsequent observations on the heavier chalcogens Se and Te followed [3–5], and in each case some evidence of a paramagnetic state was uncovered. While the properties of these states (temperature dependence of hyperfine parameters, relaxation rates, and visibility using various μ SR techniques) remain incompletely clarified, discussion has coalesced around the possible role of diatomic “hydride” radicals such as SMu (the muoniated isotopomer of the mercapto radical) and its Se and Te analogs. S, Se, and Te in the solid state are structurally similar: rhombic sulfur (the most stable of the allotropes under standard conditions) is distinctly molecular, consisting of S_8 rings; selenium, too, has an Se_8 form (α -monoclinic Se), but it is higher in energy than a trigonal form (t-Se) consisting of 3_1 chains; the single form of Te stable under standard conditions is isostructural with this trigonal form, but shows less evidence of covalent bonding, consistent with its greater metallicity. Oxygen, by contrast, consists of strongly covalently bound diatomic molecules both in the gaseous and in the solid state, and discussions of positive muon behavior in various forms of oxygen have focused upon the possible rôle of MuO_2 or MuO_2^+ ; while Kempton

accounted for the repolarization behavior observed as a result of muon attachment to O_2 on the surface of silica grains in terms of the neutral radical [6], Bermejo et al. found that observations in solid oxygen were best explained if all magnetic interactions are dipolar in nature, implying a state such as *singlet* MuO_2^+ , an excited state [7]. The results presented here primarily deal with the hyperfine properties of the diatomic hydride radicals OH, SH, SeH, and TeH, calculated at a consistent level of theory, and with zero-point corrections appropriate for the muonium isotopomers included. Some additional consideration is given to specific possible muonium states in rhombic sulfur.

2. Computational details

Calculations on the diatomic hydride species mainly used the ORCA quantum chemistry program [8], with some supplementary calculations being carried out using *Gaussian 03* [9]. Very few high-quality all-electron basis sets are available for all chalcogens up to Te; those used were the segmented basis sets of triple-zeta quality created by Koga and co-workers [10], which were employed in both contracted and uncontracted forms: in more detail, these sets provide a 6s3p2d basis for H, a 10s5p3d2f basis for O, a 12s9p4d2f basis for S, a 17s14p10d2f basis for Se, and a 20s17p13d2f basis for Te. Other calculations use the correlation-consistent basis sets of Woon and Dunning [11]. Methods used include standard post-Hartree–Fock treatments such as CISD, as well as density functional theory methods. The highest-quality DFT calculations (on the diatomics) use the “double hybrid” B2PLYP method of Grimme [12], in which the correlation energy

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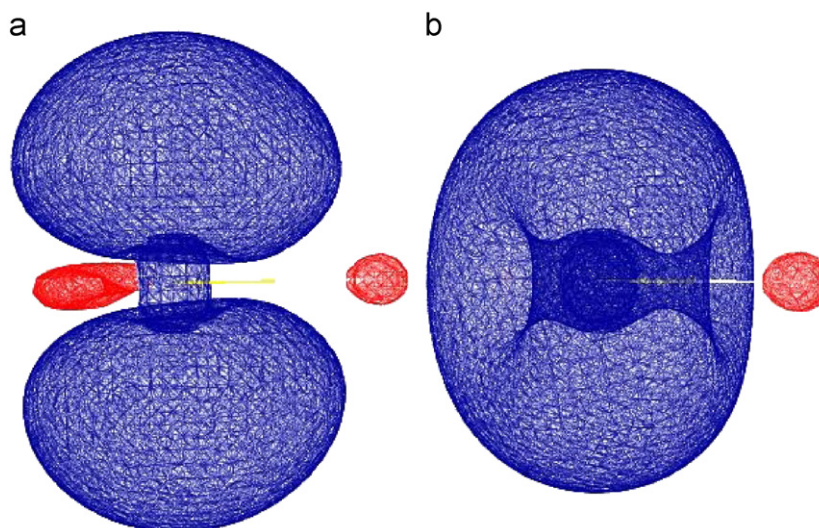


Fig. 1. Distribution of alpha (blue) and beta (red) spin density in the SH radical at $r = 134$ pm (0.005 a.u. contour) with (a) conventional wavefunction and (b) wavefunction enforcing fractional occupancy.

incorporates a second-order perturbative component. Other DFT calculations use the standard B3LYP approach.

A further complication in the wavefunction of the diatomics in their $X^2\Pi_{3/2}$ ground states is that it must yield an electron density distribution which has the same symmetry as the nuclear geometry, in other words axial symmetry. Almost all previous electronic structure calculations on these species have however used standard Hartree–Fock or DFT approaches using a basis set incorporating real (rather than complex) p-orbitals. In such a case the minimum energy configuration typically features a SOMO in which the unpaired electron breaks the symmetry of the hamiltonian and resides in a π_x or π_y orbital. For this reason earlier work on SMu obtained a hyperfine tensor which the anisotropic component was non-axial [13]. The single exception to this appearing in the literature seems to be a study by Bendazzoli et al. [14] on OH and SH, in which the fractional occupation operator of Slater [15] was generalized to be used in unrestricted molecular wavefunctions, resulting in a totally symmetric Hartree–Fock hamiltonian. (Their calculations were, however, limited to the UHF and ROHF-CIS methods, and are consequently subject to the errors in the treatment of spin polarization implicit in those methods.) A similar operator is available in ORCA and was used in the following.

Fig. 1 illustrates the effect of fractional occupancy upon the spin density distribution obtained for SH at $r = 134$ pm (the experimentally measured bond length).

3. Discussion

3.1. Chalcogen monohydrides

No attempt is made here at a comprehensive review of the experimental and theoretical literature on the diatomic hydrides; such a review will be presented elsewhere in a more complete treatment of these systems.

Bond-coordinate scans were carried out on the four diatomic species using the B2PLYP functional and the appropriate Koga basis, and with fractional orbital occupancy enforced. The dependence of the Fermi contact term upon r for each of the four species is illustrated in Fig. 2. The qualitative behavior is the same in each case: the coupling is negative over the entire range of r , and has an absolute magnitude which passes through a shallow

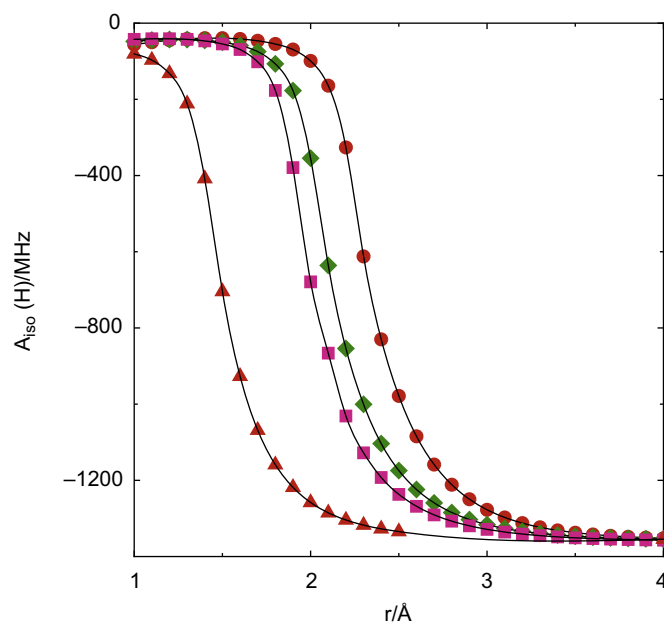


Fig. 2. Fermi contact term vs. r for OH (triangles), SH (squares), SeH (diamonds), and TeH (circles). The curve is a spline fit for illustrative purposes.

minimum at some $r < r_e$, then increases monotonically with r over the remainder of the range studied. In the valence region where there is significant orbital overlap, $|dA_{iso}/dr|$ is small, but the slope increases sharply in the bond breaking region before the coupling asymptotically tends to $-A_{iso,H}$ (the hyperfine constant of the free hydrogen atom) at large r . The asymptote is $-A_{iso,H}$ rather than $A_{iso,H}$ because the state remains overall doublet in character; the paramagnetic 3P state of the chalcogen and 2S state of H couple antiferromagnetically.

A comparison of density functional methods and CISD was conducted on SH using *Gaussian 03* [9] and the cc-pVTZ basis set [11]; B3LYP yielded $r_e = 135$ pm and $A_{iso} = -37$ MHz, while CISD yielded $r_e = 134$ pm and $A_{iso} = -52$ MHz. The experimental values are 134 pm and -53 MHz, respectively. Superficially this suggests that CISD is superior to DFT for this calculation, but it should be noted that these values do not include any zero-point vibrational

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