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The First Infrared Spectra and Quasirelativistic DFT Studies of the US, US$_2$, and US$_3$ Molecules

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Laser-ablated U atoms react with discharged sulfur vapor in excess argon to form the US, US$_2$, and US$_3$ molecules, which are identified from matrix infrared spectra using sulfur isotopic substitution. Vibrational frequencies from quasirelativistic DFT calculations support these assignments and provide an insight into the bonding and structure. Unlike linear UO$_2$, US$_2$ is bent because of more favorable U(6d)–S(3p) overlap, and US$_2$ has a 118 ± 5° (experimental based on isotopic shift) or 121° (calculated $^3B_2$ ground state, B3LYP) S–U–S bond angle.

Uranium chemistry has attracted tremendous interest because uranium oxides are widely used as nuclear fuel.[1] Compared to the amount of research performed on uranium oxides, the analogous uranium sulfides have received much less attention both experimentally and theoretically. Bulk uranium sulfides have been prepared, and their crystal structures, phase systems, and physical properties have been reported.[2−7] To our knowledge, the study of isolated uranium sulfide molecules is entirely unexplored. The more diffuse nature of sulfur 3p orbitals compared to oxygen 2p may lead to differences in bonding to uranium 5f and 6d orbitals, and the resulting structures may be different.

The uranium oxides UO and UO$_2$ were definitively identified by Gabelnick, Reedy, and Chasanov in solid argon matrixes.[8] The ceramic nature of uranium oxides required temperatures near 2000 °C for evaporation of molecular species. We have employed laser ablation as a source of U atoms for reaction with small molecules to form the linear UO$_2$, NUN, NUO, and CUO molecules and characterized them by means of matrix infrared techniques coupled with density functional theoretical (DFT) calculations.[9−14] Here, we will apply these methods to the first observation of isolated uranium sulfides. Although many metal sulfides are analogous to their oxide counterparts,[15] we will show a distinct structural difference between UO$_2$ and US$_2$.

Sulfur atoms and small molecules were generated by a microwave discharge in argon seeded with sulfur vapor using a quartz discharge tube similar to the one used in earlier sulfur experiments.[16] The presence of significant quantities of S$_2$ in the discharge was indicated by the characteristic sky-blue emission.[17]

The experiment for laser ablation and matrix isolation has been described in detail.[18] Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz, 10 ns) was focused to ablate the rotating uranium metal target (Oak Ridge National Laboratory) using low energy (5−20 mJ/pulse). Laser-ablated uranium atoms were co-deposited with the sulfur-doped argon spray-on stream onto a 7 K CsI window at 3−5 mmol/h for 0.5−1.5 h. Infrared spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 550 spectrometer.

Quasirelativistic density functional theoretical (DFT) calculations were performed using the GAUSSIAN 98

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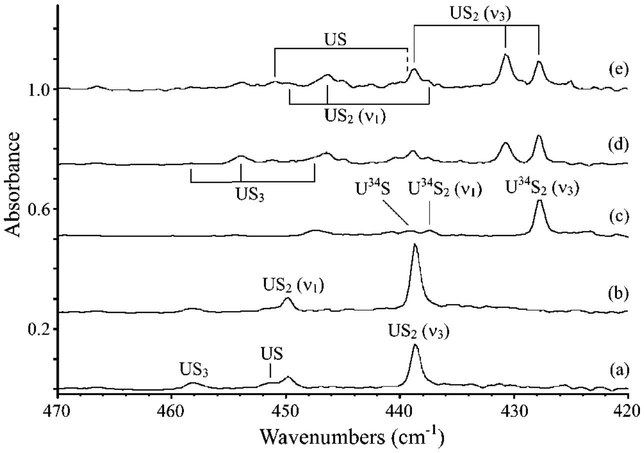

Figure 1. Infrared spectra in the 470−420 cm^{-1} region for laser-ablated U co-deposited with discharged isotopic S in argon at 7 K: (a) ^{32}S with higher concentration, (b) ^{32}S with lower concentration, (c) ^{34}S, (d) 35/65 ^{32}S + ^{34}S mixture, and (e) 50/50 ^{32}S + ^{34}S mixture.

program[19] and the hybrid B3LYP[20] functional as this method was effective for describing uranium oxide molecular species.[14] A small-core uranium pseudopotential (32 electrons treated explicitly) together with sulfur pseudopotential (6 electrons treated explicitly) was used, together with flexible bases (double-ζ plus polarization plus diffuse quality for S, nearly triple-ζ for U) as described in detail elsewhere.[14]

Figure 1 shows the 470−420 cm^{-1} region of infrared spectra of argon matrix samples following the reaction of laser-ablated U atoms with discharged isotopic sulfur vapor in excess argon during condensation at 7 K. Spectra a and b were obtained in two consecutive experiments with U and ^{32}S, using higher sulfur concentration for a, and lower sulfur concentration for b, with all other experimental conditions the same. Spectrum c is from the reaction between U and ^{34}S, and spectra d and e are from the reactions between U and two different sulfur isotopic mixtures.

In ten U + ^{32}S experiments using various conditions of sulfur and uranium concentration, the prominent feature at 438.7 cm^{-1} and the weaker absorption at 449.8 cm^{-1} showed a consistent absorption intensity ratio of 6:1. In the ^{34}S isotopic experiment, these two bands red-shifted to 427.8 and 437.4 cm^{-1}, with ^{32}S/^{34}S isotopic frequency ratios of 1.0255 and 1.0283, respectively. These ratios are lower and higher than the harmonic U^{32}S/U^{34}S diatomic frequency ratio (1.0270), which is expected for the antisymmetric (ν_3) and symmetric (ν_1) stretching modes, respectively, of a triatomic S−U−S molecule. In the mixed ^{32}S + ^{34}S experiment, both bands split into asymmetric triplets: the two new intermediate bands at 430.7 and 446.5 cm^{-1} are 2.6 cm^{-1} lower and 2.9 cm^{-1} higher, respectively, than the medians of the corresponding pure isotopic bands. The matching shifts show that these two modes couple in the lower symmetry mixed-isotopic molecule. It is evident that two equivalent sulfur atoms are involved in two U−S stretching modes, and hence, the US$_2$ molecule is identified with a *bent* geometry. Here, we use low laser power and produce low uranium atom concentrations such that major product species contain a single U atom. The agreement between similar laser-ablated U reactions with O$_2$ and thermal effusion of UO$_2$ for the infrared spectrum of UO$_2$ in solid argon[8,9] supports this conclusion. Accordingly, the 438.7 and 449.8 cm^{-1} bands are assigned to the antisymmetric (ν_3) and symmetric (ν_1) modes, respectively, of US$_2$. Using appropriate G-matrix elements and the isotopic ν_3 frequencies,[21] the upper limit for the S−U−S bond angle is estimated at 118 ± 5°, which, on the basis of results of a similar calculation for S$_3$,[16] should be close to the actual value.

The weak band at 451.1 cm^{-1}, partially covered by the US$_2$ ν_1 mode, shifted to 439.2 cm^{-1} in the ^{34}S isotopic experiment. The ^{32}S/^{34}S isotopic frequency ratio of 1.0271 is very close to the harmonic diatomic US isotopic frequency ratio. In the mixed ^{32}S + ^{34}S experiment, a doublet splitting pattern was observed although the bands are weak. The 451.1 cm^{-1} band is assigned to the US fundamental in the argon matrix.

Another weak band at 458.2 cm^{-1} shifted to 447.4 cm^{-1} in the ^{34}S experiment, with ^{32}S/^{34}S frequency ratio of 1.0241. This band showed the triplet splitting pattern with an intermediate band at 454.1 cm^{-1} in the mixed ^{32}S + ^{34}S experiment, which indicates that two equivalent sulfur atoms are involved in this vibrational mode. In experiments using different sulfur concentrations while keeping other conditions the same (Figure 1a,b), the 458.2 cm^{-1} band is clearly favored by higher sulfur concentration as indicated by more intense S$_3$ absorption in the infrared spectrum.[16] Furthermore, the US fundamental at 451.1 cm^{-1} increased slightly, whereas the US$_2$ absorptions decreased in this higher S$_3$ concentration experiment. The 458.2 cm^{-1} band is assigned to the antisymmetric stretching mode of the near-linear S−U−S unit in the T-shaped US$_3$ molecule, which is similar to the T-shaped UO$_3$ analogue.[14,22]

To support the infrared assignments, and to provide structure and bonding properties for these three uranium sulfides, quasirelativistic DFT/B3LYP calculations were performed. These calculations neglect spin-orbit coupling. However, very recent CASSCF/CASPT2 calculations[23,24] show that spin-orbit effects make little difference in the computation of the antisymmetric stretching frequency of UO$_2$. Table 1 lists a comparison of calculated and observed

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Table 1. Comparison of Observed and Calculated Uranium−Sulfur Stretching Frequencies (cm^{-1}) for the Ground State US, US$_2$, US$_3$ Molecules

			Observed			Calculated		
identity	state	mode	^{32}S	^{34}S	^{32}S/^{34}S	^{32}S	^{34}S	^{32}S/^{34}S
US	^{5}H/$^5\Pi^a$		451.1	439.2	1.0271	445.0	433.3	1.0270
US$_2$	^{3}B$_2$	ν_1	449.8	437.4	1.0283	440.4	428.2	1.0285
US$_2$	^{3}B$_2$	ν_3	438.7	427.8	1.0255	432.1	421.4	1.0254
US$_3$	^{1}A$_1$	b$_2$	458.2	447.4	1.0241	463.4	452.5	1.0241

[a] See text for discussion.

Table 2. Calculated (B3LYP) Structures and Frequencies for Uranium Sulfide Molecules

molecule	lengths, angles	frequencies, cm^{-1} (intensities, km/mol)
US (^{5}H/$^5\Pi$)^a	2.378 Å	445 (74)
US$_2$ (^{3}B$_2$) (0.0)^b	2.380 Å, 121.4°	440 (a$_1$, 18), 432 (b$_2$, 157), 61 (a$_1$, 8)
US$_2$ (^{3}B$_1$) (16.0)	2.363 Å, 116.0°	445 (b$_2$, 167), 444 (a$_1$, 28), 88 (a$_1$, 5)
US$_2$ (^{3}A$_1$) (16.2)	2.362 Å, 115.7°	445 (b$_2$, 161), 444 (a$_1$, 28), 88 (a$_1$, 5)
US$_2$ (^{3}H$_g$/$^3\Pi_g$) (16.5)	2.401 Å, 180°	428 (σ_u, 244), (417 (σ_g, 0), 56i (π_u)
US$_3$ (^{1}A$_1$)	2.333 Å, 150.8° 2.342 Å, 104.6°	463 (b$_2$, 174), 452 (a$_1$, 26), 423 (a$_1$, 71)

[a] See text for discussion. [b] Relative energies, kJ/mol.

vibrational frequencies for the ground-state molecules, and Table 2 gives other calculated properties of three uranium sulfide molecular species.

The ground state of US is predicted to be a quintet with the unpaired electrons distributed as $(\sigma)^1(\sigma)^1(\delta)^1(\phi)^1$ and bond length 2.378 Å. This configuration gives two different spectroscopic states, ^{5}H and $^5\Pi$. The Gaussian/DFT results are a mixture of the two. Because the δ and ϕ orbitals are nonbonding 5f, the coupling of the angular momenta of electrons in these open shells should have little influence on the frequency. The computed harmonic frequency is 445 cm^{-1}, which supports the experimental assignment.

The calculation on US$_3$ located a T-shaped (C_{2v}) singlet ground state, with bond lengths 2.342 Å for the unique U−S, and 2.333 Å for other two equal U−S bonds, and the larger S−U−S angle is 150.8°. A similar structure was found for UO$_3$ at the SCF level[25] and at the B3LYP level,[14] and the B3LYP frequencies are in very good agreement with experimental results.[8,9] Three vibrational stretching modes were predicted for the US$_3$ molecule, at 463, 452, and 423 cm^{-1}, with infrared intensities of 174, 26, and 71 km/mol, respectively. The strongest b$_2$ mode is primarily antisymmetric stretching of the near-linear S−U−S unit with little involvement of the third S atom; this result explains the triplet splitting pattern of the observed 458.2 cm^{-1} band in the mixed ^{32}S + ^{34}S experiment and supports the assignment to US$_3$.

The spectroscopic observation of US$_2$ with a bent geometry is of major interest, since the analogous UO$_2$ is a well-known linear molecule.[8,9,14,23,24] The DFT calculation predicts the ground state for US$_2$ as ^{3}B$_2$ (unpaired electrons in a$_1$ and b$_2$ orbitals, atoms in the *yz* plane), with bond length of 2.380 Å, and bond angle of 121.4°. The ν_1 and ν_3 vibrational modes were computed at 440 and 432 cm^{-1}, with infrared intensities of 18 and 157 km/mol, respectively, which are comparable to the bands observed at 449.8 and 438.7 cm^{-1} with 1:6 relative intensity. Two other slightly higher bent states, ^{3}B$_1$ and ^{3}A$_1$ with $(a_1)^1(b_1)^1$ and $(a_1)^1(a_1)^1$ configurations, respectively, are predicted to have almost coincident 445 cm^{-1} frequencies, which is not in agreement with the experimental spectrum. Although the observed spectrum shows that US$_2$ is bent, both from the observation of a weak ν_1 (a$_1$) mode and the sulfur isotopic shift of the ν_3 (b$_2$) mode, calculations were performed on different linear states of US$_2$; however, *all* have higher energies and imaginary bending frequencies.

Mulliken population analyses can provide helpful insight into the bonding, though they must be interpreted with caution because the numerical values are sensitive to details of the basis. The net charge on U in the ^{3}B$_2$ state is only +0.67 at the B3LYP level, giving 5.33 “valence electrons”, with 5f and 6d populations of 2.96 and 1.93. The spin density on U is 2.45, essentially in the 5f orbitals (2.20). The U−S overlap population is dominated by contributions from the 6d orbitals (75% of the total), with the 5f contributing only 28%, s-type orbitals just 7%, and a net antibonding interaction (−9%) from the p-type orbitals. For comparison, in U−O species, the 5f orbitals on U play the largest role, as their contribution to the overlap population in the uranyl ion (directly comparable bases used in the two cases) is 18% larger than that from the 6d orbitals.[14] The reduced importance of the 5f orbitals in US$_2$ is directly due to their size (mean radius 0.76 Å), as they are notably more contracted than the 6d (radius 1.70 Å).[26] Accordingly, they overlap effectively with other small orbitals, such as 2p on O (radius 0.66 Å), but are less suitable for overlap with more diffuse valence orbitals such as 3p on S (radius 1.09 Å).

The differing pattern of orbital participation on U leads to the different shapes of UO$_2$ and US$_2$. The uranyl ion is linear, as are UO$_2^+$, UO$_2$, and UO$_2^-$,[14] because of the predominant role played by f-type orbitals on U. However, MO$_2$ species where M uses mostly d-type orbitals are bent, at least where M has few d electrons. The ThO$_2$ molecule is bent (122 ± 2°),[27] d participation is favored over f by orbital energies, and d−f mixing leads to the observed bond angle.[28−30] As the open-shell 5f orbitals on U contribute relatively little to the bonding in US$_2$, the pattern of their occupation has little influence on the total energy. These observations show that the bent geometry found here for US$_2$ is due to the dominance of 6d bonding by uranium.

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