Photoinduced Nucleation of CS_2 Vapor in a Flow Photochemical Reactor

Honghai He and Richard H. Heist*

Department of Chemical Engineering, University of Rochester, Rochester, New York 14627-0166

Received: November 18, 1996; In Final Form: June 11, 1997[⊗]

Photoinduced nucleation (PIN) experiments using CS_2 and CS_2/ethanol vapors have been carried out in a flow photochemical reactor. Following ultraviolet irradiation of the CS_2-containing vapors, photoinduced nucleated particles were captured and characterized using mass spectrometry and Raman spectroscopy. Results of the analysis confirm the presence of S_8 molecules in the particles produced by PIN of CS_2 vapor. Additional results consistent with these data but involving PIN of CS_2 in supersaturated 1-propanol also from this laboratory are reviewed. The role of sulfur in the PIN mechanism is discussed in the context of these particle characterization results and the gas-phase photochemistry of CS_2 and is shown to be consistent with an earlier description of CS_2 PIN from this laboratory.

Introduction

Research involving carbon disulfide has recently been reported involving applications in aerosol formation,[1−3] chemical vapor deposition of novel electronic materials, such as C_3S,[4] growth of light-emitting and electroluminescent ZnS thin films,[5] and plasma-polymerized thin film rechargable batteries.[6] Most of these applications involve excitation (usually optical) of the CS_2 followed by particulate formation. While gas-phase photoinduced nucleation (PIN) of CS_2 has been of considerable interest for some time,[7] the formation of particles by PIN, in general, has given rise to considerable interest in the mechanism of formation of these particles and in the identification of the nucleated products (to aid in the understanding of the PIN process).

In the specific case of CS_2, systems of interest involve either pure (supersaturated or undersaturated) CS_2 vapor or CS_2 vapor mixed with a second (supersaturated or undersaturated host) vapor (e.g., ethanol, 1-propanol), which are irradiated with light of an appropriate wavelength (usually ultraviolet) and intensity. We note that in the systems employing supersaturated vapors, the supersaturation required for PIN is generally significantly lower than that required for homogeneous nucleation (the so-called critical supersaturation). Although solid products are known to form during the irradiation of undersaturated CS_2 vapor,[8] the mechanism of the process is not clear.[9−13] Understanding the role of CS_2 in the PIN process is important to our better understanding the role of CS_2 in materials and aerosol applications.

Investigations involving PIN in thermal diffusion cloud chambers (TDCC) were, by and large, first reported in the late 1970s. The observation of PIN in the TDCC led to attempts (largely phenomenological) to explain the mechanism of PIN that often involved postulating the existence of exotic intermediates, such as long-lived, host-stabilized, photoaffected species[13a] or massive clusters with PIN intermediates with lifetimes on the order of minutes.[13b] The great interest of the nucleation community in PIN at the time led to research from our laboratory in which we carried out a careful study of CS_2 PIN in the diffusion cloud chamber and came to the conclusion that the observed PIN could be entirely explained by postulating the photochemical production of sulfur followed by the nucleation of sulfur to produce nucleation sites for the supersaturated host vapor.[10] We were able to apply this general model to PIN of supersaturated CS_2 and also to PIN of CS_2 in other supersaturated vapors. There was (and still is) considerable controversy with this model[13c] since the difficulty with all such research involving the diffusion cloud chamber (even to this day) arises due to the fact that the diffusion cloud chamber is a closed system. All efforts to study the PIN process were necessarily phenomenologically based and did not allow isolation (and subsequent identification) of the small amounts of PIN products. While results of photochemical studies of undersaturated CS_2 are available in the literature and clearly indicate sulfur formation, it was argued that these investigations, carried out under conditions quite distinct from those within the diffusion cloud chamber, were not necessarily proof of the role of sulfur in the PIN process. Recent examples of such photochemical studies include Matsuzaki et al.'s observation of sulfur polymer S_n ($n = 3-8$) in aerosol formed from N_2 laser irradiated CS_2 vapor at pressures of 50−100 Torr[11] and Desai et al. using TOF mass spectrometry to identify S_m^+ ($m \leq 6$) present in the van der Waals clusters in a molecular beam at low pressures when CS_2 is irradiated by 239.53 nm light.[9] Clearly, these studies support the role of polymers of elemental sulfur in the PIN of CS_2 vapor as originally proposed by Kalisky and Heist,[10] but the criticism remains that the conditions of these investigations do not correspond to those commonly found within the diffusion cloud chamber.

The objective of a recent investigation from our laboratory which we report here was to capture and characterize particles formed during the PIN of CS_2 vapor under conditions closer to those found within the diffusion cloud chamber in order to clearly demonstrate the presence of sulfur in the PIN process involving CS_2 and attempt to resolve the questions pertaining to PIN of CS_2 that have existed since the original investigations.[10,13] To accomplish this objective, we designed a flow photochemical reactor to produce particles by PIN of CS_2 vapor (neat or in the presence of other vapors, e.g. ethanol) and to permit the subsequent capture of these generated particles for chemical analysis. We report experimental results of our investigations involving both CS_2 vapor and a variety of CS_2/ethanol vapor mixtures that address the characterization of these PIN-generated particles. We also review, briefly, results (reported elsewhere, see below) of a similar investigation from our laboratory involving PIN of CS_2 in a flow diffusion cloud chamber in which supersaturated 1-propanol vapor was the host

---

* To whom all correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

S1089-5639(96)03842-X CCC: $14.00 © 1997 American Chemical Society

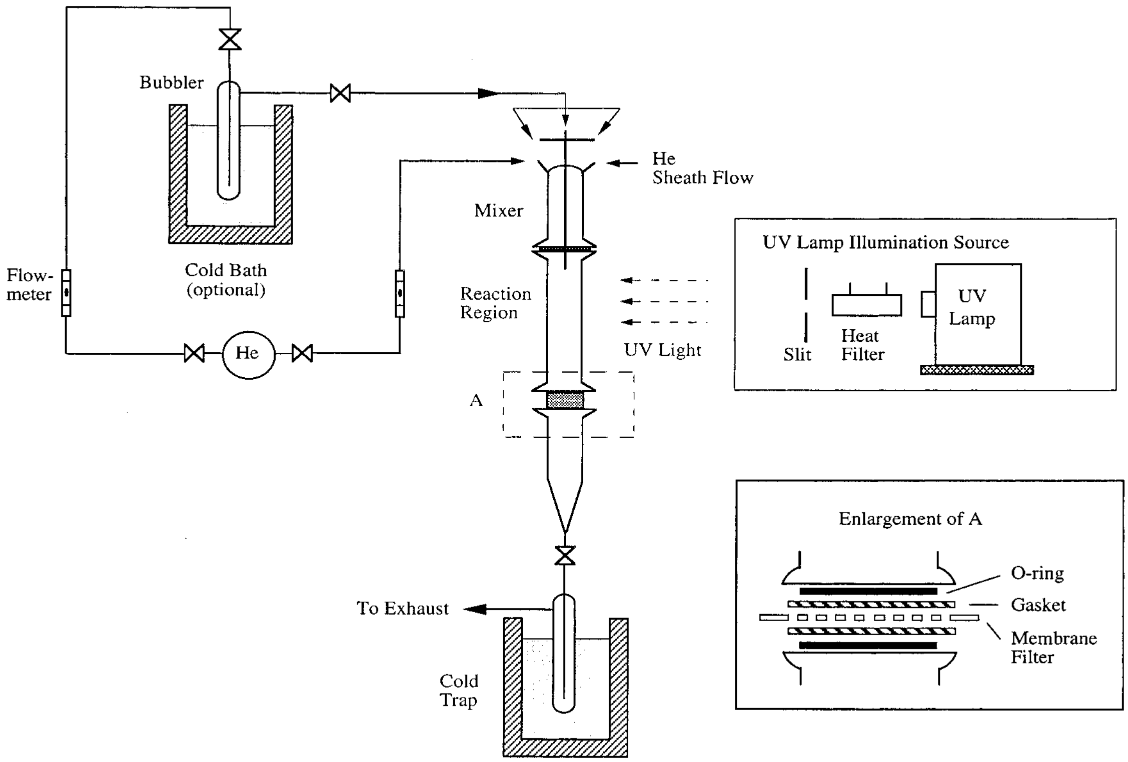


Figure 1. Schematic description of the flow photochemical reactor (FPR) experiment setup.

vapor. All these results will be shown to support the sulfur formation PIN mechanism proposed by Kalisky and Heist.[10]

Experiment Description

A flow photochemical reactor (FPR) system was designed and constructed to allow production and collection of photonucleated products for subsequent chemical analysis. The FPR system, shown schematically in Figure 1, consists of a gas stream mixer, a quartz flow reactor, a bubbler, a gas-handling line, a background gas cylinder (helium for these investigations) with appropriate flow controls, and an exhaust trap. The setup, except for the gas cylinder and flow control elements, was assembled and maintained in a ventilation hood and kept at ambient temperature. The function of the gas flow mixer was to produce a core flow stream (system gases) surrounded by a sheath flow stream (background gas). The gas mixer contains two concentric Pyrex tubes (10.4 mm i.d. and 20 mm i.d., respectively) and five flow ports (6 mm i.d. Pyrex tubing) for gas/vapor input. The gas mixer is connected to the quartz flow reactor using O-ring joints and a FETFE O-ring with pinch clamps. The quartz flow reactor is 50 mm in length with a 20 mm i.d. and with an O-ring joint fused to each end. The mixer and reactor assembly are mounted to produce a vertical flow. A Nucleopore polycarbonate membrane filter (0.1 or 0.015 μm pore size) is mounted in the cross-section plane of the flow axis at the lower end of the flow reactor and held in place by the O-ring and O-ring joints.

The system vapor (CS_2 or CS_2/ethanol) is introduced into the flow stream by bubbling helium through a glass frit into CS_2 or CS_2/ethanol liquid in the bubbler tube. This mixture of working vapor and helium enters the gas mixer via two symmetrically positioned T-junctions and flows into the center region (core) of the quartz tube reactor at a velocity in the range 0.5−1.0 cm/s. The sheath flow of pure helium flowing at the same velocity as the core enters the gas mixer via two other symmetrically positioned ports and surrounds the core. The purpose of maintaining a core and sheath flow configuration is to minimize wall deposition. The quartz flow reactor section has a 3 cm by 2 cm irradiation area and is irradiated using a high-pressure xenon arc lamp (Schoeffel, 1000 W), which provides a broad UV irradiance of optical wavelengths down to about 190 nm. Carbon disulfide has strong absorption in the 190−210 nm range and moderately strong absorption bands in the 280−360 nm range. The output of this arc lamp extends over all these bands, although the intensity below 200 nm is small. The flow rates used in our investigations produced a steady, laminar flow with a residence time in the irradiated zone ranging from 2 to 6 s. PIN that occurs within the irradiation region is followed by rapid growth to micrometer-size (visible) particles that are entrained within the laminar flow. Particles generated in the flow are collected as the stream flows through the membrane filter. We note that the core and sheath flow arrangement was generally successful in avoiding wall deposits, although on occasion we still observed a small amount of deposition on the wall, particularly during experiments requiring long irradiation times. We also note that it took a significant amount of time to produce an amount of sample sufficient for subsequent characterization. When we used dilute solutions of CS_2 in ethanol, we often had to collect samples for up to 12 h at a time.

In this investigation we used as our working vapors pure CS_2, pure ethanol, and a series of CS_2/ethanol vapor mixtures prepared from solutions containing 1%, 10%, 30%, and 50% CS_2 by volume. Reagent carbon disulfide (J. T. Baker, 99.95%), absolute ethanol (EM Science, 99%), and research grade helium (Air Products, 99.9999%) were used in this investigation with no attempt at further purification. The entire experiment system was purged thoroughly with background gas prior to each experiment to minimize atmospheric contamination.

The collected particle samples were characterized ex situ using field desorption mass spectrometry (FDMS), scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDXA), and Raman spectroscopy. Raman spectroscopy was

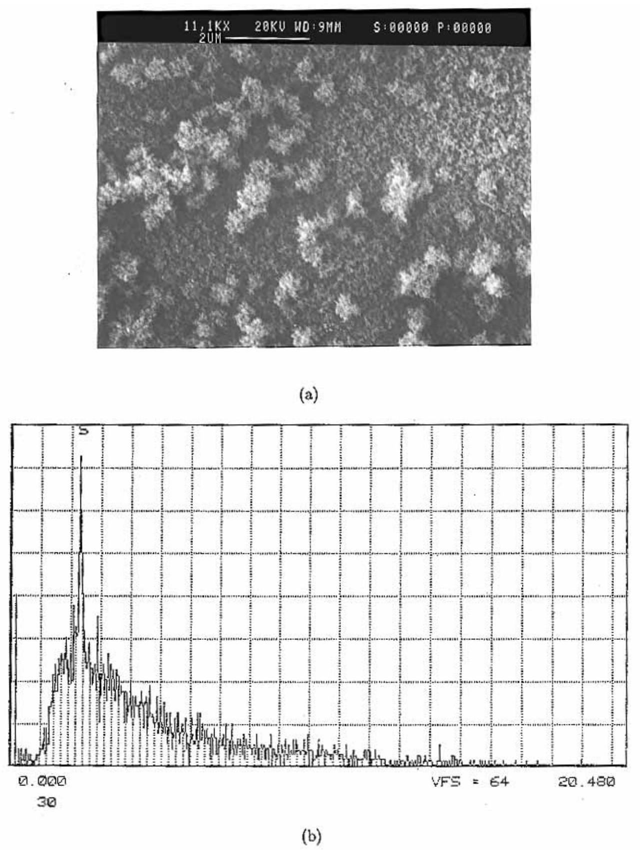


Figure 2. (a) SEM micrograph of submicrometer particles produced in the FPR by PIN of CS_2 vapor during continuous UV irradiation; (b) EDXA spectrum of PIN particles indicating the abundant presence of sulfur.

chosen because the sulfur double bond vibrational frequency is Raman active.

The experimental arrangement for the PIN of CS_2 in a flow diffusion cloud chamber has been described elsewhere, and appropriate results of that investigation will be reviewed below.

Results and Discussion

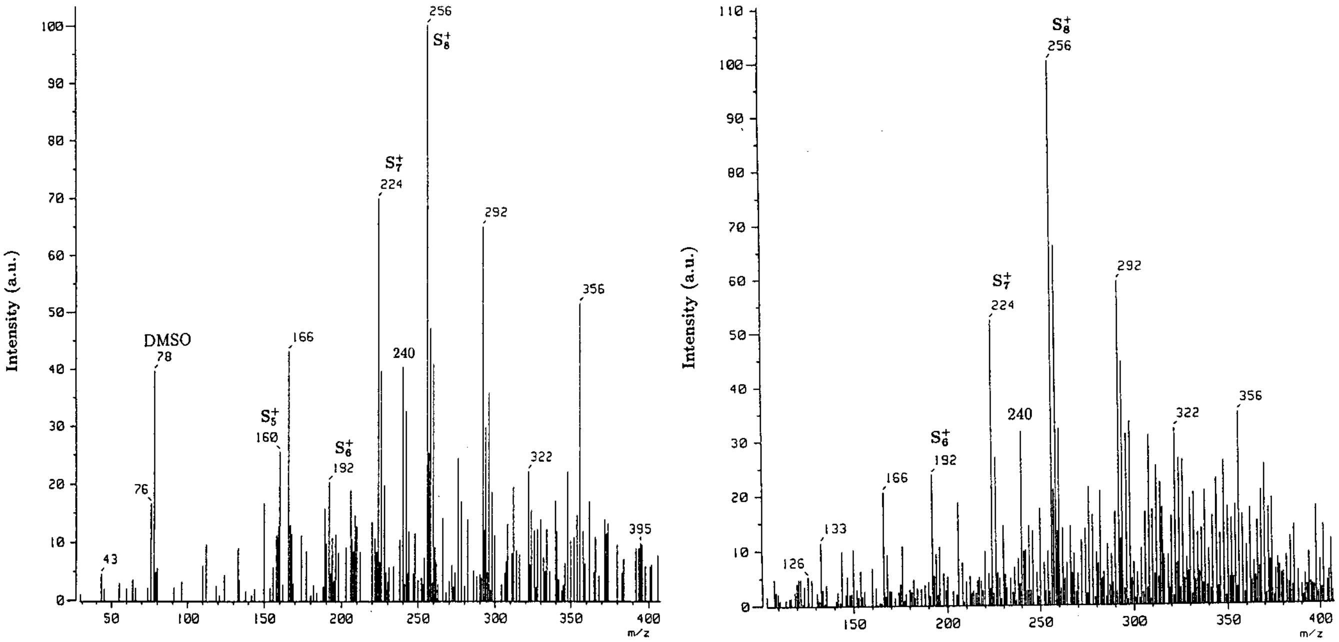
During all our experiments, we were unable to detect particle formation without using UV excitation of the gas/vapor flow and without using CS_2 in the flow stream. When visible, the particles collected on the membrane filters appeared to the eye as light yellow to dark yellow/brownish deposits against the white background of the filter. A typical scanning electron microscope (SEM) micrograph shown in Figure 2a illustrates the roughly 1 μm size aggregates deposited on the filter during a PIN experiment with pure CS_2 vapor. These aggregates appear to be composed of large numbers of ultrafine sulfur particles produced by the PIN. A repesentative EDXA spectrum, shown in Figure 2b, clearly indicates that the dominant chemical component of these particles is sulfur. The FDMS spectra in Figure 3 provide additional, confirmatory fingerprint details.

Figure 3 shows a typical mass spectrum of particles formed during gas-phase PIN of pure CS_2 vapor in helium. Figure 3b shows a typical mass spectrum of particles formed during gas-phase PIN of a 10% CS_2 in ethanol mixture. The two spectra present similar features. The S_8^+ (m/z 256) peak clearly dominates both spectra. Mass spectra lines for S_5^+ (m/z 160), S_6^+ (m/z 192), and S_7^+ (m/z 224) can also be assigned with confidence. Both spectra are consistent with the mass spectrum of elemental sulfur.[14] Matsuzaki et al.[11] performed mass spectrometry on the sedimental materials formed following N_2 laser irradiation of CS_2 vapor. Their mass spectrum showed lines analogous to those shown in Figure 3, which they also assigned to S_5, S_6, S_7, and S_8. The general appearance of the particles collected during our experiments is consistent with the appearance of solid S_8, S_7 (both yellow), and S_6 (orange yellow).[15,16] Other lines (e.g., with m/z's of 166, 240, 292, 308, 322, and 356) in the mass spectra (Figure 3) can be assigned to various C−S moieties of the form C_xS_y (e.g., m/z 308 for the $(CS)_7^+$ species). This is also consistent with an earlier analysis of results of continuous UV irradiation of CS_2 to form a mixture of photopolymer including $(C_3S_2)_x$.[17] These various spectroscopic studies suggest that the formation of C_xS_y moieties and CS polymerization, in addition to S_8 formation, may also play a role in the PIN (and/or subsequent growth of nucleated particles) of CS_2.[18,19]

Raman spectroscopy was used to analyze a number of our particle samples. In Figure 4, we show a typical Raman spectrum of particles formed by PIN of pure CS_2 vapor during our investigation. The spectrum features three Raman peaks at 155, 221, and 474 cm^{-1}, respectively. These peaks match the literature Raman spectrum of elemental sulfur[20,21] and are consistent with the presence of S_8 molecules in these nucleated particles. Interestingly, these three Raman peaks match those obtained from Raman spectra of elemental sulfur at elevated temperatures, e.g. > 258 °C,[21,22] which may further suggest the polymeric nature, e.g. $S_n + S_8$, of the sulfur in the nucleated particles.[20,22] Our Raman spectrum supports the suggestion made by Matsuzaki et al.,[11] based on their Raman and infrared spectroscopic studies, that S_8 was present in the sedimental materials formed during their investigations of N_2 laser irradiation of CS_2 vapor. The fact that our Raman spectrum matches that of sulfur at elevated temperatures may indicate a "freezing in" of a nonequilibrium structure as the vapor nucleates (or condenses) from the vapor to a liquidlike phase which is unable to relax to the more stable equilibrium structure representative of the low-temperature form of solid sulfur.

Both the mass spectrum in Figure 3 and the Raman spectrum in Figure 4 strongly suggest the presence of S_8 molecules in particles formed during PIN of CS_2 and CS_2/ethanol vapor mixtures. The analysis of these particles provides direct spectroscopic evidence that polymeric sulfur and C_xS_y moieties are, indeed, involved in the PIN of CS_2 vapor. These conclusions support the PIN model proposed by Kalisky and Heist that suggested sulfur and sulfur clusters play a key role in gas-phase PIN of pure CS_2 and CS_2/ethanol mixtures.[10]

Additional experiments have been carried out in our laboratory, but reported elsewhere, involving PIN of CS_2 vapor in supersaturated 1-propanol vapor,[23] again, the objective being to investigate PIN of CS_2 under conditions consistent with those in the TDCC studies. A flow diffusion cloud chamber was used to produce supersaturated alcohol vapor in the presence of dilute CS_2 vapor (using 1% and 25% CS_2 solutions by liquid volume). Helium was used as a background gas in these experiments. PIN of CS_2 was observed using the same 1000 W Xe excitation source. The resulting 1-propanol nucleated droplets containing the PIN precursor were collected using a filter arrangement similar to that described above. The rate of PIN was maintained low (e.g. 5−20 drops/cm^3/s) to avoid 1-propanol vapor depletion. Quite long collection times were required due to the small rate of PIN and the fact that the amount of photonucleated solid in any one aerosol particle collected by the filter was small. Following the optical excitation and particle collection, the filter was removed and dried and the collected particles were analyzed using EDXA spectroscopy. Results of the analysis of those PIN products were entirely consistent with results reported here.[23]



(a)

(b)

Figure 3. FDMS spectrum of particles formed during gas-phase PIN of (a) pure CS_2 and (b) CS_2/ethanol vapor mixture formed from solution of 10% CS_2 in ethanol. In both cases, S_8^+ species are found to be most abundant along with S_6^+ and S_7^+. These spectra are consistent with the mass spectrum of elemental sulfur[14] and mass spectra of aerosols formed during N_2 laser irradiated CS_2 vapor.[11] $C_xS_y^+$ ions also appear to be present in the spectra. See text for details.

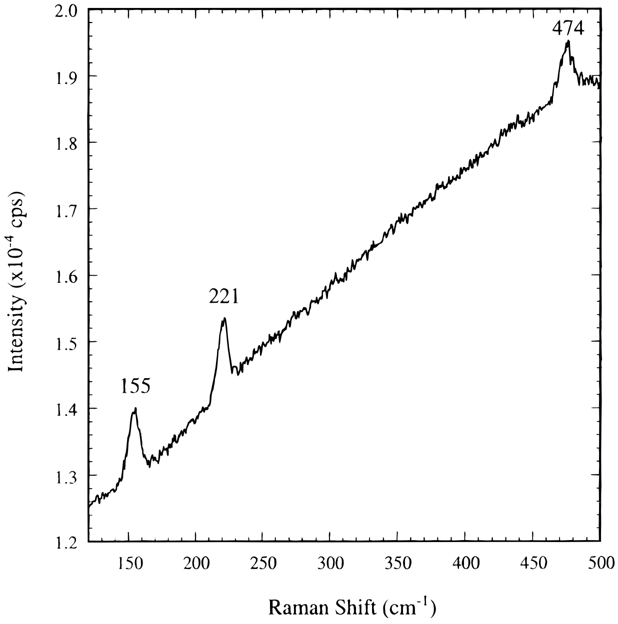


Figure 4. Raman spectrum of particles formed during gas-phase PIN of pure CS_2. The Raman shifts match those of pure sulfur obtained at elevated temperatures. See text for details.

Although photoinduced nucleation of CS_2 has been actively investigated for some time, the mechanism underlying the nucleation process is still not clear. Previously, investigators used phenomenological modeling to correlate nucleation delay time data and nucleation rate measurements obtained from TDCC.[10,13,24] Although Kalisky and Heist[10] proposed that sulfur formation was responsible for PIN of CS_2, other investigators ruled out sulfur as playing an important role because of the low concentration of CS_2 used in their experiments and because of results of their diffusion-based photonucleator size calculations.[13,24] To date there is still controversy over the mechanism of the CS_2 PIN, due in large part to the fact that products of the PIN process under conditions similar to that in the diffusion cloud chamber have never been captured and analyzed. The photochemical literature[18] tends to support the contention that, under optical excitation (laser, flashlamp, etc.), CS_2 molecules in the vapor phase are excited and dissociate into S, CS, and S_2 (as determined by time-of-flight mass spectrometry, vacuum UV spectroscopy, and optical absorption studies).[9,25−27] On the basis of the results of our investigation, it appears increasingly reasonable to suggest that nucleated particles formed during PIN of CS_2 contain sulfur (and probably C_xS_y moieties, as well). While the detailed, elementary mechanism is still not clear (and not absolutely necessary to achieve the objective of this investigation), the results presented here, along with earlier results from our other investigations, provide strong support for the Kalisky and Heist model for PIN in CS_2 vapor.

Concluding Remarks

In summary, the results of our investigations support the following description: PIN of CS_2 begins with the UV dissociation of CS_2. The photodissociation products, i.e., S, CS, and S_2, of this process serve as precursors for the subsequent production of (primarly) S_8 and C_xS_y moieties. This step is followed by nucleation and growth of these vapors into clusters. If a second condensable (host) vapor (e.g., supersaturated ethanol, 1-propanol, or CS_2) is present, these nucleated clusters induce host vapor (heterogeneous) nucleation and growth at supersaturations below the host vapor critical supersaturation. In this sense, we use the host vapor nucleation and growth to detect the presence of the nucleated sulfur particles. If a second, supersaturated host vapor is not present or if the second vapor is not supersaturated, the nucleated sulfur clusters continue to grow (to macroscopic size if sufficient material is available) by sulfur (and possibly C_xS_y) addition. These results are consistent with and support the earlier phenomenological model proposed by Kalisky and Heist to explain results of PIN studies using a thermal diffusion cloud chamber.[10]

Acknowledgment. We thank Mr. Xinye Liu of the University of Rochester Chemistry Department for assisting with the

Raman spectroscopy measurements. We acknowledge the assistance of Mr. Brian McIntyre of the University of Rochester School of Engineering and Applied Sciences Electron Microscopy Laboratory during the SEM studies. We also acknowledge the help of Dr. Thomas Jackson of Eastman Kodak with the mass spectrometry measurements. The financial support of the Department of Chemical Engineering of the University of Rochester is acknowledged.

References and Notes

(1) Gingell, J. M.; Mason, N. J. Sutherland, J.; Taylor, M. *Meas. Sci. Technol.* **1994**, *5*, 1281.

(2) Vlahoyannis, Y. P.; Patsilnakou, E.; Fotakis, C.; Stockdale, J. A. D. *Radiat. Phys. Chem.* **1990**, *36*, 523.

(3) Matsuzaki, A.; Morita, H.; Hamada, Y. *Chem. Phys. Lett.* **1992**, *190*, 331.

(4) Spiro, C. L.; Banholzer, W. F.; McAtee, D. S. *Thin Solid Films* **1992**, *220*, 122.

(5) Takata, S.; Minama, T.; Miyata, T.; Nanto, H. (a) *Jpn. J. Appl. Phys.* **1988**, *27*, L247; (b) *J. Cryst. Growth* **1988**, *86*, 257.

(6) Sadhir, R. K.; Schoch, K. F., Jr. *Chem. Mater.* **1996**, *8*, 1281.

(7) Heist, R. H.; He, H. *J. Phys. Chem. Ref. Data* **1994**, *23*, 781.

(8) Sorgo, M. D.; Yarwood, A. J.; Strausz, O. P.; Gunning, H. E. *Can. J. Chem.* **1965**, *43*, 1886.

(9) Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Phys. Chem.* **1995**, *99*, 1786.

(10) Kalisky, O.; Heist, R. H. *J. Chem. Phys.* **1985**, *83*, 3668.

(11) Matsuzaki, A.; Hamada, Y.; Morita, H.; Matsuzaki, T. *Chem. Phys. Lett.* **1992**, *190*, 337.

(12) Colman, J. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 11270.

(13) (a) Katz, J. L.; McLaughlin, T.; Wen, F. C. *J. Chem. Phys.* **1981**, *75*, 1459. (b) Chen, C. C.; Wen, F. C.; Katz, J. L. *J. Chem. Phys.* **1986**, *84*, 3843. (c) Chen, C. C.; Katz, J. L. *J. Chem. Phys.* **1988**, *88*, 5007.

(14) Grupe, Von K.-H.; Hellwig, K.; Kolditz, L. *Z. Phys. Chem. Leipzig* **1974**, *255*, 1015.

(15) Voronkov, M. G.; Vyazankin, N. S.; Deryagina, E. N.; Nakhmanovich, A. S.; Usov, V. A. *Reactions of Sulfur with Organic Compounds*; Consultants Bureau: New York, 1986; Chapter 1.

(16) *Dictionary of Inorganic Compounds*; Chapman & Hall: London, 1992; Vol. 3.

(17) Cataldo, F. *Inorg. Chim. Acta* **1995**, *232*, 27.

(18) Gattow, G.; Behrendt, W. *Carbon Sulfides and Their Inorganic and Complex Chemistry*; George Thieme: Stuttgart, 1977.

(19) Moltzen, E. K.; Klabunde, K. J.; Senning, A. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 391.

(20) Grasselli, J. G.; Snavely, M. K.; Bulkin, B. J. *Chemical Applications of Raman Spectroscopy*; John Wiley & Sons: New York, 1981.

(21) Ward, A. T. *J. Phys. Chem.* **1968**, *72*, 4133.

(22) Rosasco, G. J.; Simmons, J. H. *Am. Ceram. Soc. Bull.* **1975**, *54*, 590.

(23) (a) Vohra, V. Ph.D. Thesis, University of Rochester, 1996. (b) Vohra, V.; Heist, R. H. *J. Chem. Phys.* **1996**, *104*, 382.

(24) Wen, F. C.; Mclaughlin, T.; Katz, J. L. *Phys. Rev. A* **1982**, *26*, 2235.

(25) Callear, A. B. *Proc. R. Soc. (London) Ser. A* **1963**, *276*, 401.

(26) Wright, F. J. *J. Phys. Chem.* **1960**, *64*, 1648.

(27) Ernst, K.; Hoffman, J. J. *Chem. Phys. Lett.* **1979**, *68*, 40.