# Dinitrogen Sulfide, N₂S, Revealed by Photoelectron Spectroscopy

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**Abstract:** The reactive dinitrogen sulfide molecule, $N_2S$, has been confirmed by He I photoelectron spectroscopic measurements as a major product of the thermal decomposition of 5-phenyl-1,2,3,4-thiatriazole. The adiabatic ionization energy of $N_2S$ is 10.55 eV, and its spectrum is characterized by two sharp ionization bands assigned as the ground $^2\Pi$ ($\pi_s$) and first excited $^2\Sigma$ ($\sigma_{NN}$) states of the $N_2S^+$ ion. A broad band is tentatively assigned to the second excited $^2\Pi$ ($\pi_{NN}$) ion state. Comparison with the spectrum of its stable analogue, OCS, indicates that the N–S bond is relatively weak, so that the S atom effects only small perturbations of the $\sigma_g$ and $\pi_u$ molecular orbitals of $N_2$ within the linear $N_2S$ molecule. Molecular orbital calculations provide data in good agreement with these observations, including estimates of the geometry and vibration frequencies of $N_2S$ and $N_2S^+$. The photoelectron spectra also show that diatomic sulfur, $S_2$, is produced in the thermal decomposition of 5-phenyl-1,2,3,4-thiatriazole, from which it is concluded that $N_2S$ is undergoing bimolecular decomposition. This confirms that $N_2S$ is not only just an unstable but also probably a highly reactive 1,3-dipole similar to diazomethane, $CH_2N_2$, and potentially useful in chemical synthesis.

The highly reactive molecule, $N_2S$, has recently been identified by IR spectroscopy and mass spectrometry as a product of the thermal decomposition of 5-phenyl-1,2,3,4-thiatriazole.[1] This



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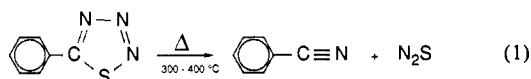
was in spite of earlier work[2,3] which had discounted this route for the thermal decomposition.[3] While there had been no substantial experimental identification of $N_2S$ previously, Powell[4] had nominated it as the carrier in a $N_2$–$CS_2$ laser system. He suggested that $N_2S$ is linear and claimed it to be relatively unreactive at room temperature. However, the IR study[1] showed it to be unstable in argon matrices on warming to 160 K. It was also easily detectable by mass spectrometry[1] by using a 5-cm path to the ion source, whereas it had not been detected by Holm and co-workers[3] who used a longer path.

The technique of He I photoelectron spectroscopy has proved to be most useful in the study of small reactive molecules produced by flash vacuum pyrolysis[5] as well as by high-temperature vaporization.[6] Numerous reactive small molecules containing sulfur have been studied in this way. These include CS,[7] $CH_2S$,[8] SO,[9] $S_2$,[6] $S_2O$,[5] NS,[10] $N_2S_2$,[11] and $N_3S_3$.[12]

$N_2S$ is potentially a synthetically important 1,3-dipole. Therefore, information on its reactivity, which might be deduced from its HOMO energy, and hence from its photoelectron spectrum is highly desirable. Furthermore, as has become clear from the present investigation, the chemistry associated with $N_2S$ production is also a source of diatomic sulfur, $S_2$. This is of current interest since disulfur units are finding application in cycloaddition chemistry.[13]

Molecular orbital calculations on $N_2S$[14,15] confirmed the linear NNS structure and estimated the N–S bond length to be 1.63 Å. This is longer than the double bond in HNSO ($R_{NS} = 1.51$ Å)[16] but shorter than the single bond in [$(CH_3)_2N]_2S$ ($R_{NS} = 1.69$ Å).[17] However, it is similar to the N–S bond length in 1,2,5-thiadiazole ($R_{NS} = 1.63$ Å)[18] which involves nominally single bonds shortened by conjugation with the ring $\pi$ system.

## Experimental Section

The He I photoelectron spectra were measured on a spectrometer specially designed for the study of transient molecular species. It consists of separately pumped ionization and analyzer chambers, with a helium discharge lamp of standard design, and an electron analyzer which is a 150° double-hemispherical electrostatic-focussing type. The spectrometer

is controlled by an enhanced Apple IIe microcomputer which operates a repetitive 1024 point analyzer sweep voltage over any chosen range and counts and stores the pulses from the electron detection and amplification system.

A heated inlet system was used to measure the He I spectrum of 5-phenyl-1,2,3,4-thiatriazole (1) which required a temperature of 65 °C to produce a satisfactory vapor pressure. Flash vacuum pyrolysis of the flowing vapor was achieved by passing it through a narrow quartz tube wound near its end with a short coil of shielded heating wire. The pyrolysis products emerging from the tube travelled about 1 cm before intersecting the He I ionizing beam.

The thermal decomposition products of 1, in particular benzonitrile and $N_2$, were first observed at a pyrolysis temperature of 165 °C, and at 190 °C about half of 1 appeared to be decomposed. This was effected by observing the count rate at 11.5 eV where only 1 shows significant intensity. At 310 °C the count rate at 11.5 eV was relatively low indicating nearly complete (>95%) decomposition of 1.

The He I spectra illustrated in Figure 1 represent increasing degrees of thermal decomposition at temperatures of 95, 165, 190, and 310 °C. The bottom frame of Figure 1 is a composite of the spectra of the stable decomposition products, benzonitrile and $N_2$, measured for pure samples at a temperature of 100 °C. The ionization energy scale was based on

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N₂S

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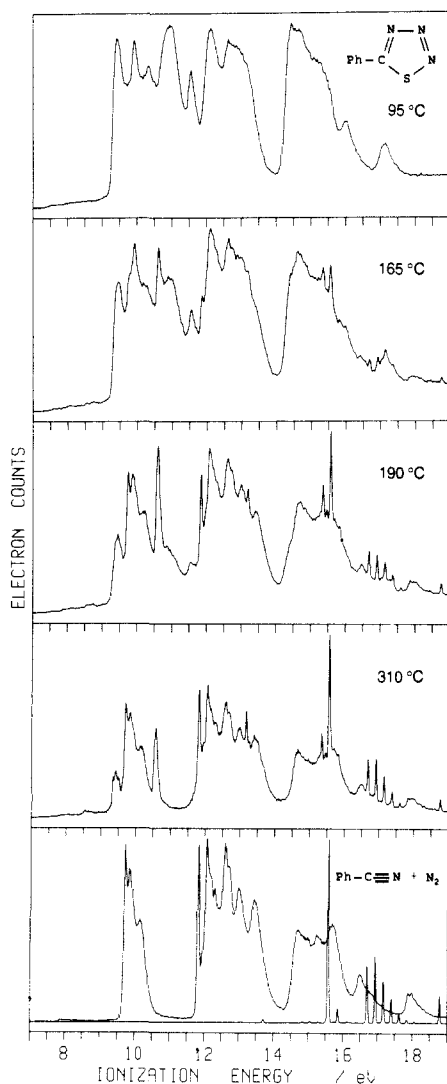


**Figure 1.** He I photoelectron spectra of 5-phenyl-1,2,3,4-thiatriazole measured at 95 °C and at pyrolysis temperatures of 165, 190, and 310 °C. The bottom frame is of superimposed spectra of the stable pyrolysis products benzonitrile and nitrogen.

$CH_3I$ and $N_2$ calibrant lines, and the operating resolution of the spectrometer was 35 meV. The time-averaged spectra were obtained by using run times of 2–3 h.

## Results

Visual observation of the spectra in Figure 1 indicates the presence of a number of new bands. These are seen more clearly in Figure 2 which is a spectrum obtained by subtraction of the benzonitrile and $N_2$ spectra from the pyrolysis product spectrum at 310 °C. This spectrum is representative of a mixture of $S_2$ and $N_2S$. The $S_2$ spectrum, originally described by Jonathan and co-workers[5] is prominent, with its structured first band at 9.41 eV and sharp fourth band at 13.20 eV, being easily assigned. After locating the other $S_2$ bands the remaining bands which are assigned to $N_2S$ are its first band with a vertical IE of 10.60 eV and a sharp higher band at 15.36 eV. While these two bands have rather different total intensities they are observed to have the same relative intensities in each of the elevated temperature spectra in Figure 1. Consequently they are indicative of the same species, and their simple appearance suggests that $N_2S$ and its ions are each of linear geometry.

A number of broad underlying bands are also observed in Figure 2, but most of these can be assigned to residual traces of **1** enhanced by the spectrum subtraction. However a weak low IE band is observed near 8.5 eV, increasing in relative intensity with increase in pyrolysis temperature. This can only be due to a large molecule, for which phenyl isothiocyanate, PhNCS, is the obvious candidate as it has been observed as a minor product of the thermal
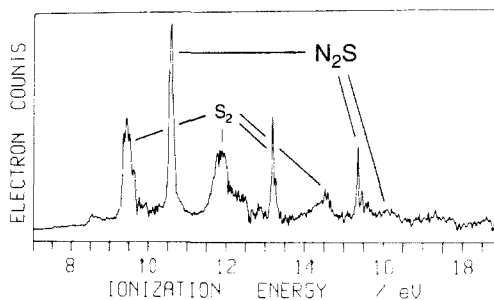


**Figure 2.** He I photoelectron spectrum of the unstable pyrolysis products, $S_2$ and $N_2S$, obtained by subtraction of PhCN and $N_2$ spectra from the 310 °C spectrum in Figure 1.

decomposition of **1**.[1,3] This is verified by comparison with the He I spectrum of PhNCS,[19] which displays a structured first band with a vertical IE measured at 8.53 eV.

On the basis of the PE spectrum of its isoelectronic analogue, OCS, a third ionization band of $N_2S$ is expected below 18 eV. The broad bands with maxima at ∼14.3 and ∼16.2 eV include contributions from residual **1**, while a weaker band around ∼17.3 eV is contaminated by residual $N_2$ data. As argued later the band at 16.2 eV is tentatively assigned to the third ionization of $N_2S$. The sharp 15.36 eV ionization is then assigned as the second band.

The first and second $N_2S$ bands show evidence of fine structure. The first band which has a vertical IE of 10.60 eV has a low IE shoulder at 10.55 eV and a suggestion of a higher IE shoulder at 10.65 eV. The band has a profile similar to that of the first band in the PE spectrum of OCS,[20] which is analyzed in terms of a vibration frequency of ∼650 cm⁻¹ and a spin-orbit splitting of ∼350 cm⁻¹. The $^2\Pi$ state of $S_2^+$ shows spin-orbit splitting of ∼470 cm⁻¹.[6] So the enhanced width observed for the apparently single peak in the first $N_2S$ band is likely to be due to a similar mixing of spin-orbit and vibrational levels. We are able to simulate the shape of the band by using a spin-orbit parameter of 400 cm⁻¹ and a vibrational spacing of 500 cm⁻¹ with $v' = 0, 1, 2$ intensities in the ratio 1:0.3:0.1 convoluted with a Gaussian function of 500 cm⁻¹ halfwidth. A value of ∼500 cm⁻¹ is a reasonable value for the N–S stretching vibration in $N_2S^+$.

The second band of $N_2S$ is characterized by a strong peak at 15.36 eV which is clearly an adiabatic value, and it is followed by a weaker peak at 15.47 eV indicating a vibration of 820 ± 50 cm⁻¹. This can only be assigned as the N–S stretching vibration of the first excited state of $N_2S^+$, though its value is considerably higher than the ∼500 cm⁻¹ value presumed for the ground state of $N_2S^+$.

No monatomic sulfur (IEs of 10.36, 12.12, and 13.40 eV) is detected in the spectrum of Figure 2. However if monatomic S was produced in this gas-phase reaction, its photoelectron spectroscopic detection would have been expected, even though diatomic $S_2$ is the form of sulfur predominating at low pressure.[6] Other possible thermolysis products containing sulfur can also be eliminated as the source of the new bands. So $H_2S$ ($I_1 = 10.48$ eV) is not observed, and related transient molecules such as NS,[10] $S_2N_2$,[11] and $S_3N_3$[12] cannot be seen.

## Calculations and Discussion

The assignment of the HeI PE spectrum of $N_2S$ is most usefully made by comparison with the spectrum of its isoelectronic analogue OCS, which was measured and interpreted by Brundle and Turner.[20] It is also instructive to compare each of these with $N_2$ and CO, respectively. The ionization energies below 18 eV for these molecules are shown in the correlation diagram given in Figure 3. In addition, data obtained from ab initio calculations on these and their ground and excited ion states are presented in Table I. The $N_2O$ molecule might also be considered as an analogue of $N_2S$. However its electronic structure is similar to

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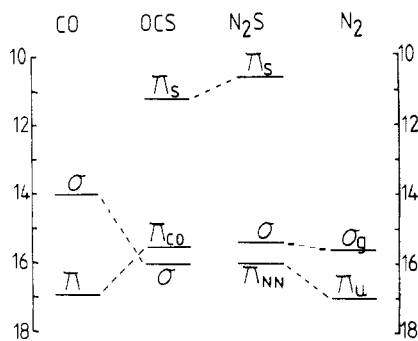
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**Figure 3.** Correlation diagram for the vertical ionization energies, in eV, of CO, OCS, N₂S, and N₂.

**Table I.** Theoretical and Experimental Data for N₂S and Related Molecules[a]

| | $N_2(^1\Sigma_g^+)$ | | $N_2^+(^2\Sigma_g^+)$ | | $N_2^+(^2\Pi_u)$ | |
|---|---|---|---|---|---|---|
| | theor | expt | theor | expt | theor | expt |
| $R_{NN}$ | 1.078 | 1.098 | 1.094 | 1.116 | 1.138 | 1.18 |
| $\nu_{NN}$ | 2758 | 2360 | 2563 | 2191 | 1575 | 1850 |
| $E$ | 0.0 | 0.0 | 15.59 | 15.58 | 16.14 | 16.69 |

| | $N_2S(^1\Sigma)$ | | $N_2S^+(^2\Pi)$ | | $N_2S^+(^2\Sigma)$ | |
|---|---|---|---|---|---|---|
| | theor | expt | theor | expt | theor | expt |
| $R_{NN}$ | 1.086 | | 1.082 | | 1.167 | |
| $R_{NS}$ | 1.652 | | 1.720 | | 1.502 | |
| $\nu_{NN}$ | 2602 | 2030[c] | 2510 | | 2142 | |
| $\nu_{NS}$ | 583 | | 491 | ~500[b] | 974 | 820[b] |
| $E$ | 0.0 | 0.0 | 9.91 | 10.60[b] | 15.58 | 15.36[b] |

| | $CO(^1\Sigma)$ | | $CO^+(^2\Sigma)$ | | $CO^+(^2\Pi)$ | |
|---|---|---|---|---|---|---|
| | theor | expt | theor | expt | theor | expt |
| $R_{CO}$ | 1.114 | 1.128 | 1.098 | 1.115 | 1.223 | 1.244 |
| $\nu_{CO}$ | 2440 | 2143 | 2393 | 2200 | 1075 | 1549 |
| $E$ | 0.0 | 0.0 | 13.90 | 14.02 | 15.92 | 16.54 |

| | $OCS(^1\Sigma)$ | | $OCS^+(^2\Pi)$ | | $OCS^+(^2\Sigma)$ | |
|---|---|---|---|---|---|---|
| | theor | expt | theor | expt | theor | expt |
| $R_{CO}$ | 1.131 | 1.157 | 1.104 | 1.136 | 1.218 | ~1.16 |
| $R_{CS}$ | 1.572 | 1.561 | 1.672 | 1.634 | 1.494 | ~1.56 |
| $\nu_{CO}$ | 2307 | 2079 | 2335 | 2069 | 1969 | |
| $\nu_{CS}$ | 889 | 859 | 654 | 610 | 938 | |
| $E$ | 0.0 | 11.19 | 10.69 | 11.19 | 16.85 | 16.04 |

[a] The theoretical data are for optimized geometries obtained by using the GAUSSIAN 82 program with 6-31G* atomic basis sets. The UHF calculations on the ions are for the ground and first excited states in each case. Bond lengths $R$ are in Å, vibration frequencies $\nu$ are in cm⁻¹, and relative total energies $E$ in eV are referred to the ground-state molecule. [b] Experimental data from present study. [c] From ref 1.

that of CO₂ where the terminal atoms contribute equally to all MOs. The differences in orbital size and electronegativity of the S atom compared with the O atom mean that N₂S varies considerably from N₂O in its structure and consequently has more in common with OCS.

The expectation that the N–S bond in N₂S is weaker than the corresponding C–S bond in OCS is confirmed by the calculated geometries. The GAUSSIAN 82 program[21] was used with the 6-31G* basis sets to derive these optimum geometries, which show an $R_{NS}$ of 1.652 Å compared with an $R_{CS}$ of 1.572 Å. By comparison the calculated $R_{NN}$ in N₂S is 1.086 Å, shorter than the $R_{CO}$ of 1.131 Å in OCS. The latter values show small increases over the respective calculated diatomic values of 1.078 Å for N₂ and 1.114 Å for CO. The calculated rotational constant of 0.210 cm⁻¹ for N₂S agrees well with the value of 0.22 ± 0.01 cm⁻¹ estimated by Powell.[4] An estimate of the N–S bond energy in N₂S is obtained from the total energies at the MP3 level of approximation for the 6-31G* wave functions of N₂, CO, N₂S, and OCS. The appro-

**Table II.** Experimental Ionization Energies of N₂S

| $I_A$[a] | $I_V$[b] | MO($C_{\infty v}$) | ion state |
|---|---|---|---|
| 10.55 | 10.60 | $3\pi$ | $^2\Pi$ |
| 15.36 | 15.36 | $9\sigma$ | $^2\Sigma$ |
| ~15.7 | ~16.2 | $2\pi$ | $^2\Pi$ |

[a] Adiabatic ionization energy in eV. [b] Vertical ionization energy in eV.

priate difference formula gives a value of –60 kcal mol⁻¹ relative to that of the C–S bond in OCS. By using the known OC–S bond energy of 128 kcal mol⁻¹, a value of 68 kcal mol⁻¹ is hence estimated for the N₂–S bond energy. Consequently, as illustrated in Figure 3, the effect of addition of the S atom to N₂ is to produce weaker perturbations of the $\sigma$ and $\pi$ ionizations of N₂ than in the case of S atom addition to CO represented by OCS.

Below 18 eV, the OCS spectrum consists of three bands, with the sharp first band at 11.20 eV being associated with the effectively nonbonding $\pi$ electrons of the S atom, designated as $\pi_S$. The second band ($I_A$ = 15.08 eV, $I_V$ = 15.52 eV) is broad and assigned to the bonding $\pi$ orbitals and the sharp third band ($I_A$ = $I_V$ = 16.04 eV) to the $\sigma$ orbital. These latter bands can be correlated with the $\sigma$ ($I_V$ = 14.01 eV) and $\pi$ ($I_V$ = 16.91 eV) ionizations of CO, which demonstrate similar nonbonding and bonding character, respectively. If the S atom in OCS is regarded as perturbing these uppermost $\sigma$ and $\pi$ MOs of CO, then its effect is to increase the $\sigma$ IE by 2.03 eV and to decrease the $\pi$ IE by 1.39 eV. However these shifts can be considered to arise from the lengthening of the C–O bond (from 1.128 Å in CO to 1.157 Å in OCS), which increases 2p$\sigma$–2p$\sigma$ overlap and decreases 2p$\pi$–2p$\pi$ overlap, rather than to S3p orbital mixing with the respective $\sigma$ and $\pi$ MOs of CO. This is the same effect which is seen for the IEs of CO ligands in transition-metal complexes[22] and for CO adsorbates on clean metal surfaces.[23]

Consequently the weaker S interaction in N₂S can be seen as effecting smaller perturbations on the $\sigma_g$ and $\pi_u$ ionizations of N₂. The first PE band of N₂S at 10.60 eV is clearly of nonbonding S character, being associated with the essentially localized 3p$_x$,3p$_y$ orbitals and designated as of $\pi$ symmetry. This $\pi_S$ IE is lower by 0.60 eV than the comparable ionization in OCS. The difference can be attributed to an enhanced C⁺–O⁻ polarity in OCS arising from the lengthened C–O bond and producing an electrostatic shift contribution to the $\pi_S$ ionization energy.

Since the sharp third band of OCS is related to the $\sigma$ ionization of CO, it is likely that the sharp band of N₂S at 15.36 eV is related to the $\sigma_g$ ionization of N₂. It is hence assigned as the second IE band of N₂S and represents the $\sigma_g$ MO stabilized by only 0.20 eV due to small S 3p$\sigma$ admixture.

The third band of N₂S is expected to be below 18 eV, and since the S interaction has been shown to be weak in the first and second PE bands, it is possible that the broad band with a vertical IE at ~16.2 eV is the $\pi$ ionization of N₂S related to the $\pi_u$ band in N₂. Its IE indicates that it is destabilized by 0.8 eV relative to $\pi_u$ due, as in OCS but to a lesser extent, to the reduced 2p$\pi$–2p$\pi$ overlap with the slight lengthening of the N–N bond in N₂S. This rather tentative assignment is also consistent with the pattern observed in OCS where the second and third bands are separated by less then 1 eV. Also while allowing for the limitations inherent in using the Koopmans approximation, the molecular orbital calculation on N₂S suggests a separation of 1.4 eV for the corresponding ionizations. The experimental IE data for N₂S are summarized in Table II.

The calculated IEs given in Table I are adiabatic values obtained as the difference in ion and molecule total energies at the MP3 level of approximation for their respective 6-31G* SCF equilibrium geometries. While this procedure is the obvious

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alternative to using the Koopmans approximation, which fails in the classic case of $N_2$, the open-shell calculations on the doublet ion states are not without their own complications. These calculations are susceptible to varying amounts of high spin contamination and for the excited triatomic ions are plagued by convergence difficulties both in the SCF procedure and in the geometry optimization. The vibration frequency calculations for the excited $^2\Sigma$ states of $N_2S^+$ and $OCS^+$ can only be performed for the linear vibrations, as angle deformation leads to variational collapse. So the second derivatives of the total energy must be obtained from single-point calculations. Consequently the calculated properties for the excited ion states must be accepted with caution. Where experimental geometries are available for comparison, the calculated geometries are less accurate than in the cases of the corresponding molecule and ion ground states. For $N_2^+(^2\Pi_u)$ and $CO^+(^2\Pi)$ the calculated frequencies are significantly lower than the experimental values, which is the reverse of the usual trend. Nevertheless the measurable difference in first ionization energies of $N_2S$ (calculated 9.91 eV, experimental 10.69 eV) and OCS (calculated 11.21 eV, experimental 11.20 eV) is well simulated by the calculations, which indicate that in each case the highest occupied degenerate $\pi$ MOs are dominated by S 3p character (87% for $N_2S$, 77% for OCS). The calculated Mulliken charges indicated by $N^{-0.02}N^{0.08}S^{-0.06}$ and $O^{-0.36}C^{0.43}S^{-0.07}$ show that the CO subunit in OCS is highly polarized and hence more electronegative than the $N_2$ subunit in $N_2S$. This causes the higher $\pi_S$ IE for OCS.

The calculated vibration frequencies of $N_2S$ and OCS listed in Table I are interesting in their comparison. In general, theoretical values based on the harmonic approximation are around 10% higher than experimental frequencies,[24] so the $\nu_{CO}$ and $\nu_{CS}$ data for OCS and ground-state $OCS^+$ are consistent with expectation. However the calculated value of $\nu_{NN}$ for $N_2S$ is larger than that of $\nu_{CO}$ in OCS, in contrast to the matrix value[1] of $\nu_{NN}$ = 2030 cm$^{-1}$ which is marginally lower than the gas-phase value of $\nu_{CO}$ = 2079 cm$^{-1}$.

The $\nu_{NS}$ vibration frequencies for $N_2S$ and ground-state $N_2S^+$ are considerably lower than the comparable $\nu_{CS}$ values for OCS and ground-state $OCS^+$ consistent with the weaker N–S bond. The approximate value of 500 cm$^{-1}$ estimated from the first PE band of $N_2S$ agrees well with the theoretical value of 491 cm$^{-1}$ obtained as the harmonic $\nu_{NS}$ frequency for the ground $^2\Pi$ state of $N_2S^+$. The $\nu_{NS}$ vibration frequency of 820 cm$^{-1}$ measured for the $^2\Sigma$ excited state of $N_2S^+$ suggests that a stronger N–S bond is involved than in either of the ground states $N_2S$ or $N_2S^+$. This might be explained by the fact that the excited ion has its positive hole localized on the $N_2$ unit, with the geometric relaxation of $N_2^+S$ tending to decrease the N–S bond length. The calculated geometry of $N_2S^+(^2\Sigma)$ lends support to this description, and the theoretical $\nu_{NS}$ value of 974 cm$^{-1}$ relates well to the observed frequency. There is some discrepancy however in that such a change in geometry between the neutral and ion states would be expected to result in a more complex photoelectron band for the second ionization of $N_2S$. While the observed vibration frequency suggests a reasonable change in geometry, the strong adiabatic peaks suggests otherwise.

Comparison with the third PE band of OCS and its associated $^2\Sigma$ ion state does not greatly assist in a resolution of this apparent anomaly. The band as measured[20] shows poorly resolved structure and has been interpreted as being dominated by the adiabatic peak suggesting an ion geometry identical with that of neutral OCS.[25] However there is an indication that a vibration of ~800 cm$^{-1}$ may be involved, which would be consistent with the calculated $\nu_{CS}$ of 938 cm$^{-1}$.

With the identification of $S_2$ and $N_2S$ in the HeI spectra of the gas-phase thermal decomposition of **1**, it is clear that both products are found at all temperatures used for the measurements. We can examine two alternative mechanisms for their production, in particular a concerted reaction leading directly to atomic sulfur (eq 2) and the bimolecular decomposition of $N_2S$ following its formation from **1** (eq 3). In the photoelectron spectra in Figure

$$2N_2S \longrightarrow 2N_2 + S_2 \qquad (3)$$
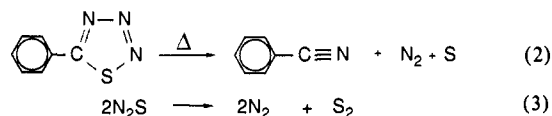
**1** we can follow the various pyrolysis products via a single sharp peak of each, of benzonitrile at 11.84 eV, of $N_2$ at 15.58 eV, of $S_2$ at 13.20 eV, and of $N_2S$ at 15.36 eV. Relative to the benzonitrile product the increase in temperature results in a decrease in the proportion of $N_2S$ formed and increases in the proportions of $N_2$ and $S_2$. While the respective peak heights cannot be used as quantitative measures of the amounts of each compound present, there seems to be more $N_2S$ produced than $S_2$ at the lowest pyrolysis temperature, 165 °C, where they are both observed.

This suggests that $S_2$ is a secondary product arising from the bimolecular decomposition of $N_2S$ according to eq 3. Since we are dealing with a very short path-length gas-phase reaction, it seems inconceivable that S atoms could arise by eq 2 and escape detection. Likewise, only $S_2$ and not monoatomic S was detectable in the short path high vacuum mass spectrometric study.[1] Moreover the operation of eq 2 was deemed unimportant on the basis of absence of a nitrogen kinetic isotope effect.[3] It is likely that bimolecular association is often a prelude to formal "sulfur" extrusion from labile compounds in the form of $S_2$, for example, as in eq 4 or 5. Further investigations on this point using other sulfur-containing compounds (e.g., nitrile sulfides[1]) are underway.

$$2 \ \bar{N} = \overset{+}{N} = S \longrightarrow \bar{N} = N - S - S - \overset{+}{N} \equiv N \longrightarrow 2N_2 + S_2 \qquad (4)$$
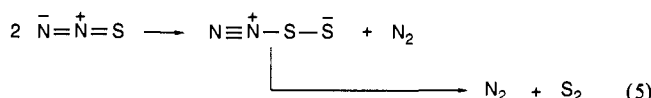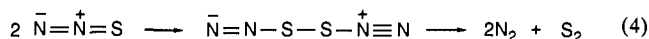
The fact that there is probably more $N_2$ present at 165 °C again indicates that either or both of reactions 2 and 3 are occurring with reservations concerning eq 2 as stated above. It is also conceivable that some sulfur is removed as polymeric $S_n$ prior to detection. Elemental sulfur only produces $S_2$ slowly on heating in vacuum, but this process does not appear to be important under the experimental conditions used here. The observation of a relative decrease in the proportion of $N_2S$ clearly indicates that it is kinetically less stable at the higher temperatures, decomposing to $N_2$ and $S_2$.

## Conclusion

The He I photoelectron spectrum of dinitrogen sulfide, $N_2S$, was measured in the mixture of products of the thermal decomposition of 5-phenyl-1,2,3,4-thiatriazole. Both the adiabatic ionization energy of 10.55 eV which is 0.63 eV lower than that of its analogue OCS and its second ionization energy of 15.36 eV which is only 0.22 eV lower than the first IE of $N_2$ with which it correlates are indicative of a comparatively weak N–S interaction in the linear $N_2S$ molecule. The high reactivity of $N_2S$ is indicated by the presence of $S_2$ in all spectra, suggesting that a bimolecular decomposition of $N_2S$ is also occurring at all pyrolysis temperatures. $N_2S$ is likely to prove to be a highly reactive 1,3-dipole, similar to $CH_2N_2$, and is of potential use in chemical synthesis.

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