

Photodissociation of (OCS)₂ and (CS₂)₂: Competing Photochemical Pathways

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The photochemistry of (OCS)₂ and (CS₂)₂ is investigated by using resonance-enhanced multiphoton ionization. The competition between van der Waals and covalent bond chemistry occurring upon electronic excitation of the dimers is probed, and the energetic and kinetic factors affecting this competition are examined. Photodissociation of the ¹Σ⁺ state of OCS in a dimer is investigated and found to produce a significant amount of S₂. Photodissociation of the ¹B₂(¹Σ_u⁺) state of CS₂ in a dimer leads to the production of S₂ and C₂S₂ photoproducts. These fragments are obtained as a result of covalent bond photochemistry of the respective dimers. There appears to be a greater tendency toward van der Waals bond dissociation in (CS₂)₂ compared with (OCS)₂, in agreement with expectations based on differences in energetics and excited-state dynamics of the two dimers.

Introduction

The photodissociation of isolated small molecules has been an area of intense experimental and theoretical research.¹⁻⁷ Molecular clusters of these small molecules provide the opportunity to design experiments that probe solvent effects on reactivity.

Since the first results of the photofragmentation of a van der Waals molecule were reported,⁸ only a handful of experiments have been performed to study the photodissociation of molecular clusters.⁹⁻¹⁵ Wittig et al. have reported the use of CO₂-HBr and CO₂-DBr complexes to study orientation effects in bimolecular reactions.^{9a,b} Soep and co-workers used Hg-H₂ complexes for similar studies.¹⁰ Recent photodissociation studies of OCS¹¹ and CS₂^{12,13} clusters have reported evidence of photoproducts resulting from photochemistry occurring within the clusters. In the case of OCS, the internal energy of S₂ photoproducts resulting from photoexcitation of the ¹Δ state at 222 nm was investigated.¹⁴

The approach chosen here relies on the dimers of OCS and CS₂. The mechanisms responsible for energy transfer and the competition between energy flow to the weak bonds and covalent bond photodissociation are investigated.

The isoelectronic molecules OCS and CS₂ were chosen for this study for several reasons: (1) The spectroscopy and photochemistry of the monomers are well-known. (2) Clusters of these molecules are readily produced, and the binding energies and ionization potentials of the clusters have been determined. (3) The C-S bond strengths in OCS and CS₂ are respectively stronger and weaker than the S₂ bond formed in the dimer photolysis. (4) The excited-state dynamics are sufficiently different to allow for

a comparative study.

This paper reports the results of resonance-enhanced multiphoton ionization studies of OCS, CS₂, and their respective dimers, to probe the competition between the photodissociation of van der Waals and covalent bonds. Consequently, the energetic and dynamical factors affecting this competition are investigated.

Experimental Section

In this experiment, dimers of OCS and CS₂ were created by supersonic expansions of neat samples. The composition of the expansions was estimated by using electron impact ionization. The photochemistry of the dimers was then probed via resonance-enhanced multiphoton ionization (REMPI) techniques.

OCS was obtained from Matheson Gas Products and used without further purification. Reagent gas CS₂ was obtained from Fisher Scientific and used after outgassing by pumping on a small sample of the liquid. Stagnation pressures from 20 to 200 Torr of OCS and CS₂ were expanded through a pulsed nozzle (General Valve) with a 50-μm-diameter orifice. The driving pulse to the nozzle had a pulse width of 160 μs but resulted in actual pulse widths on the order of 1 ms as measured by electron impact (EI). The repetition rate of the nozzle was 10 Hz, resulting in an average chamber background pressure of 1 × 10⁻⁵ Torr when 200-Torr stagnation pressure was used. The nozzle was located 2.75 cm (550 nozzle diameters) from the entrance of the ionization region and was directed along the axis defined by the ionization region, a set of ion optics, the quadrupole mass filter, and the detector. The supersonic beam is fully expanded when it reaches the ionization region.

In the electron impact ionization experiments, the molecular beam was bombarded with electrons produced by two tungsten filaments located directly above and below the beam axis in the center of the ionization region. The electron energy was chosen to be 25 eV for the following reasons: (1) Lower electron energies produced much smaller signals due to a decrease in the ionization cross section. (2) Larger electron energies resulted in extensive fragmentation of the ions. (3) While the overall signal intensities increased, the ratios (OCS)₂⁺/OCS⁺ and (CS₂)₂⁺/CS₂⁺ were not greatly affected as the electron energy was varied from 12 to 25 eV.

All positive ions formed by EI were subsequently directed into a quadrupole mass filter (Extranuclear 4-270-9) by a set of ion optics. The ionizer and ion optics form a single unit that was manufactured by Extranuclear Corp. (Model 041-2).

Ions transmitted by the quadrupole are detected and amplified by a conversion dynode electron multiplier (De-Tech Model 305A) and a current amplifier (Keithley Model 427). The CDEM has a gain of about 10⁷, and the current amplifier has a variable gain of 10⁴-10⁶ V/A. The output voltage of the current amplifier is then signal averaged for 500-1000 nozzle pulses by a gated integrator (EGG 164) and the averaged signal monitored on a chart recorder. Corrections for contributions to the ionization signal from the background are made by subtracting out any ion signal

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present when the nozzle is closed.

The resonance-enhanced multiphoton ionization experiments were performed using the same apparatus. However, the tungsten filaments were left off because ionization was provided by laser excitation. The REMPI experiments of OCS at 308 nm employed a Lambda Physik EMG-101 excimer laser operating on the XeCl excimer with pulse energies from 2 to 8 mJ. A Lumonics TE-861T-4 excimer laser operating on the ArF excimer at 193 nm was used in the REMPI experiments of CS₂, using pulse energies from 0.03 to 0.8 mJ. The output from the appropriate laser was directed along a path perpendicular to the molecular beam and focused with a 25-cm focal length lens into the center of the ionization region of the ionizer where it intersected the molecular beam. Ion collection was identical with that used in the above EI experiments. The entire chamber was pumped by a single liquid nitrogen trapped 6-in. diffusion pump.

Results

A. EI Mass Spectra. Electron impact ionization mass spectra for OCS and CS₂ were obtained at 25 eV with stagnation pressures ranging from 20 to 200 Torr of neat sample. These nozzle conditions are identical with those used in the later REMPI experiments, and the results are used in the characterization of the molecular beam. The EI data for OCS and CS₂ are available as supplementary material. (See paragraph at end of paper regarding supplementary material.)

OCS. The largest percentage of the total ion signal comes from OCS⁺. Under the most favorable clustering conditions, (OCS)₂⁺ accounts for 0.05% of the total ion signal, while the stronger, S₂⁺ signal accounts for 7.5%. The sum of the ion signals for all daughter ions of (OCS)_n⁺ (*n* > 2) represents less than 0.01% of the total ion signal. While all of the observed ion signals are seen to increase with increasing stagnation pressure, they do not all do so in a linear fashion. The OCS⁺ and CS⁺ signals increase much less than linearly over the pressure range employed. CO⁺ and S⁺ increase almost linearly with pressure and CO⁺ being more sensitive to pressure than S⁺. The remaining ions observed are all daughters of (OCS)_n⁺ (*n* > 1) cluster ions and increase dramatically with pressure.

CS₂. The largest ion signal observed under all expansion conditions is that of the parent, CS₂⁺. When 200-Torr stagnation pressure is used, (CS₂)₂⁺ accounts for 0.3% of the total ion signal, while S₂⁺ supplies 4.5%. Here again, all ion signal intensities are seen to increase with increasing stagnation pressure, with the largest percentages of the total ion signal coming from CS₂⁺, S⁺, and CS⁺. At higher pressures a significant number of ions are formed by fragmentation of (CS₂)_n⁺ (*n* ≥ 2). However, the intensity of daughter ions of (CS₂)_n⁺ (*n* ≥ 2) is greater than those coming from (CS₂)_n⁺ (*n* ≥ 3), with the sum of the ion signals for all daughter ions of (CS₂)₂⁺ (*n* > 2) accounting for only 0.02% of the total ion signal under the most favorable clustering conditions. As expected, the fragments of these cluster ions display a nonlinear pressure dependence.

Supersonic expansions of OCS and CS₂, both neat and seeded in rare gases, have been previously investigated. OCS seeded in He and expanded from a total pressure of 1300 Torr through a 500-μm-diameter nozzle allowed the observation of OCS clusters up to (OCS)₁₀⁺.¹⁴ The neat expansion of 800 Torr of OCS through a 50-μm nozzle allowed the determination of the ionization potentials of (OCS)_n⁺ (*n* = 1–3) in a photoionization experiment.¹⁵ Similar experiments have been performed on expansions of CS₂. The expansion of 270 Torr of CS₂ in 450 Torr of Ar through a 70-μm nozzle allowed the determination of the ionization potentials of (CS₂)_n⁺ (*n* = 1–5) in a photoionization experiment.¹² Finally, in a recent photofragmentation study of CS₂, 150 Torr of CS₂ seeded in 620 Torr of He and expanded through a 127-μm nozzle produced significant amounts of photoproducts that were attributed to large clusters of CS₂.¹³ In all of these experiments the stagnation partial pressure of OCS or CS₂ was greater than in our expansions. The nozzle diameters used, with one exception, were also larger than ours. As the formation of a bound dimer requires at least a three-body collision, a condition which scales¹⁶

roughly as *P*₀²*D*, the above expansion conditions were such that they favored cluster production more so than do our expansions. The expansion conditions used in the OCS photoionization experiment by Ono et al. are very similar to ours. They expanded 800 Torr of neat OCS through a 50-μm nozzle, where we expand at most 200 Torr of neat OCS through an orifice of identical diameter. They were able to obtain trimers in sufficient quantity with which to measure the ionization potential. As our expansions were performed with significantly lower stagnation pressures, we expect the amount of clustering to be less. This is confirmed by the EI data, where very little signal arises from clusters larger than the dimer. We believe that our expansions consist of mainly monomers and dimers, with the monomer concentration being by far the greater of the two.

B. REMPI. OCS. The results of resonance-enhanced multiphoton ionization (REMPI) of OCS at 154 nm (2 × 308 nm) over a range of pressures and pulse energies are available as supplementary material. The predominant ions observed at any combination of pressure and pulse energy are S⁺ and S₂⁺. The ratio S₂⁺/S⁺ is favored at high pressure and low pulse energy, consistent with S₂ being a result of cluster photodissociation. OCS⁺ is not observed at 20-Torr stagnation pressure, even at the highest pulse energies used where ionization competes more favorably with dissociation. Only at higher pressures where efficient clustering occurs is OCS⁺ observed. Even then, the pulse energy must be sufficiently large so that ionization can compete with dissociation from the ¹Σ⁺ state. The observation of OCS⁺ at high pressures and high pulse energies might be indicative of a significantly longer excited-state lifetime in the cluster than in the monomer.

CO⁺, OCS₂⁺, and S₃⁺ were not observed. A small amount of (OCS)₂⁺ was observed at both 4- and 8-mJ pulse energies with 200-Torr stagnation pressure.

CS₂. The REMPI spectra of CS₂ at 193 nm were obtained over the same pressure range used in the OCS experiment above. Much smaller pulse energies are used here because excitation of CS₂ at 193 nm is very efficient. Laser ionization results from a (1 + 1) process at 193 nm for CS₂, while ionization at 308 nm of OCS occurs via a (2 + 1) process. One-photon absorption cross sections are known to be many orders of magnitude greater than two-photon absorption cross sections.^{17–19} This, along with the greater photon energy, partially accounts for the larger ion signals observed in the above REMPI data of CS₂ compared to OCS.

The largest ion signals observed are those for CS⁺, C⁺, and S⁺, all of which require only monomer precursors. A significant amount of CS₂⁺ is observed even at 20-Torr stagnation pressure and 0.03-mJ pulse energy. This is a tribute to the efficient of the 1 + 1 REMPI process responsible for its production. Note, however, that the CS₂⁺ signal increases with the square of the stagnation pressure when the largest pulse energy is used. As was the case with OCS, the amount of parent ion produced is enhanced when clustering occurs, again an implication of an increased excited-state lifetime in the cluster. Ions with (CS₂)_n⁺ (*n* ≥ 2) precursors show a much more dramatic and nonlinear dependence on stagnation pressure than ions with monomer precursors. A small but measurable amount of CS₃⁺ was observed within 0.8 mJ of 200-Torr stagnation pressure. S₃⁺ was not observed.

The EI data for both OCS and CS₂ showed the parent molecular ion as having the largest signal. This is consistent with the expected result of fragmentation occurring after formation of the molecular ion.²⁰ The amount of fragmentation of the ion depends on the energy difference between the relevant bond energies and the internal energy of the ion, which is itself determined

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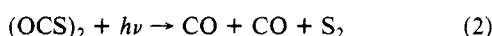
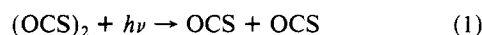
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by the difference between the ionizing electron energy and the ionization potential of the molecule. Ionization potentials are known to decrease with increasing cluster size. The ionization potentials for OCS, (OCS)₂, CS₂, and (CS₂)₂ have been measured in photoionization experiments and determined to be 11.2, 10.46, 10.1, and 9.36 eV, respectively.^{12,15} As all of the EI data were collected at 25 eV, the greatest degree of fragmentation is expected to come from (CS₂)₂⁺. On the other hand, the REMPI data for the two molecules are consistent with the primary process being photodissociation of the neutral, occurring as a result of excitation of the ¹Σ⁺ and ¹B₂(¹Σ_u⁺) states of OCS and CS₂, respectively. Consequently, the neutral photofragments are then ionized and detected.

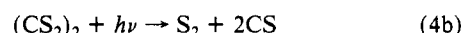
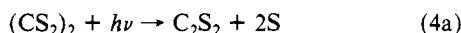
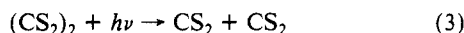
Both the EI and the REMPI data for OCS and CS₂ show a large number of ions that could not have come from fragmentation of their respective monomers. These ions show a dramatic, nonlinear dependence on stagnation pressure, as expected for clusters formed during the expansion. The increase in sample number density alone could not result in the observed pressure dependence of these ion signal intensities.

Discussion

The study presented here explores the photochemistry of dimers of two triatomic molecules, namely, carbonyl sulfide and carbon disulfide. For example, in the case of (OCS)₂, the following reactions are to be considered:



Similarly, for (CS₂)₂, one can write



These processes reflect the possible competition between the photodissociation of the weak van der Waals bond (reactions 1 and 3) and the photochemistry involving covalent bonds (reactions 2 and 4). This competition will depend on the energetics as well as the dynamics involved in the photochemical process. Consequently, we will comparatively discuss these parameters for (OCS)₂ and (CS₂)₂.

In the case of OCS, the linear ¹Σ⁺ state is accessed by using two-photon excitation with 308-nm photons. Excitation of CS₂ is performed with one 193-nm (6.42-eV) photon to the ¹B₂(¹Σ_u⁺) state. The energy deposited in the ¹Σ⁺ state of OCS and the ¹B₂(¹Σ_u⁺) state of CS₂ in this experiment is large compared with all relevant bond energies. Specifically, in (OCS)₂ the C–S bond is 3.71 eV,^{21b} the C–O bond 6.8 eV,^{21c} and the weak OCS–OCS bond only 0.03 eV.^{21a} The excitation energy of 8.05 eV is sufficient to dissociate any of these bonds. In this electronic state it is energetically possible to break both C–S bonds in (OCS)₂. In (CS₂)₂, the first C–S bond of CS₂ is 4.46 eV,^{21f} the second requires 7.8 eV for dissociation,^{21d} while the van der Waals bond is 0.05 eV.^{21e} Excitation at 193 nm makes 6.4 eV available for photodissociation. On the excited ¹B₂(¹Σ_u⁺) surface it is energetically possible to dissociate either the weak van der Waals bond of the dimer or the covalent SC–S bond, or both.

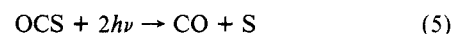
Examination of the relevant bond energies suggests that, in this experiment, energy is deposited in both (OCS)₂ and (CS₂)₂ in excess of the van der Waals bond and of the covalent dissociative C–S bond. On the basis of these energetic arguments, both the covalent (reactions 2 and 4) and van der Waals (reactions 1 and

3) photochemical pathways are possible.

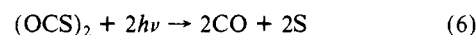
On consideration of the bond energies in the covalent channels 2 and 4, of particular importance is the energy of the covalent bond which is photodissociated (the C–S bond) with the covalent bond formed in this reaction (the S–S bond). In the case of carbonyl sulfide, the C–S bond in OCS is weaker than the S–S bond in S₂. It is probable that photodissociation of the C–S bond in (OCS)₂ leads efficiently to S₂ formation. Recent photodissociation experiments on clusters of OCS in the 222–248-nm region reported significant amounts of S₂ production. Houston et al. have shown that, in this region, photodissociation of small clusters of OCS leads to the production S₂ in both the X³Σ_g[−] and a¹Δ_g states.^{11,14} van Veen, Das, and Bersohn have provided evidence that this S₂ production takes place through a COS₂ intermediate complex.²² In what follows, we examine the effect of dimer formation on the relative yields of OCS⁺ and S₂⁺ in an attempt to establish the importance of the van der Waals vs covalent photochemical pathways.

Photodissociation of (OCS)₂. The spectroscopy and photochemistry of the linear ¹Σ⁺ state of the OCS monomer have been well-established.^{1–4,11,14,23–26} The transition at 154 nm results in excitation of the symmetric stretch in the excited state, leading to cleavage of the C–S bond to yield CO and S photoproducts with a quantum yield for dissociation of ≈1. The lifetime of this ¹Σ⁺ state is on the order of 1 × 10^{−14} s. The one-photon absorption cross section at 154 nm is ≈3 × 10^{−17} cm². Our experiment relies on the simultaneous absorption of two photons at 308 nm, where we can only estimate the two-photon absorption cross section to be ≈1 × 10^{−50} cm⁴ s.^{17–19}

The largest ion signal observed at all combinations of stagnation pressures and pulse energies is that for S⁺. Even under the most favorable clustering conditions the concentration of OCS monomers far exceeds the dimer concentration. Thus, the major source of S⁺ comes from the three-photon ionization of S (IP 10.4 eV²⁷) produced from

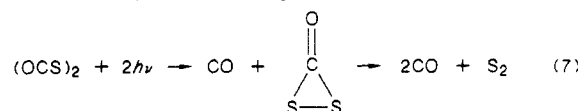


with contribution from



reaction 6 becoming more important with increasing stagnation pressure.

S₂⁺ cannot be produced from OCS monomer and is indicative of covalent chemistry occurring within the dimer, followed by photoionization (9.4 eV) of the S₂ product. This ionization step requires two to three photons, depending on the internal excitation of the S₂ photoproduct. S₂ has been observed in recent photodissociation studies of OCS clusters in the 222–248-nm region.^{15,16} The mechanism responsible for S₂ production is postulated to be²²



where one OCS molecule within the dimer is excited to the ¹Σ⁺ state and dissociates to CO + S. The photolytically generated S atom then reacts with the nearby remaining OCS molecule of the dimer to produce S₂ and CO through an OCS₂ intermediate. The energy necessary for cleavage of the C–S bond (3.71 eV) comes from the exothermic (4.4 eV) S–S bond formation and translational energy of the S atom.

Production of S₂⁺ from ion–molecule reactions of S⁺ with OCS is unlikely due to the collisionless nature of our supersonic beam in the interaction region. The observed dependence of the S⁺/S₂⁺

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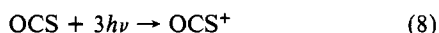
(26) Black, G.; Sharpless, R. L.; Slinger, T. G.; Lorents, D. C. *J. Chem. Phys.* **1975**, *62*, 4272.

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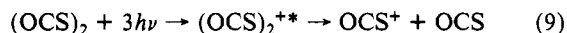
ratio on pulse energy is also inconsistent with an ion-molecule reaction, showing a decrease in the ratio with a decrease in pulse energy. This would not be expected for an ion-molecule reaction as the amount of S₂⁺ produced should be proportional to the amount of S⁺. Finally, an ion-molecule reaction would result in a broadened temporal distribution of the S₂⁺ product, which is not observed.

Fragmentation of (OCS)₂⁺ to yield S₂⁺ is not an important pathway for S₂⁺ production. Dissociation of the C-S bonds in (OCS)₂⁺ would require the absorption of additional photons. This absorption must compete with dissociation of the van der Waals bond where the energy for dissociation already exists in the dimer ion without the need for further absorption.

There are two possible pathways for OCS⁺ production:



and



We only observe OCS⁺ under conditions consistent with reaction 9 at this wavelength. In the first place, OCS⁺ is not observed at any pulse energy when 20-Torr stagnation pressure is used. Second, even when 200-Torr stagnation pressure is used, OCS⁺ is not observed at the lowest pulse energy used. The increase in sample number density alone could not account for the pressure dependence observed. These observations are consistent with an increase in the excited-state lifetime in the dimer. This would allow ionization to compete with dissociation, especially at higher pulse energies. Ionization of the dimer requires 10.46 eV, leaving 1.61 eV of excess energy behind, after the absorption of three photons. This is more than enough to dissociate the dimer ion to OCS + OCS⁺ (0.75 eV).

A trace amount of (OCS)₂⁺ is observed at 200-Torr stagnation pressure and 4- and 8-mJ pulse energies, evidence that even with the excess energy available not all of the OCS₂⁺ dissociates within the 70 μs required for the ion to travel from the interaction region to the detector.

In summary, photoexcitation of the ¹Σ⁺ state of OCS in (OCS)₂ leads to covalent bond chemistry, as evidenced by the observation of S₂⁺, as well as to dissociation of the van der Waals bond, as evidenced by the observation of OCS⁺.

Photodissociation of (CS₂)₂. In the case of (CS₂)₂, the best value available for the C-S bond (4.45 eV) is higher than that of the S-S bond (4.4 eV) in S₂. In this case, CS₂⁺ and C₂S₂⁺ are the significant photoproducts indicative of covalent chemistry occurring within the CS₂ dimer.

The photochemistry of CS₂ monomer at 193 nm has been well-established.^{1-4,12,13,28-30} The energy of a single photon excites the molecule to the bent ¹B₂(¹Σ_u⁺) state where dissociation to CS + S occurs within the lifetime of the excited state, ≈2 × 10⁻¹⁴ s, with a quantum yield for dissociation of ≈1. This transition has an absorption cross section of ≈2 × 10⁻¹⁶ cm² and leads to excitation of the symmetric stretch and bending modes in the excited state.

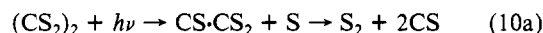
The large concentration of CS₂ monomers and the efficient photochemistry of the ¹B₂(¹Σ_u⁺) state combine to yield large amounts of CS and S. With the photon energy used, 6.42 eV, subsequent ionization of CS (IP 11.7 eV) and S (IP 10.4 eV) is performed with no more than two additional photons. Ionization of CS is further enhanced by resonance of a vibronic state at 193 nm,³¹ explaining its appearance as the largest ion signal observed. Photofragment of CS to C and S, followed by ionization, is efficient and leads to ion production.

CS₂⁺ is observed at all pressures and pulse energies. However, the dependence of the ion signal with pulse energy is very different at 20-Torr than at 200-Torr stagnation pressure. When 20-Torr

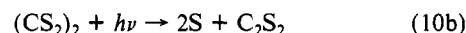
stagnation pressure is used, the magnitude of the CS₂⁺ signal changes by no more than a factor of 2 while the pulse energy is varied from 0.03 to 0.8 mJ. More importantly, the percentage of the total ion signal attributable to CS₂⁺ actually decreases from 2% to 0.4%. Conversely, at 200-Torr stagnation pressure the magnitude of the CS₂⁺ signal increases by a factor of 6 and is responsible for 5% and 8% of the total ion signal at 0.03- and 0.8-mJ pulse energies, respectively. Unlike OCS, ionization of the CS₂ monomer is a significant source of CS₂⁺. When higher stagnation pressure is used, contribution from a mechanism similar to that for OCS in reaction 9 becomes important, especially under high pulse energy conditions. This is exemplified by the strong stagnation pressure dependence of the CS₂⁺ signal when 0.8-mJ pulse energy was used.

Covalent chemistry occurring within the CS₂ dimer is evident in observed ion signals corresponding to S₂⁺ and C₂S₂⁺, which show a strong dependence on stagnation pressure. Formation of S₂ from the photodissociation of the CS₂ monomer is very unlikely. C₂S₂, on the other hand, is unambiguously the result of cluster photochemistry.

Two unlikely mechanisms for the production of S₂ and C₂S₂ from (CS₂)₂ are



and



The energy of a single photon (6.42 eV) is all that is required to cleave the C-S bond (4.45 eV) and initiate the above reaction. The energy necessary for cleavage of the second C-S bond is supplied by the exothermic S-S bond formation (4.4 eV) and translational energy of the photolytically generated S atom.

The parent dimer ion, (CS₂)₂⁺, is never observed. After ionization occurs (9.36 eV), a sufficient amount of the excess energy (3.48 eV) in the dimer ion leads to dissociation of the van der Waals bond (0.76 eV).

Analysis of the photofragmentation of (OCS)₂ and (CS₂)₂ indicates that both the covalent and van der Waals bond chemistry occur efficiently. It is not possible to get accurate quantum yields from our experiments because of the difficulty in obtaining accurate ionization cross sections for each species involved. However, fragments produced by both pathways are efficiently detected, suggesting a contribution from the covalent channel far beyond that expected statistically on the basis of the bond dissociation energies.

While a direct comparison between the OCS and CS₂ REMPI data cannot be made due to large differences in absorption cross sections, a qualitative comparison can be made on the relative amounts of observed dimer fragments from (OCS)₂ and (CS₂)₂. In OCS, the percentage of the total ion signal due to S₂⁺ varies from 5% to 17%. On the other hand, the combined ion signals of S₂⁺ and C₂S₂⁺ from CS₂ never make up more than 1% of the total ion signal. The parent ion of the dimer is never observed from CS₂ at 193 nm, but (OCS)₂⁺ is observed at 308 nm. Finally, the intensity of S₂⁺ is always greater than that for OCS⁺ in the REMPI data for OCS, while the CS₂⁺ signal is always larger than S₂⁺ and C₂S₂⁺ from REMPI of CS₂. The data suggest that the van der Waals bond in (CS₂)₂ is more prone to dissociation in the ¹B₂(¹Σ_u⁺) state than the equivalent bond in (OCS)₂ is in the ¹Σ⁺ state. This conclusion can be rationalized as follows:

1. Independent studies provide information about the time scale for photodissociation in the ¹Σ⁺ state of OCS and the ¹B₂(¹Σ_u⁺) state of CS₂ from the spectroscopy of these jet-cooled molecules. When the sample is cooled to low temperatures, the homogeneous line width can be obtained in favorable cases where the spectra are not congested. Such studies have been performed for both of the molecules investigated here,^{24,28} and from the homogeneous line width at the excitation energy employed here one obtains a lifetime of 0.01 and 0.02 ps for OCS and CS₂, respectively. These estimates are based on the very reasonable assumption that the major nonradiative channel is photodissociation, which is known to occur with a quantum yield of ≈1. The lifetime of the ¹B₂(¹Σ_u⁺)

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state in CS₂ is approximately twice as long as the ¹Σ⁺ state in OCS, allowing for a longer period of time for energy to flow into a mode responsible for dissociation of the weak bond in (CS₂)₂ before covalent dissociation takes place.

2. The exchange of a S-S bond for a C-S bond is exothermic in OCS by 0.7 eV but is endothermic by 0.05 in CS₂. If the dimer covalent chemistry takes place through a mechanism as presented in reactions 7 and 10, then on the basis of the above energetics covalent chemistry in the CS₂ dimer would be less favorable than in the OCS dimer.

3. The geometry of the dimers and the vibrational excitation in the excited states may play an important role as well. For example, the transition to the linear ¹Σ⁺ state of OCS leads to excitation of the symmetric stretch. Given the proposed "staggered parallel" geometry of the OCS dimer,¹⁵ this mode would not be disruptive to the van der Waals bond. In CS₂ on the other hand, the transition to the bent ¹B₂(¹Σ_u⁺) state leads to excitation in both the symmetric stretch and bending modes. Given the proposed linear geometry of the CS₂ dimer,¹⁵ both of these modes could be considered disruptive to the weak van der Waals bond.

It is obvious from these results that photochemistry competes efficiently with energy transfer and that the covalent bond dissociates on a time scale shorter than that required for energy flow to complete randomization.

Conclusions

In summary, the photodissociation of dimers of OCS and CS₂, prepared in supersonic expansions, was investigated by using REMPI techniques. The results indicate that a significant amount of covalent chemistry occurs in the dimer, even though the van der Waals bond is much weaker. These results are consistent with recent studies of OCS cluster photodissociation¹⁴ in the ¹Δ state at 222 nm and with evidence of CS₂ cluster photodissociation¹³ of the ¹B₂(¹Σ_u⁺) state at 193 nm. Comparatively more covalent chemistry is found to occur in the OCS dimer than in the CS₂ dimer. This difference is presumed to be due to the difference in the energetics involved as well as the difference in excited-state dynamics for the two systems.

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Registry No. (OCS)₂, 463-58-1; (CS₂)₂, 75-15-0; S₂, 23550-45-0; C₂S₂, 83917-77-5.

Supplementary Material Available: Tables of relative signal intensities from electron impact ionization of OCS and CS₂ (4 pages). Ordering information is given on any current masthead page.

HOD Spectroscopy and Photodissociation Dynamics: Selectivity in OH/OD Bond Breaking

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We present a study of HOD photodissociation dynamics in the first electronically excited state for transitions originating from the ground as well as a few vibrationally excited states. The electronic absorption as well as emission spectra are calculated for the first time by using a quantum mechanical time-dependent formalism in the two stretching coordinates, and they are compared with those of H₂O and D₂O. Good agreement between the calculated and experimental emission spectra is observed. Nuclear dynamics on *both* the ground and excited states are examined. A connection between the observed spectra and the photodissociation reaction is made. Branching ratios (H + OD)/(D + OH) as a function of laser frequency are obtained. There is generally a higher probability to break the OH bond than the OD bond, but to achieve selectivity in bond breaking to yield *exclusively* one of the two possible products requires a two-photon (IR + UV) scheme. Such a scheme is designed and presented.

I. Introduction

The spectroscopy and photodissociation dynamics of water in its first absorption band have been the subject of many recent investigations. The first electronically excited state, the ¹Δ state, is known to be repulsive, and the molecule dissociates directly to give H(2S) + OH(2Π). The water molecule presents a unique situation in which only one Born-Oppenheimer electronically excited state needs to be considered and no curve crossing is involved. Moreover, the small size of this molecule makes it feasible to calculate the relevant potential energy surfaces (PES) from first principles. The *ab initio* PES for the ¹Δ state has been calculated by Palma et al.¹ and has since been used in several dynamical and spectroscopic studies.²⁻⁶ Schinke and co-workers^{2,4}

have calculated the absorption spectrum and photodissociation final product-state distributions, treating all three vibrational modes, and obtained good agreement with experimental results.^{7,8} We have very recently used the same surface to study the absorption³ and emission⁵ spectra. Our study was done in the two stretch coordinates while keeping the bend fixed at the ground-state equilibrium geometry. We obtained excellent agreement with the absorption spectrum calculated by Schinke et al., which suggests that the photodissociation can to a good approximation be described in the two stretch coordinates. This is supported by the

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