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Infrared and Mass Spectroscopic Study of the Reaction of Silyl Iodide and Ammonia. Infrared Spectrum of Silylamine

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The reaction of silyl iodide and ammonia has been studied under slowly flowing conditions using FTIR spectroscopy and mass spectroscopy. At low (0.01 mbar) partial pressures of silyl iodide in excess ammonia, monosilylamine, a long postulated intermediate in the synthesis of trisilylamine from halosilanes and ammonia, was the only silylamine observed by mass spectroscopy and infrared spectroscopy. At a silyl iodide pressure of 0.1 mbar (necessary to obtain a high signal-to-noise infrared spectrum of silylamine) a significant amount (~10%) of disilylamine was observed by both infrared and mass spectroscopies, demonstrating that both monosilylamine and disilylamine intermediates are produced in the gas phase. Trisilylamine was not observed as a product of the gas-phase reaction of silyl iodide and ammonia under the low-pressure conditions studied. By study of the reaction of deuterated silyl iodide and ammonia and the reaction of silyl iodide with deuterated ammonia, it was determined that the hydrogen lost in the formation of hydrogen iodide originates from the ammonia molecule. The infrared spectra of SiH_3NH_2, SiH_3ND_2, SiD_3NH_2, and SiD_3ND_2 are reported.

Introduction

The intermediate existence of monosilylamine, SiH_3NH_2, in the synthesis of trisilylamine from halosilanes and ammonia has long been postulated.[1] The proposed stepwise mechanism[2] for the formation of trisilylamine involves the initial formation of monosilylamine

$$SiH_3X + 2NH_3 \rightarrow SiH_3NH_2 + NH_4X \qquad (1)$$

$$X = \text{halogen}$$

followed by sequential disproportionation to generate trisilylamine and ammonia

$$2SiH_3NH_2 \rightarrow (SiH_3)_2NH + NH_3 \qquad (2)$$

$$2(SiH_3)_2NH \rightarrow (SiH_3)_3N + SiH_3NH_2 \qquad (3)$$

or, alternatively, stepwise reaction of the initially formed monosilylamine with halosilane

$$SiH_3NH_2 + SiH_3X + NH_3 \rightarrow (SiH_3)_2NH + NH_4X \qquad (4)$$

$$(SiH_3)_2NH + SiH_3X + NH_3 \rightarrow (SiH_3)N + NH_4X \qquad (5)$$

Although relatively little work has been done on this series of reactions, Aylett and Hakim[3] have reported the preparation of disilylamine, $(SiH_3)_2NH$, from diphenylaminosilane and ammonia at low temperatures. They determined that reaction 3 did not occur in the gas phase but that this disproportionation reaction occurred slowly in the liquid phase at 0 °C. They also observed that the reaction of disilylamine and silyl iodide (reaction 5) did not occur rapidly (if at all) in the gas phase but that this reaction is rapid and nearly quantitative in a condensed phase. These authors also sought evidence of the formation of silylamine, but none was found. The chemistry of silicon–nitrogen compounds has been the subject of a recent review.[4]

Silylamine has been the subject of considerable theoretical interest for several reasons. It is the simplest saturated Si–N–H compound, and it is the silicon analog of methylamine. The structure and properties of silylamine may be contrasted with those of methylamine,[5] and it is possible that (as in disilylamine and trisilylamine but not in methylamine) the molecule is planar about nitrogen. Molecular and electronic struture,[6] Si–N bond dissociation energy,[5,6] ionization potentials,[7,8] and dipole moments[9] have been predicted by ab initio calculations.

Gordon[9] has calculated the vibrational frequencies of silylamine by ab initio methods using the pyramidal structure predicted by geometry optimization. Silylamine possesses C_s symmetry and is expected to show 15 (9 A′ + 6 A″) absorptions in the IR. The normal modes of isostructural methylamine have been described,[10] as have the infrared spectra of the known silylamines, disilylamine[3] and trisilylamine.[11]

Recently, in situ mass spectroscopic studies of silane/ammonia chemical vapor deposition (CVD) processes have led to the detection of silylamine. Silylamine was first observed by Wu[12] in a study of the mercury-sensitized photochemistry of silane/ammonia mixtures in 1987. Wu reported that silylamine decomposed in the dark and with a half-life of 1–20 h, depending on the surface preparation of the gas cell. Silylamine has also been observed in a study of silane/ammonia plasma-enhanced CVD using a triple-quadrapole mass spectrometer.[13] We have observed silylamine, again mass spectroscopically, in the eximer

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laser (193 nm)[14] photochemistry of silane/ammonia mixtures. In our previous study, we also reported that the gas-phase reaction of silyl iodide and ammonia produced silylamine, although no details were given. In this study, we wish to report conditions under which silylamine may be prepared from silyl iodide and ammonia, mass spectroscopic studies of deuterated silylamines, and the infrared spectrum of silylamine and deuterated silylamines.

Experimental Section

Silyl iodide[15] was prepared by the reaction of phenylsilane (Petrarch) and HI (Matheson) at -45 °C and was partially purified by fractional condensation on the vacuum line using traps at -63 and -95 °C. The contents of the -95 °C trap (silyl iodide contaminated with 10% benzene) were fractionally distilled (30 cm × 1 cm column packed with glass helicies) at atmospheric pressure under nitrogen. Purity was checked by infrared spectroscopy (>99%). Deuterated silyl iodide was prepared by the reduction of (chlorophenyl)trichlorosilane (Petrarch) with $LiAlD_4$ (Aldrich) to form $ClC_6H_4SiD_3$, followed by reaction with DI (MSD) at room temperature in a glass bomb tube. The product was purified according to the literature procedure.[16] All glassware and the vacuum line were treated with D_2O and thoroughly dried before use. Infrared spectroscopy indicated the SiD_3I produced by this procedure had a chemical purity of greater than 99% and an isotopic purity of 98%. Ammonia (Matheson) and deuterated ammonia (MSD) were used without further purification. Disilylamine was prepared by the method of Aylett and Hakim[3] from diphenylaminosilane and ammonia. Disiloxane was prepared by the hydrolysis of silyl iodide with a slight excess of deoxygenated water. The purity of both compounds was checked by infrared spectroscopy and vapor pressure measurements.

A long-path-length FTIR spectrometer employing in situ mass spectroscopic sampling of gas composition was constructed from a commercial (Nicolet) 10-m-path-length multipass infrared cell. The cell had a volume of 2.5 L and was attached to a Nicolet 5pc FTIR (KBr optics, liquid-N_2-cooled MCT detector, 2-cm^{-1} resolution). A gas inlet system consisting of mass flow controllers (Vacuum General) to regulate the flow of ammonia and helium and a needle valve to control the flow of silyl iodide was attached to the inlet of the cell. The flow of silyl iodide into the cell was estimated from the observed pressure rise and the previously measured pumping speed of the system. The exhaust port of the cell was connected to a vacuum pump. The cell pressure was measured using a 0-10-Torr capacitance manometer (MKS, Baratron). Gases flowing into the cell were sampled using a differentially pumped mass spectrometer (Dycor AM200 mass spectrometer, 70-eV ionization potential, 50-μm sampling orifice pumped by a Leybold TMP 150C 150L/s turbomolecular pump). Mass and infrared spectra were obtained at a partial pressure of ~0.01 mbar of silyl iodide using the following flows and pressure: NH_3 flow = 2 mL/min, SiH_3I flow = 0.2 mL/min, He flow = 50 mL/min, total pressure ≈ 2.6 mbar. (Helium was added to increase the total pressure in the cell to partially suppress the coating of the cell mirrors with ammonium iodide. At 2.6 mbar total pressure, most of the ammonium iodide was deposited in the inlet system. Increasing the total pressure also prevented the back-streaming of oil vapor from the pumps into the cell.) In order to observe weaker bands and increase the signal-to-noise ratio, it was necessary to increase the partial pressure of silylamine by an order of magnitude. In this case, the flow rates and pressure were as follows: NH_3 flow = 10 mL/min, SiH_3I flow = 2 mL/min, He flow = 40 mL/min, total pressure = 2.6 mbar. Under these conditions of higher silyl iodide partial pressure, disilylamine was observed in significant (~10-20%) quantities. (See Results and Discussion.)

To subtract the contribution of ammonia to the spectra (necessary for all of the spectra), the sharp N-H stretching peak at 3336.0 cm^{-1} was used, and in the case disilylamine the N-H bend at 1183 cm^{-1} was used. The spectra of all of the deuterated species were obtained at 0.02 mbar partial pressure of silyl iodide to minimize contamination from disilylamine. Spectral collection times were limited by the coating of the cell optics by ammonium iodide (see Results and Discussion), and most of the spectra are averages of 128 transients.

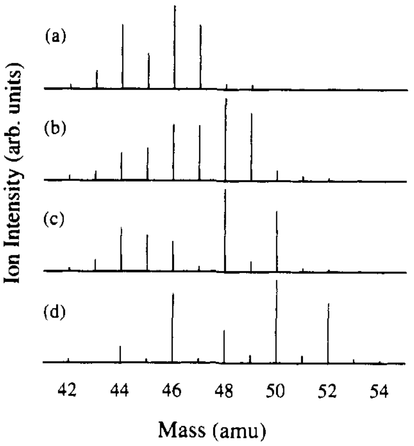

Figure 1. Mass spectra of the reaction products of SiH_3I and NH_3 (a), SiH_3I and ND_3 (b), SiD_3I and NH_3 (c), and SiD_3I and ND_3. Each spectrum is normalized to the base peak.

Results and Discussion

Mass Spectra. The mass spectra of mixtures of SiH_3I and NH_3, SiH_3I and ND_3, SiD_3I and NH_3, and SiD_3I and ND_3 in the region of 40-56 amu are shown diagrammatically in Figure 1. These spectra were obtained under experimentally determined conditions of low silylamine partial pressure and excess ammonia. The mass spectrum of silylamine is essentially the same as that which had been reported earlier,[12-14] differing only in that the peak at $m/e = 44$ is of lower intensity relative to the other peaks in the spectrum. This is readily explainable because the mass spectra recorded in silane-ammonia CVD environments contained other silicon-nitrogen species in whose mass spectra $SiNH_2^+$ is a common fragment ion.

The reaction of silyl iodide and ammonia appears to be quantitative under these conditions in that all of the silyl iodide was consumed and silylamine was the only product. By increasing the partial pressure of silyl iodide until ammonia was no longer in a large excess, it was possible to observe the appearance of peaks in the mass spectrum due to disilylamine. This implies that stepwise silylation of ammonia to silylamine to disilylamine (eqs 1 and 4) does occur and that both silylamine and disilylamine intermediates in the synthesis of trisilylamine may be formed in the gas phase. Disilylamine was also observed when the flows of ammonia and silyl iodide were increased by a factor to 10 to increase the partial pressure of silylamine for IR measurements. While this could be interpreted as evidence for disproportionation of silylamine to disilylamine and ammonia (eq 2), it was also possible that the formation of disilylamine was the result of poor gas mixing, resulting in local depletion of ammonia. Poor gas mixing could have been caused by low flow (52 mL/min at 2.6 mbar, 20 L/min pumping seed) through the cell due to the limited conductance of the small (6 mm) inlet and outlet ports of the cell. To test this hypothesis, the flow of He was discontinued and the flow of ammonia was increased to maintain the same total flow. The partial pressure of ammonia was increased from 0.5 to 2.5 mbar and resulted in an approximately 3-fold decrease in the disilylamine peaks relative to those of silylamine. Since the gas residence time was unchanged, this indicates that disproportionation was not the major cause of the observed disilylamine and that reaction of silylamine with silyl iodide is primarily responsible for the production of disilylamine. (Unfortunately, it was not possible to obtain IR spectra at higher ammonia partial pressures because absorption of radiation by ammonia reached saturation.)

By deuterating either the ammonia (Figure 1b) or the silyl iodide (Figure 1c), it was possible to determine that the H atom of the HI produced in the reaction of silyl iodide and ammonia originated from ammonia. Reaction of SiH_3I and ND_3 yields

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SiH_3ND_2 (m/e = 49), while SiD_3I and NH_3 yields SiD_3NH_2 (m/e = 50). Since it is known that silyl iodide readily forms stable, isolable adducts with tertiary amines, it is reasonable to think that the reaction of silyl iodide and ammonia proceeds through the formation of an ammonia–silyl iodide adduct followed by the 1,2-elimination of HI from a four-centered intermediate.

The cracking pattern of the partially deuterated species gives additional information about the stability of ions formed by electron impact ionization of silylamine. The base peak at m/e = 46 is $H_2SiNH_2^+$, formed by the loss of H from Si. This gives rise to peaks at m/e = 48 in both SiH_3ND_2 and SiD_3NH_2, which are also the base peaks in both spectra. Similarly, the peak at m/e = 45 is due to $HSiNH_2^+$, in which two H atoms have been lost from the Si atom of the molecular ion. This gives rise to peaks at m/e = 47 and m/e = 46 in the mass spectra of SiH_3ND_2 and SiD_3NH_2, respectively. The peak at m/e = 44 in the mass spectrum of SiH_3NH_2 is due to both $SiNH_2^+$ and $HSiNH^+$ ions. These ions give rise to peaks at m/e = 45 and 46 in the mass spectrum of SiH_3ND_2 and peaks at m/e = 44 and 45 in the mass spectrum of SiD_3NH_2. The peak at m/e = 43 in the mass spectrum of SiH_3NH_2 is due to $SiNH^+$, which gives rise to peaks at m/e = 44 in the spectrum of SiH_3ND_2 and m/e = 43 in the mass spectrum of SiD_3NH_2.

Infrared Spectra. The collection of infrared spectra was made difficult by several factors, primary of which was the extreme ease of hydrolysis of silyl iodide and silylamine. While the metal inlet system and mass spectrometer could be heated under vacuum to an acceptable state of dryness, this was not possible for the IR cell used in this study because the fixed mirrors were attached to the cell walls using an epoxy cement. It was impossible to completely dry the cell; however, after a number of exposures of the cell to silyl iodide, the cell became somewhat passivated. Using the 1106-cm^{-1} peak in the spectrum of disiloxane (the hydrolysis product of both silyl iodide and silylamine), it was estimated that the half-life for the hydrolysis of silyl iodide at a pressure of 0.01 mbar was approximately 3 min. Since the calculated plug-flow gas residence time under the conditions of measurement was approximately 7 s, hydrolysis in the passivated cell became negligible for flow measurements but ruled out any static measurements of gas composition using the IR cell.

The production of ammonium iodide as the other product of the reaction caused some experimental difficulty in that periodic disassembly and cleaning of the cell optics were required. To some extent, the problem was alleviated by raising the total pressure to 2.6 mbar using helium as an inert diluent, causing most of the deposition of ammonium iodide to occur in the inlet system. To minimize absorption of water during cleaning, the cell was sealed, removed from the optical bench, disassembled, cleaned, and reassembled in an inert-atmosphere drybox.

Another problem in obtaining the IR spectra was the limitation in pumping speed imposed by the small inlet and exhaust ports of the cell, as discussed eariler. Attempts to raise the pressure of silylamine by increasing the flow of silyl iodide and ammonia led to formation of disilylamine, probably due to poor gas mixing in the inlet system. Disilylamine contamination is evident in Figure 2 where the spectrum of silylamine taken at approximately 0.01 and 0.1 mbar are shown. The spectrum of the 0.1-mbar sample (Figure 2b) has bands at 1183 and 930 cm^{-1} characteristic of disilylamine, consistent with the mass spectral measurements. Figure 2c shows the spectrum resulting from the subtraction of a spectrum of disilylamine obtained from a sample prepared by the method of Aylett and Hakim.[3] Parts a and c of Figure 2 are identical, differing only in intensity and signal-to-noise ratio.

To further illustrate that the spectrum of silylamine is free of impurities, the spectra of silyl iodide, disiloxane, disilylamine, and silylamine (obtained at 0.01 mbar) in the region 1250–500 cm^{-1} are shown in Figure 3. Besides differing in the Si–H bending region (900–1000 cm^{-1}) in both band shape and position, the spectrum of silylamine lacks bands at 1106 cm^{-1} characteristic of disiloxane and at 1183 cm^{-1} characteristic of disilylamine. Silyl iodide, if present, would have appeared in the region 940–890 cm^{-1}.

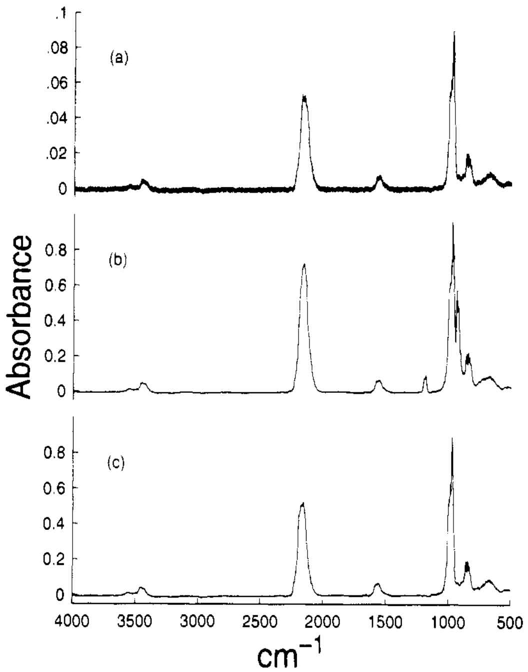

Figure 2. Infrared spectra of silylamine at (a) 0.01 mbar and (b) 0.1 mbar partial pressure of silyl iodide. Spectrum c is spectrum b after the subtraction of peaks due to disilylamine (see text).

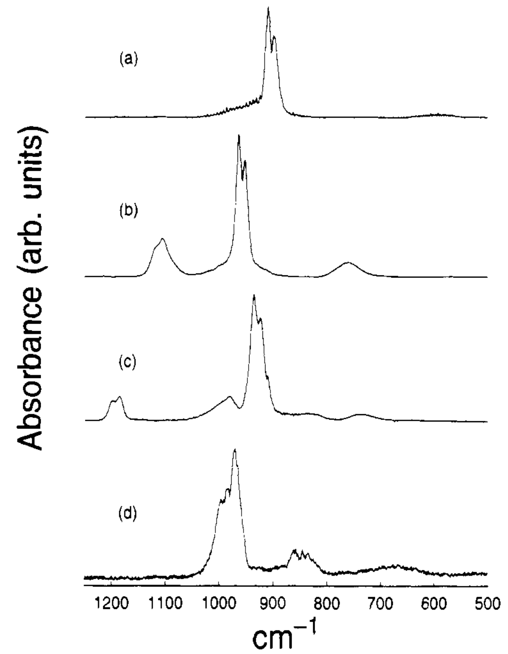

Figure 3. Infrared spectra of (a) silyl iodide, (b) disiloxane, (c) disilylamine, and (d) silylamine. All spectra are normalized to the most intense peak in the spectrum.

The spectrum of silylamine is composed of six major bands, several of which may be assigned by inspection. The N–H stretching (3400–3600 cm^{-1}) region shows a band with two peaks assignable to the symmetric and asymmetric stretching modes of NH_2. The next lowest energy band (centered at 2167 cm^{-1}) is readily assigned to the Si–H stretching modes. The single band at 1560 cm^{-1} is assigned to the N–H bending mode and is characteristic of a primary amine. The band at 970 cm^{-1} is in a region of the spectrum associated with Si–H bending vibrations.

Table I. Fundamental Vibrational Frequencies of Silylamine and Deuterated Silylamines[a]

assgnt	SiH_3NH_2	SiH_3ND_2	SiD_3NH_2	SiD_3ND_2	calc[b]
NH(D) str					
asym	3547	2611	3538	2599	3886
sym	3445	2528	3435	2523	3792
SiH(D) str	2172	2171	1570	1574	2370 (SiH_2, sym)
					2364 (SiH_2, asym)
					2317 (SiH)
NH(D) bend	1564	1127		1118	1733
SiH(D) bend	996 (sh)	989 (sh)	700	702	1082 (SiH_3)
	983 (sh)	960			1072 (SiH_3)
	970				1011 (SiH_2)
					999 (SiH_2–NH_2)
SiN str	859 r		839 r	826 r	
	845 q	835	828 q	815 q	872
	834 p		816 p	798 p	
SiH_3 bend	670 (b)	710			768
SiH_2–NH_2 bend	670 (b)				671

[a] sh = shoulder; b = broad. [b] From ref 9.

As an aid to the assignment of the lower energy bands, the observed spectrum may be compared with that predicted by ab initio methods.[9] The observed and calculated stretching frequencies for silylamine are tabulated in Table I. As a test of the validity of this approach, the bands which may be assigned unambiguously (N–H stretch and bend, average Si–H stretch and bend) are compared with calculated values. The calculated values are systematically 8–10% too high, as has been previously observed and discussed.[17] The calculation predicts that the Si–N stretch will have a frequency of 872 cm^{-1}, and the observed band at 845 cm^{-1} is assigned to this mode. The calculation also predicts two other low energy bands due to SiH_3 and NH_2–SiH_2 bending modes. A single very broad peak at 670 cm^{-1} is observed in the spectrum and is assigned to these two modes.

In order to confirm these assignments, the spectra of SiH_3ND_2, SiD_3NH_2, and SiD_3ND_2 were recorded. The observed stretching frequencies are tabulated in Table I. The only peak not to show a large shift on deuterium substitution was the peak at 845 cm^{-1}, thus confirming the assignment of this band to the Si–N stretching mode. This peak was also the only peak to show a recognizable band contour. In the 80-mTorr spectrum of the parent compound, reproduced in expanded form in Figure 4a, this band is split into three peaks. A more distinct PQR band contour in the expanded spectra of SiD_3NH_2 and SiD_3ND_2 is shown in Figure 4b,c, respectively. Although silylamine is not a symmetric top, this pseudoparallel band might be expected to show this PQR contour, as does the C–N band of methylamine.[18] The band assigned to the Si–N stretch in the spectrum of SiH_3ND_2 did not show a discernible band contour, possibly due to the overlap of an N–D bending mode.

Formation of Trisilylamine. Although trisilylamine was not detected in the flow measurements performed in this study, several new pieces of information concerning its formation were obtained. First, this study confirms that monosilylamine is the reaction product formed by the gas-phase reaction of ammonia and silyl iodide. Second, the monosilylamine formed is sufficiently basic to rapidly react with a second molecule of silyl iodide to form disilylamine, even in the gas phase. This is in contrast to the reactivity of disilylamine with silyl iodide, which do not react in the gas phase but only in a condensed phase.[3] Third, monosilylamine does not rapidly disproportionate, even in the presence of excess ammonia, consistent with the observation of Wu,[12] who observed only slow a slow disproportionation reaction, probably occurring at the reactor walls. Disilylamine also does not disproportionate in the gas phase.[3] Finally, monosilylamine and disilylamine do not rapidly react to form trisilylamine. These observations indicate that the primary pathway for the synthesis of trisilylamine from halosilane and ammonia is the stepwise silylation of ammonia to monosilylamine to disilylamine and ultimately to trisilylamine.

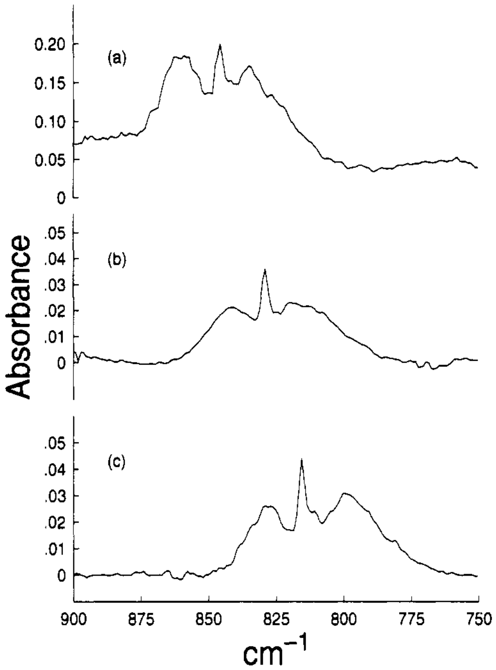

Figure 4. Infrared spectra of (a) SiH_3NH_2, (b) SiD_3NH_2, and (c) SiD_3ND_2 in the Si–N stretching region.

Conclusions

It was shown that silylamine may be produced at low pressure in a flow reactor by the reaction of silyl iodide and ammonia in sufficient concentration to obtain its infrared spectrum. This observation suggests that it should be possible to structurally characterize this molecule using high-resolution infrared and microwave spectroscopy, and it may also be possible to characterize the electronic structure of this molecule using electron spectroscopy.

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