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Decomposing the First Absorption Band of OCS Using Photofragment Excitation Spectroscopy

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ABSTRACT: Photofragment excitation spectra of carbonyl sulfide (OCS) have been recorded from 212–260 nm by state-selectively probing either electronically excited S(1D) or ground state S(3P) photolysis products via 2 + 1 resonance-enhanced multiphoton ionization. Probing the major S(1D) product results in a broad, unstructured action spectrum that reproduces the overall shape of the first absorption band. In contrast, spectra obtained probing S(3P) products display prominent resonances superimposed on a broad continuum; the resonances correspond to the diffuse vibrational structure observed in the conventional absorption spectrum. The vibrational structure is assigned to four progressions, each dominated by the C=S stretch, $\nu_{\text{f}}$, following direct excitation to quasi-bound singlet and triplet states. The S(3P) products are formed with a near-statistical population distribution over the J = 2, 1, and 0 spin–orbit levels across the wavelength range investigated. Although a minor contributor to the S atom yield near the peak of the absorption cross section, the relative yield of S(3P) increases significantly at longer wavelengths. The experimental measurements validate recent theoretical work characterizing the electronic states responsible for the first absorption band by Schmidt and co-workers.

INTRODUCTION

Carbonyl sulfide (OCS) is the most abundant sulfur-containing compound in the atmosphere. OCS is relatively unreactive in the troposphere, where it is present at near constant mixing ratios of $\sim$500 ppt, but concentrations drop off sharply in the stratosphere, as shorter wavelength photolysis becomes increasingly important. As a source of atomic sulfur, photolysis of OCS makes a significant nonvolcanic contribution to the stratospheric sulfate aerosol layer. The compound in the atmosphere.

The first absorption band of OCS is the most abundant sulfur-containing compound in the atmosphere. OCS is relatively unreactive in the troposphere, where it is present at near constant mixing ratios of $\sim$500 ppt, but concentrations drop off sharply in the stratosphere, as shorter wavelength photolysis becomes increasingly important. As a source of atomic sulfur, photolysis of OCS makes a significant nonvolcanic contribution to the stratospheric sulfate aerosol layer. The band appears as a broad, weak continuum spanning 190–260 nm and has diffuse vibrational structure superimposed. The diffuse structure was first observed by Breckenridge and Taube and assigned to four different progressions. One progression was identified as a hot band arising from bend-excited ground state molecules, which was later confirmed by Wu et al. The red wing of the continuum absorption also depends strongly on temperature, largely due to population in excited levels of the low frequency bend, $\nu_{\text{f}}$, which significantly enhances the transition strength. Additional diffuse structure has also been observed in the long wavelength tail of the absorption spectrum between 270–300 nm, where the cross section is around 4 orders of magnitude smaller than at the peak.

The first absorption bands of OCS arise from $\pi\pi^*$ excitations and lead to $1\Sigma^-$, $1\Sigma^+$, and $1\Delta$ states in linear geometries, while $\sigma\pi^*$ excitations lead to $1\Pi$ states at higher energy. The first absorption band primarily results from excitation to the $1\Delta$ and $1\Sigma^-$ states. Formally, electric dipole transitions to both states are forbidden in linear geometries because of the $\Delta\Lambda = \pm 1$ and $\Sigma^- \rightarrow \Sigma^+$ selection rules. Bending deformation reduces the symmetry to $C_2$ and splits the $1\Delta$ state into the $2\Delta'$ and $2\Delta''$ states, which form a Renner–Teller pair. The $1\Sigma^-$ state becomes the $1\Pi^+$ state, which has a bent minimum. All transitions are weakly allowed in $C_2$ symmetry. Several groups have performed electronic structure calculations to characterize the electronic structure, calculate the absorption spectrum, and provide insight into the photodissociation dynamics. Multireference configuration interaction (MRCI) calculations have shown that the $2\Delta'$ ($1\Pi^-$) state predominantly and the $1\Pi^+$ ($1\Sigma^+$) state to a lesser extent are primarily responsible for the first absorption continuum. Schmidt and co-workers re-evaluated the transition dipole moment functions finding that the $1\Pi^+$ state a made significantly greater contribution to the absorption spectrum than previously thought. One-dimensional cuts through the potential energy surfaces along the Jacobi coordinate defining the distance between the S atom and the center of mass of the CO molecule are depicted in Figure 1. Other key characteristics of the states are summarized in Table 1. The topographies of the $2\Delta'$ and $1\Pi^+$ states are very similar. Both are highly repulsive along the C=S bond in near-linear geometries, but have minima in bent geometries that lie below the S(1D) + CO product asymptote. These potential wells can support bound states and are responsible for the structure in the long-wavelength tail of the absorption band.

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Figure 1. One-dimensional cuts along the Jacobi coordinate $R$ for the lowest singlet (black) and triplet (red) states for $r = 2.2 \ a_0$ and $\gamma = 5^\circ$. Solid and dashed lines indicate states of $\Lambda^\prime$ and $\Lambda^\alpha$ symmetry, respectively. Adapted from Schmidt et al.17

Table 1. Summary of OCS Electronically Excited States48

<table>
<thead>
<tr>
<th>label</th>
<th>$C_s$</th>
<th>$C_{\text{ave}}$</th>
<th>$E$/eV</th>
<th>type</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1$\Lambda^\prime$</td>
<td>1$\Sigma^\gamma$</td>
<td>0</td>
<td>bound</td>
</tr>
<tr>
<td>A</td>
<td>2$\Lambda^\prime$</td>
<td>1$\Delta$</td>
<td>5.82</td>
<td>dissociative</td>
</tr>
<tr>
<td>B</td>
<td>1$\Lambda^\prime$</td>
<td>1$\Sigma^\gamma$</td>
<td>5.73</td>
<td>dissociative</td>
</tr>
<tr>
<td>C</td>
<td>2$\Lambda^\prime$</td>
<td>1$\Delta$</td>
<td>5.88</td>
<td>bound</td>
</tr>
<tr>
<td>a</td>
<td>1$\Lambda^\prime$</td>
<td>1$\Sigma^\gamma$</td>
<td>5.05</td>
<td>dissociative</td>
</tr>
<tr>
<td>b</td>
<td>1$\Lambda^\prime$</td>
<td>1$\Delta$</td>
<td>5.42</td>
<td>dissociative</td>
</tr>
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<td>1$\Sigma^\gamma$</td>
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</tr>
<tr>
<td>d</td>
<td>2$\Lambda^\prime$</td>
<td>1$\Delta$</td>
<td>5.45</td>
<td>bound</td>
</tr>
</tbody>
</table>

$E$ is the vertical excitation energy. Adapted from Schmidt et al.17

Spin–orbit coupling to the strongly absorbing and near-degenerate 2$\Lambda^\alpha$ state.17,20–22 Inclusion of higher order correlation effects in the electronic structure calculations critically influence the potential energy surfaces (PESs) and transition dipole moment functions.25

It has long been known46 that excitation of OCS in the first absorption band leads to dissociation to form CO + S, and the photodissociation dynamics has received significant attention.20,27–40 Various groups have attempted to quantify the photodissociation quantum yield, $\Phi$.5,6,9,41 Although the earliest measurements reported $\Phi \approx 1$, others suggested smaller values when probing the yield of CO.6,9 The secondary reaction S + OCS $\rightarrow$ S$_2 +$ CO was assumed to go to completion, leading to an anticipated total CO quantum yield of $\Phi = 2$. The current JPL evaluation42 recommends a primary CO quantum yield of unity across the 220–254 nm wavelength range, based primarily on the tunable diode laser absorption measurements made by Zhao et al. probing CO concentration after photolysis at 248 nm.41 Sulfur atoms are formed predominantly in the electronically excited 1$\Delta$ state with a far smaller fraction produced in the 1$\Sigma^\gamma$ ground state. Early measurements of the branching between singlet and triplet S atom photoproducts inferred that S(1$\Delta$) accounted for around 75% of the total atomic sulfur yield.42,43 although measurements in collisional environments were complicated by quenching. Two-photon LIF measurements by van Veen et al. probed the time-dependent formation of S(3$P$) and S(1$D$) atoms following photolysis at 248 nm.44 While S(1$D$) atoms were detected promptly, the S(3$P$) fluorescence signal grew in over a millisecond time scale. However, the experiments lacked sufficient time resolution to demonstrate exclusive production of S(1$D$). Sivakumar et al. suggested a S(3$P$) branching fraction of 0.15 after 222 nm excitation, but subsequently revised this to $<0.02$.27,28 Doppler profile measurements by Nan et al. using VUV laser-induced fluorescence at a photolysis wavelength of 222 nm demonstrated the direct formation of S(3$P$) radicals with a S(3$P$)/S(1$D$) branching ratio of 0.05.29 Fully state-resolved velocity-map imaging measurements at 230 nm probed CO($J = 63$) products and determined a S(3$P$)/S(1$D$) branching ratio of 0.038, consistent with the rotationally averaged result.37

In this work, photofragment excitation (PHOFEX) spectroscopy has been used to record action spectra of the first absorption band of OCS while probing ground state S(3$P$) and electronically excited S(1$D$) atoms by 2 + 1 resonance enhanced multiphoton ionization. The PHOFEX spectra are structureless when probing S(1$D$) atoms, but show resonances corresponding to vibrational progressions in two different bound electronic states when probing S(3$P$) atoms. The wavelength dependence of the ground state fine-structure branching and the overall singlet–triplet branching fractions are determined.

**EXPERIMENTAL METHODS**

PHOFEX spectra were recorded in a velocity-map ion imaging mass spectrometer, previously described in detail.45 In these experiments, however, it was operated as a conventional Wiley–McLaren time-of-flight mass spectrometer. Dilute mixtures of OCS (Matheson, > 97% purity) in Ar or He carrier gas were expanded into high vacuum from a stagnation pressure of 1 atm using a solenoid pulsed valve (Parker Series 9). The expansion was skimmed (Beam Dynamics) to form a molecular beam before being intersected by counter-propagating pump and probe laser beams that dissociated OCS and state-selectively ionized S(1$D$) or S(3$P$) products via well-known 2 + 1 resonance-enhanced multiphoton ionization (REMPI) transitions. Pump laser pulses spanning the 212–260 nm wavelength range were generated using a midband Nd:YAG-pumped optical parametric oscillator (OPO) (Continuum Surelite EX and Horizon II). The OPO generated a broadly tunable UV beam with a linewidth of $S\sim 7$ cm$^{-1}$. The pulse energy increased from 0.5 to 1.1 mJ across the scanned range. A frequency doubled Nd:YAG-pumped dye laser (Continuum Surelite II–10, Lambda Physik Scanmate) operating with Rhodamine 590 or 640 laser dyes generated the REMPI probe pulses with typical pulse energies of $<1.5$ mJ. The pump and probe beams, temporally separated by <30 ns, were focused into the ionization region of the mass spectrometer with fused silica lenses of focal lengths $f = 1000$ mm and 300 mm, respectively. A stack of electrodes accelerates the resultant ions toward a time-gated MCP/phosphor assembly (Photonis).

The phosphorescence corresponding to selected features in the mass spectrum was monitored as a function of pump wavelength by a silicon photomultiplier (SenSL MicroSL 10020-X18) to generate PHOFEX spectra. Pump and probe laser pulse energies were monitored with a photodiode (Thorlabs DET10A) that had been calibrated against an energy meter (Gentec Maestro). Optogalvanic Ne spectra were
PHOFEX action spectra of OCS were recorded by repeatedly scanning the pump wavelength from 212 to 260 nm, while monitoring the total m/z = 32 (S⁺) signal with the probe laser wavelength tuned to be resonant with a known 2 + 1 REMPI transition of sulfur atoms. On its own, the pump laser-induced background signals when tuned over sharp two-photon resonances of atomic sulfur. A weaker, broad background S⁺ signal also appeared at pump wavelengths <225 nm. This signal coincided with the observation of the OCS⁺ parent ion at m/z = 60 and was attributed to dissociative ionization. The probe laser was held fixed at 288.17 nm to ionize S(1D) atoms via the 3p³4p 1F₃ level. S(3P) atoms were ionized via the 3p³4p 1P₃ levels at one-photon wavelengths 308.20, 310.09, and 310.96 nm, which probed the J = 2, 1, and 0 levels, respectively. The trace amount of CS₂ present as a contaminant in the OCS sample (<0.2%) makes no significant contribution to the PHOFEX spectra in the wavelength range studied.

The PHOFEX spectrum of OCS obtained probing electronically excited S(1D) atoms is shown in Figure 2. Background signal induced by the pump laser alone has been subtracted and the spectrum has been normalized for the wavelength dependence of the pump laser power. The spectrum reproduces the overall shape of the absorption spectrum reasonably well, although some differences are evident. First, the diffuse vibrational structure in the absorption spectra is absent from the S(1D) action spectrum. Second, despite cooling in the supersonic expansion, the long-wavelength (λ > 235 nm) region of the PHOFEX spectrum is more similar to the absorption spectrum measured at 295 K than 170 K. The maximum S(1D) yield appears red-shifted by ∼2 nm relative to the maxima of the absorption spectra. Several groups have investigated the temperature dependence of the absorption spectrum, finding that excitation in ν₂ in the ground electronic state is responsible for absorption in the red wing of the band.10−12,16 Low frequency vibrational excitation, which greatly enhances the absorption cross section, appears not to be effectively relaxed in the expansion, as has been observed previously in ion imaging experiments.36 Third, the relative S(1D) yield measured in the PHOFEX spectrum deviates from the conventional absorption spectrum at shorter wavelengths (λ < 225 nm), where the absorption band is least affected by the temperature. The dissociation threshold to form CO + S(1S) does not become energetically accessible until λ < 211 nm and the S(1P) yield, described below, is too small to compensate for the apparent deviation between the S(1D) yield and the OCS absorption spectrum. The deviation does coincide, however, with the appearance of OCS⁺ and S⁺ peaks in the mass spectrum induced by the pump laser alone. Multiphoton dissociative ionization likely competes with neutral dissociation at the typical pump energies used in the experiment, reducing the apparent yield of neutral sulfur atoms in this wavelength range.

The action spectrum presented in Figure 2 differs somewhat from that measured previously by Suzuki et al., who found a relatively smaller S(1D) yield at longer wavelengths, although the Feshbach resonances predicted in the wavepacket calculations are not observed in our spectrum either.20 The absence of structure in the PHOFEX spectrum is consistent with the theoretical view that the absorption spectrum is dominated by excitation to the repulsive 2¹A″ and 1¹A″ states.17,22,23 The measurements reported here do not distinguish the relative contributions of each state to the S(1D) yield, although previous measurements of the photo-fragment angular distributions indicate that both contribute significantly.20,34,47

In contrast to S(1D), the equivalent PHOFEX spectra recorded when state-selectively probing S(3P) atoms show distinct resonances superimposed on a similar broad continuum; pump-only background subtracted and pump power normalized spectra are shown in Figure 3. Aside from the relative yield of each S(3P) spin–orbit level, the triplet PHOFEX spectra are qualitatively similar. The relative population in each spin–orbit level can be obtained directly.
from the REMPI signal intensity, since the line strengths for the transitions used to probe the $J = 0, 1,$ and 2 spin−orbit levels are almost identical. A correction is applied to account for incomplete sampling of the total REMPI spectrum at the fixed probe wavelengths. Each nominal transition probing $S(^3P)$ comprises two or three partially resolved spectral lines due to the small spin−orbit splitting in the resonant electronically excited state. Figure 4 shows $S$ atom REMPI spectra following photodissociation of OCS at 225 nm. The fractional contribution made to the total REMPI signal at each fixed probe wavelength was used to scale the PHOFEX spectra in Figure 3 such that the intensity is proportional to the yield. The $J = 2$ spin−orbit level is the major triplet product, with progressively smaller yields of $J = 1$ and $J = 0$. The resonances account for <10% of the total $S(^3P)$ yield: the underlying continuum absorption is predominantly responsible for the production of $S(^3P)$ atoms.

The continua in the triplet and singlet PHOFEX spectra have very similar shapes, suggesting the same underlying electronically excited states are primarily responsible. Following initial excitation to the repulsive $2^1A'$ or $1^1A''$ states, intersystem crossing must occur to yield $S(^3P)$ products. The dissociative $2^1A'$ and $1^1A''$ states are likely too short-lived for intersystem crossing in the Franck–Condon region to be important. One-dimensional cuts through the PESs (see Figure 1) show that the bound $2^3A''$ state becomes repulsive at longer range (Jacobi coordinate, $R > 5.2\,\text{a}_0$) in linear geometries as a result of an avoided crossing with an unidentified repulsive surface (likely $3\Sigma^-$), and the outer limb crosses both the repulsive $2^1A'$ and $1^1A''$ singlet surfaces. Alternatively, the products could be formed on the repulsive $1^3A'$ state, which lies very close in energy to the $2^1A'/1^1A''$ exit channel conical intersection at bend angles of ~60°. The transition dipole moments for direct spin-forbidden excitation to the lowest dissociative triplet states, $1^3A'(1\Sigma^-)$ and $1^3A''(1\Delta)$, are predicted to be too small to account for the observed $S(^3P)$ yield. However, these transition dipole moments were not updated in a more recent paper that identified problems with the earlier calculations and could be in error.

The wavelength dependence of the spin−orbit population distributions are more clearly observed in Figure 5, which shows the fractional contributions of each level to the total $S(^3P)$ yield. Across the absorption band, the fractional populations in the $J = 2, 1,$ and 0 spin−orbit levels are broadly at the $(2J + 1)$ statistical limit (i.e., 5:3:1), albeit with some subtle deviations. First, the resonances appear distinctly in Figure 5 as peaks in the fractional population in the $J = 2$ level and dips in $J = 1$. The fractional yield of the $J = 0$ level appears to be unaffected by the resonances. Second, a slight reduction in the fractional $J = 2$ population across the center of the absorption band is compensated by local increases in $J = 1$, centered near 226 nm, and $J = 0$, centered near 238 nm. The wavelength-dependent enhancements in the fractional $J = 1$ and $J = 0$ populations match well the predicted absorption spectra for excitation to the repulsive $1^1A''(1\Sigma^-)$ and $1^3A''(1\Delta)$ states, respectively.

It is not clear, however, why initial excitation to the $1^1A'$ and $1^3A''$ states would result in an increased propensity for production of $S(^3P_1)$ and $S(^3P_0)$, respectively. Brouard et al. identified an additional translationally fast (i.e., low-$J$ CO) component in $S(^3P_0)$ ion images that was not present for $S(^3P_2)$ or $S(^3P_1)$ at a photolysis wavelength of 248 nm. The spin−orbit branching was also found to be weighted even more heavily in favor of the $J = 2$ level at 248 nm. While it is possible that the fast component could arise from direct excitation to the repulsive $1^3A'$ state, one-dimensional cuts through the PES suggest that it is highly anisotropic, which would lead to rotationally excited CO coproducts. The adiabatic model discussed by Brouard et al. shows that $S(^3P_0)$ does not correlate with the $1^1A''$ state, but rather to the higher-lying bound $2^3A''(1\Sigma^-)$ state in both bent and linear geometries. A more detailed understanding of the photodissociation mechanism is likely to require further theoretical work, in particular, calculation of the fully spin−orbit coupled PESs.

The wavelengths and relative intensities of the resonances in the triplet PHOFEX spectra shown in Figure 3 reproduce the diffuse vibrational structure observed in conventional absorption measurements and indicate excitation to bound, or rather quasi-bound, states. Dissociation to form $S(^3P) + CO$ must be faster than the time scale of the experiment, i.e., < 30 ns, the

![Figure 4](image4.png)

**Figure 4.** Two $+1$ REMPI spectra of (a) $S(^1D)$, (b) $S(^3P_2)$, (c) $S(^3P_1)$, and (d) $S(^3P_0)$ atoms arising from the photolysis of OCS at 225 nm. Sticks indicate the positions and relative intensities of the transitions.

![Figure 5](image5.png)

**Figure 5.** Spin−orbit branching fractions among $S(^3P)$ products. The dashed horizontal lines indicate the statistical limits.
time delay between the pump and probe laser pulses, to produce the action spectrum. Prompt predissociation is also supported by anisotropy in the photofragment angular distributions. Figure 6 shows a higher resolution OCS PHOFEX spectrum of the structured region between 216 and 238 nm that was obtained probing S(3P2) products. Lorentzian distributions supported by anisotropy in the photofragment angular distributions.

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Table 2. Band Progressions Identified in the S(3P2) PHOFEX Spectrum of OCSa

<table>
<thead>
<tr>
<th>Progression</th>
<th>(\nu/cm^{-1})</th>
<th>(\lambda/nm)</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>42719 (61)</td>
<td>234.09</td>
<td>0.24</td>
<td>(2^3\Sigma^+ (1^1\Sigma^-))</td>
</tr>
<tr>
<td></td>
<td>43389 (43)</td>
<td>230.47</td>
<td>0.70</td>
<td>(n\nu_1)</td>
</tr>
<tr>
<td></td>
<td>44071 (56)</td>
<td>226.91</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44745 (51)</td>
<td>223.49</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45111 (46)</td>
<td>220.21</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>42352 (77)</td>
<td>236.12</td>
<td>0.18</td>
<td>hot bands (2^3\Sigma^+ (1^1\Delta))</td>
</tr>
<tr>
<td></td>
<td>43045 (51)</td>
<td>232.31</td>
<td>0.25</td>
<td>(n\nu_1)</td>
</tr>
<tr>
<td></td>
<td>43755 (68)</td>
<td>228.55</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44488 (52)</td>
<td>224.88</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>42868 (123)</td>
<td>233.27</td>
<td>0.14</td>
<td>(2^1\Delta (1^3\Delta))</td>
</tr>
<tr>
<td></td>
<td>43588 (105)</td>
<td>229.42</td>
<td>0.24</td>
<td>(n\nu_1)</td>
</tr>
<tr>
<td></td>
<td>44292 (65)</td>
<td>225.78</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44992 (101)</td>
<td>222.26</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45701 (65)</td>
<td>218.81</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>46261 (50)</td>
<td>224.11</td>
<td>0.27</td>
<td>(2^3\Sigma^+ (1^3\Sigma^-))</td>
</tr>
<tr>
<td></td>
<td>45314 (50)</td>
<td>220.68</td>
<td>0.41</td>
<td>(n\nu_1+2\nu_2)</td>
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<tr>
<td></td>
<td>46007 (55)</td>
<td>217.36</td>
<td>0.40</td>
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</tr>
<tr>
<td></td>
<td>46679 (74)</td>
<td>214.23</td>
<td>0.30</td>
<td></td>
</tr>
</tbody>
</table>

aThe uncertainty (1σ) in the reported band centers is ±3 cm⁻¹ and the values in parentheses are the FWHM of the Lorentzian fits.

homogeneous lifetime broadening is responsible for the width of the resonances, the lifetimes of the quasi-bound excited states are expected to be ~100 fs. The resonances dissociate exclusively to form S(3P) products—no structure is identifiable within our signal-to-noise in the PHOFEX spectrum when probing S(1D).

Figure 6. High-resolution PHOFEX spectrum of OCS probing S(3P2) atoms. Progressions I and IV (red comb) are assigned to \(n\nu_1\) and \(n\nu_1+2\nu_2\) in the \(2^3\Sigma^+ (1^1\Sigma^-)\) state. Progressions II and III (blue combs) are assigned to \(n\nu_1\) in the \(2^1\Delta (1^3\Delta)\) state, the former originating from bend excited ground state molecules. The predicted absorption spectrum for excitation to the \(2^3\Sigma^+ (1^3\Sigma^-)\) state from Schmidt et al. is also shown, offset by 3 nm (dashed red).

The diffuse vibrational structure in the conventional absorption spectrum has been assigned to four progressions (labeled here as I–IV), one of which was found to be a hot band arising from bend-excited ground state molecules. The four strongest transitions in the spectrum shown in Figure 6 are evenly spaced and identified as progression I. The weak feature at 234.09 nm (42719 cm⁻¹) also appears to be associated with this progression and is presumed to be the origin band. The average separation of 673 ± 7 cm⁻¹ is close to the predicted harmonic C–S stretch (\(\nu_1\)) frequency in the bound \(2^3\Sigma^+ (1^1\Sigma^-)\) state of 688 cm⁻¹. The positions and intensities are in excellent agreement with the calculated spectrum for direct excitation to the bound \(2^3\Sigma^+ (1^3\Sigma^-)\) state, which also is shown in Figure 6, offset by 3 nm. The transition to the \(2^3\Sigma^+\) state gains intensity through spin–orbit coupling with the neighboring \(2^1\Delta\) state and it is predicted to undergo electronic predissociation by recoupling with a lifetime of ~300 fs. The calculated lifetime is in reasonable agreement with the ~100 fs lifetime estimated from the homogeneous broadening of the resonances. Once on the \(2^1\Delta\) surface, dissociation could proceed as described for the continuum S(3P) yield as described above. However, this mechanism would suggest that the vibrational resonances should be present in the PHOFEX spectrum obtained probing S(1D), since some fraction of the molecules that hop onto the \(2^3\Sigma^+\) surface would not undergo the second transition required to reach triplet products. The relative yields of S(3P) and S(1D) suggest that the likelihood of forming triplet products starting from the repulsive singlet surfaces is small at these wavelengths. Since the S(1D) yield is dominated by direct excitation to the \(2^3\Sigma^+\) and \(2^1\Delta\) surfaces, the signature of the resonances may be lost in the noise. Alternative interpretations are possible, in which the dissociation occurs exclusively within the triplet system. The \(2^3\Sigma^+\) state could predissociate by tunneling through the barrier to form S(3P), although inspection of the potential energy surface does not show any

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geometries for which the barrier is lower than \( \sim 1 \text{ eV} \). A tunneling mechanism may be expected to lead to a decrease in the excited state lifetime following excitation to bound states higher in the \( 2^1\text{A}^\ast \) well. While the range of excitation energies is somewhat limited, no variation in the homogeneous broadening is observed. The bound \( 2^1\text{A}^\ast \) state can interact with the dissociative \( 1^1\text{A}^\ast \) state via nonadiabatic coupling. However, the strength of this interaction is not known, and the states remain reasonably well separated in the Franck–Condon region. Elucidating the details of the dissociation mechanism will require additional experimental and theoretical work.

The weak and longest wavelength feature at 236.12 nm (42352 cm\(^{-1}\)) was previously assigned to a hot band.\(^7,12\) It is the first member of progression II with average separations of \( 705 \pm 11 \text{ cm}^{-1} \), which is also close to that expected for \( \nu_2 \). All of the bands in progression II match those identified as hot bands in temperature-dependent measurements of the absorption cross section.\(^7,12\) The \(-367 \text{ cm}^{-1} \) offset from the first member of progression I, however, is inconsistent with the frequency of \( 520 \text{ cm}^{-1} \) for the bending vibration, \( \nu_3 \), in the electronic ground state.\(^52\) A third progression (labeled III) with an effectively identical average separation of \( 708 \pm 9 \text{ cm}^{-1} \) and origin at 233.27 nm (42868 cm\(^{-1}\)) can also be identified. Progression III is red-shifted by \( 516 \pm 1 \text{ cm}^{-1} \) from the first band in progression II, consistent with the frequency of \( \nu_2 \) in the ground state. The slight increase in the average separation of the bands and small \( 149 \text{ cm}^{-1} \) shift of the apparent origin band relative to progression I suggests that progressions II and III involve excitation to a different quasi-bound and near degenerate electronic state.

The \( 2^1\text{A}^\ast \) (\( 1^1\Delta \)) and \( 2^3\text{A}^\ast \) (\( 1^3\Delta \)) states, which are the Renner–Teller partners of the \( 2^1\text{A}^\ast \) and \( 1^1\text{A}^\ast \) states, are also predicted to be bound.\(^17,22\) Progressions II and III are unlikely to be attributable to the \( 2^1\text{A}^\ast \) state for two reasons. First, the transition dipole moment was calculated to be an order of magnitude smaller than that of the \( 2^1\text{A}^\ast \) state, albeit with the caveat that these values come from the earlier work of Schmidt et al.\(^22\) and were not updated using the improved methods reported in McBane et al.\(^23\) Second, the predicted absorption spectrum appears to be significantly broader than experiment, with structure extending to longer wavelengths. Excitation to the \( 2^1\text{A}^\ast \) state on the other hand is predicted to have a transition dipole moment of comparable magnitude and lie much closer in energy to the \( 2^1\text{A}^\ast \) state. The bound \( 2^3\text{A}^\ast \) state can dissociate by nonadiabatic coupling to the dissociative \( 1^1\text{A}^\ast \) state, but this pathway would lead to predominantly singlet products. Intersystem crossing to the \( 2^1\text{A}^\ast \) state, which is nearly degenerate could lead to dissociation within the triplet system via the mechanisms suggested above.

The remaining bands in the spectrum are relatively intense and form progression IV with a characteristic spacing of \( 686 \pm 12 \text{ cm}^{-1} \), similar to that observed for progression I. The first band in this progression lies at 224.11 nm (44621 cm\(^{-1}\)), which corresponds to an offset of \( +1902 \text{ cm}^{-1} \) from the origin band of progression I. The C–O stretch, \( \nu_3 \), is predicted to have a frequency of only \( 1711 \text{ cm}^{-1} \) in the \( 2^1\text{A}^\ast \) state and a possible assignment to \( \nu_1+2\nu_3 \) is rejected.\(^17\) The average peak separation suggests additional bands should be observable near 227.6 and 231.2 nm; the latter would be offset from the origin band by \( 539 \text{ cm}^{-1} \), which is close to the predicted wavenumber of \( 522 \text{ cm}^{-1} \) for two quanta of \( \nu_2 \) in the \( 2^1\text{A}^\ast \) state and suggests an assignment to a combination band \( \nu_1+2\nu_2 \).\(^5\) Reassuringly, a very weak band is indeed visible in the PHOFEX spectrum at 227.7 nm but the predicted longest wavelength band is not observed, presumably on Franck–Condon overlap grounds.

Previously, Hishikawa et al. measured PHOFEX spectra of the \( 2^1\Sigma^+\rightarrow 1^1\Sigma^+ \) transition in the vacuum ultraviolet region (144–158 nm), probing electronically excited \( \text{S}(\text{S}) \) atoms by laser-induced fluorescence.\(^50\) A vibrational progression was observed with spacing of \( \sim 800 \text{ cm}^{-1} \). Across the progression, the peaks had varying Lorentzian linewidths and asymmetric Fano lineshapes,\(^52\) that furthermore displayed a reversal in the \( \varphi \) parameter. In contrast to the \( 2^1\text{A}^\ast \) state, which is bound, the electronically excited \( 2^1\Sigma^+ \) state is purely dissociative along the C–S coordinate, but features a broad plateau associated with C–O bond extension. Wavepacket calculations allowed the progression to be assigned to transient Feshbach resonance states associated with in-phase C–O and C–S stretching motion, that is, motion perpendicular to the dissociation coordinate. The resonances observed in the PHOFEX spectrum probing \( \text{S}(\text{P}) \) shown in Figure 6, have a different physical origin, arising from excitation to a bound state, and do not display any variation in linewidth or evidence of asymmetric Fano lineshapes.

The \( \nu_4 \) and combination band \( \nu_4+2\nu_3 \) vibrational progressions (I and IV) associated with the \( 2^1\text{A}^\ast \) state have different C–S stretch frequencies, indicating that coupling between the C–S stretch and the bend occurs. Anharmonic coupling constants are extracted by fitting the progressions to an anharmonic oscillator expression:

\[
E_V = \left( \nu_1 + \frac{1}{2} \right) \omega_1 + \left( \nu_2 + \frac{1}{2} \right) \omega_2 + \left( \nu_1 + \frac{1}{2} \right) x_{11} + \left( \nu_2 + \frac{1}{2} \right) x_{12} + \nu_3 x_{13} + \nu_4 x_{14} + \frac{1}{2} x_{22} + \frac{1}{2} x_{33} + \frac{1}{2} x_{44} + \frac{1}{2} x_{12} x_{13} - \frac{x_{12} x_{13} + x_{13} x_{22} + x_{12} x_{12}}{4}
\]

\( E_V \) is the vibrational energy in \( \text{cm}^{-1} \) above that of the electronic origin, which is assumed to be 42719 cm\(^{-1}\), the position of the first identified band in progression I. \( \omega_1 \) and \( \omega_2 \) are the zero-order frequencies of the C–S stretch and bend, while \( x_i \) are the diagonal and off-diagonal anharmonicity constants. No significant progression is observed in the bend and consequently \( x_{12} \) is held at zero. Spectroscopic constants derived from the fit are summarized in Table 3. The standard deviation between the fit and the experimental peak positions is less than \( 5 \text{ cm}^{-1} \).

| Table 3. Spectroscopic Constants from Anharmonic Oscillator Fit to the \( 2^1\text{A}^\ast \) State |
|---------------------------------|---------|
| parameter | value/cm\(^{-1}\) |
| \( E_0 \) | 42719 |
| \( \omega_1 \) | 679 \pm 6 |
| \( \omega_2 \) | 244 \pm 6 |
| \( x_{11} \) | \(-2.4 \pm 1.2\) |
| \( x_{22} \) | 0 |
| \( x_{12} \) | 11.6 \pm 1.9 |

Finally, we turn to the wavelength dependence of the quantum yield of \( \text{S}(\text{P}) \). The REMPI detection sensitivity of \( \text{S}(\text{D}) \) relative to \( \text{S}(\text{P}) \) is unknown and must be characterized. S atom REMPI spectra, equivalent to those shown in Figure 4, were recorded at a photolysis wavelength of 222 nm. After normalization for variations in pump and probe fluences the \( \text{S}(\text{D}) \) signal was approximately 61 times greater than that of
S(1D). Using the $^3P_2/^1D_3$ branching ratio of 0.05 at 222 nm measured by Nan et al., the relative REMPI detection sensitivity for S(1D) is 3.1 ± 0.8 times that of S(1P). The PHOFEX spectra can be used to estimate the wavelength dependence of the S(1P) product yield, as shown in Figure 7.

Figure 7. Wavelength dependence of the S(1P) and S(1D) photolysis quantum yields (black) and the OCS absorption cross section measured by Wu et al. at 295 K (gray). A total photolysis quantum yield of unity is assumed.

Enhanced production of S(1P) is observed when the wavelength coincides with the vibrational progressions observed in the OCS absorption and PHOFEX spectra. At wavelengths <230 nm, the S(1P) quantum yield is consistently around 0.1, but increases steadily with increasing wavelength. Hot bands arising from residual vibrationally excited OCS molecules in the ground electronic state may affect this trend.

CONCLUSIONS

Photofragment excitation action spectroscopy has been used to decompose the first absorption band of OCS. The PHOFEX spectrum obtained probing the major S(1D) products is consistent with the prompt dissociation following excitation to the repulsive 21A″ state. These states have been predicted to rapidly predissociate following direct absorption to the 11A″ state or nonadiabatic transitions between the 11A″ and 11A″ states, respectively, although subsequent intersystem crossing would be required to form S(1P) products. Alternative mechanisms for dissociation within the triplet system may involve nonadiabatic transitions between the 21A″ state and the repulsive 11A″ state; further experimental and theoretical work is needed to clarify the detailed photodissociation mechanism. Direct absorption to the dissociative 11A″ state may contribute near the red-edge of the band, leading to changes in the spin–orbit branching and an increase in relative yield of S(1P) products.

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