Infrared Spectra of Binary Selenium–Nitrogen Species Formed by Condensation of Microwave Discharge Products

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Condensation of a microwave discharge excited stream of argon–nitrogen–selenium gives NSe, NSe_2 and NSe_2^+ which are characterized by IR spectroscopy with ^{15}N, ^{76}Se and ^{80}Se isotopic substitution.

A large number of binary sulfur–nitrogen species have been prepared and isolated including SN^+, SNS^+, $S_3N_2^+$, S_2N_2 and S_4N_4.[1,2] Under the proper conditions S_4N_4 can be oxidized and the $[NS_2^+][AsF_6^-]$ salt isolated;[2] the extensive chemistry of SNS^+ has been recently reviewed.[3] However, early attempts to prepare Se–N cations from reactions of alkali metal azides with $[Se_4][AsF_6]_2$ were not successful.[4] Reactions of Se_4N_4 and AsF_5 in liquid SO_2 have been shown to give $Se_3N_2^+$ and $Se_3N_2^{2+}$, which may involve the intermediate cations $SeNSe^+$ and SeN^+, but unlike the analogous sulfur cations, the small intermediate cations are not stabilized with the more reactive selenium species.[5,6] The only known neutral selenium nitrides are Se_4N_4 and the transient SeN diatomic radical.[5–7]

We report here the identification of binary selenium-nitrogen species SeN, NSe_2 and NSe_2^+ in a solid argon matrix, which are analogous to the sulfur–nitrogen species reported earlier.[8] The experimental methods for microwave discharge and FTIR matrix spectroscopy have been described previously.[8,9] This work was greatly facilitated by the use of ^{76}Se (>99%) and ^{80}Se(>92%) isotopic samples obtained from the Kurchatov Institute, Moscow, and $^{15}N_2$ gas.

IR spectra are shown in the 1270–1200 and 1030–910 cm^{-1} regions in Figs. 1 and 2 for ^{76}Se–$^{14}N_2$, ^{80}Se–$^{14}N_2$, ^{n}Se–$^{14}N_2$ and ^{n}Se–$^{15}N_2$ passed through the argon supported discharge. The observed isotopic frequencies are listed in Table 1 for the ^{n}Se (natural isotopic selenium), ^{76}Se and ^{80}Se reactions. The observation of doublets in mixed nitrogen isotopic experiments indicates that the product species contain a single nitrogen atom.

Weak bands at 955.0 and 947.9 cm^{-1} with ^{76}Se are shifted to 951.4 and 944.4 with ^{80}Se (Fig. 2). These bands bracket the high-resolution gas phase fundamentals of $^{76}Se^{14}N$ at 948.198 and $^{80}Se^{14}N$ at 944.542 cm^{-1}.[7] The 76–80 isotopic ratios of the matrix and gas phase bands, 1.00378, 1.00371 and 1.00387, are in excellent agreement. The higher matrix site is blue shifted 6.8–6.9 cm^{-1} from the gas phase values and the lower is red shifted 0.1–0.3 cm^{-1}. The 76–14/76–15 isotopic ratios are 1.0290 and 1.0292 slightly under the 1.0293 harmonic value as expected for the small amount of cubic anharmonicity in the observed fundamentals. Clearly two different argon packing arrangements (matrix sites) around SeN are important: one is more repulsive (probably completely surrounded) than the other (probably a surface site).

The very strong 1021.2 cm^{-1} band dominates the spectrum. Following assignment of the strongest product band in the sulfur–nitrogen discharge system to the bent (153 ± 5°) NS_2 radical, where mixed sulfur isotopic spectra revealed two equivalent S atoms,[8] the 1021.2 cm^{-1} band is assigned to ν_3 of the bent NSe_2 radical. The selenium and nitrogen isotopic frequencies confirm this assignment and indicate a similar

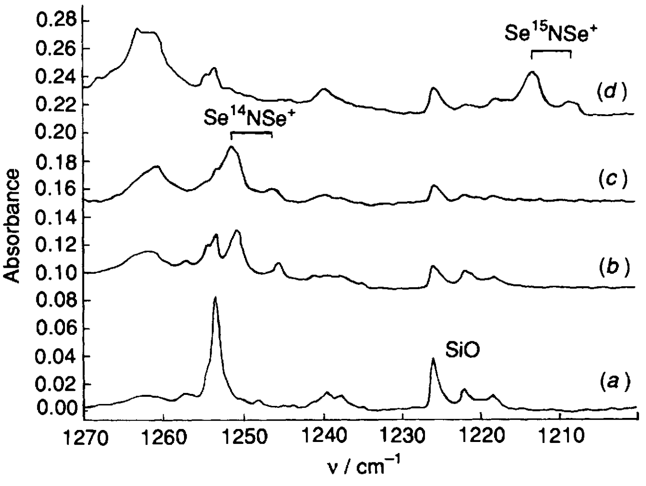

Fig. 1 IR spectra in the 1270–1200 cm^{-1} region for selenium seeded Ar/N_2 = 50/1 microwave discharged stream condensed at 12 ± 1 K for 10 h. (*a*) ^{76}Se + $^{14}N_2$, (*b*) ^{80}Se + $^{14}N_2$, (*c*) ^{n}Se + $^{14}N_2$, and (*d*) ^{n}Se + $^{15}N_2$. The bands at 1225.7, 1221.9 and 1218.3 cm^{-1} are due to SiO from the discharge tube: see J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, 1969, **51**, 4189.

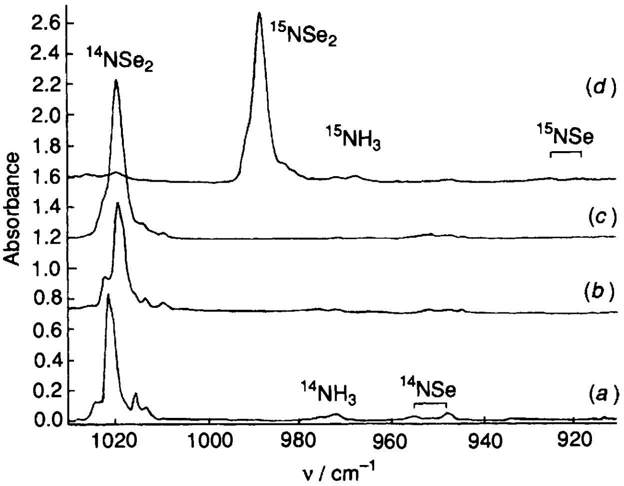

Fig. 2 IR spectra in the 1030–910 cm^{-1} region for same samples described in Fig. 1 caption. Weak bands at 974.6, 971.7 cm^{-1} are due to $^{14}NH_3$ and weak bands at 970.1, 967.2 cm^{-1} are due to $^{15}NH_3$: see S. Suzer and L. Andrews, *J. Chem. Phys.*, 1987, **87**, 5131.

Table 1 Major IR absorptions (cm^{-1}) observed in condensed argon–nitrogen–selenium stream subjected to microwave discharge

^{76}Se + ^{14}N	^{80}Se + ^{14}N	^{76}Se + ^{15}N	^{80}Se + ^{15}N	^{n}Se + ^{14}N	^{n}Se + ^{15}N	Identification
1300.1	1297.8	1300.1	1297.8	1298.1	1298.1	CSe_2
1253.3	1250.7	1215.0	1212.4	1251.3	1213.0	$SeNSe^+$ site 1
1248.1	1245.6	1210.1	1207.4	1246.2	1208.0	$SeNSe^+$ site 2
1021.2	1019.0	990.3	988.0	1019.2	988.2	SeNSe
955.0	951.4	928.1	924.3	951.3	924.2	NSe site 1
947.9	944.4	921.0	917.5	944.4	917.5	NSe site 2

geometry for NSe_2. As for NS_2, the ν_1 and ν_2 modes of NSe_2 are too weak to be observed in the infrared spectrum.

Isotopic ν_3 frequency ratios have been used to calculate valence angles for bent C_{2v} molecules such as SO_2, O_3, S_3 and NS_2.[8,10–12] Substitution in the terminal position gives an upper limit and in the central position a lower limit, and the average provides a measure of the valance angle.[10] The selenium 76–80 isotopic frequency ratios for ^{14}N and ^{15}N (1.00216 and 1.00233) define 165° and 159° upper limits and the nitrogen 14–15 isotopic ratios for ^{76}Se and ^{80}Se (1.03120 and 1.03138) define lower limits of 130° and 129°, respectively. The average value 146° is expected to be accurate to $\pm 5°$ and is close to the $153 \pm 5°$ value determined for NS_2.[8]

The 1253.3 cm^{-1} band decreases by 20–30% on Hg arc photolysis and is almost destroyed on annealing to 30 K. Such behaviour is analogous to the 1499.7 cm^{-1} band in the S–N system; this band exhibited a sharp triplet with $^{32,34}S$, a sharp doublet with $^{14,15}N$, and isotopic ratios appropriate for an antisymmetric S–N–S vibration with a large obtuse angle.[8] Following experience with N_2–O_2 discharges that give NO, NO_2 and N_2O_3,[13] the 1499.7 cm^{-1} band was assigned to N_2S_3.[8] However, the isotopic frequency ratios in Table 2 show excellent agreement with calculated ratios for the ν_3 vibration of a linear molecule. The great reactivity of this species and its relationship to the 1225.2 cm^{-1} NS_2 fundamental suggest reassignment to SNS^+. The infrared observation of (SNS^+) in (AsF_6^-) and ($SbCl_6^-$) salts[2] at 1494 and 1498 cm^{-1} supports reassignment of the 1499.7 cm^{-1} band to SNS^+ isolated in solid argon.

It follows that the analogous 1253.3 cm^{-1} band and 1248.1 cm^{-1} site in the Se–N system (Fig. 1) above NSe_2 at 1021.2 cm^{-1} can be assigned to $SeNSe^+$.† The observed isotopic frequency ratios and harmonic ratios calculated for the linear model are in excellent agreement (Table 2). Owing to cubic anharmonicity the observed values fall slightly below the calculated harmonic values. The cation is made by photoionization of the radical with argon resonance radiation in the discharge.[14] The cation absorbance in these experiments is typically 3% of the radical absorbance. The electron removed is antibonding thus leading to an increase in bond angle and ν_3 frequency for the cation as compared to the radical.

Additional support for the identification of $SeNSe^+$ at 1253.3 cm^{-1} is found in observation of the isoelectronic SeCSe molecule at 1300.1 cm^{-1}.[15] Again the observed and calculated 76–80 isotopic ratios are in excellent agreement (Table 2). The strong ν_3 CS_2 fundamental at 1528.2 cm^{-1} in solid argon[16] is likewise above SNS^+ at 1499.7 cm^{-1} in solid argon.

Table 2 Observed and calculated isotopic frequency ratios for linear SNS^+, $SeNSe^+$, and SeCSe ν_3 fundamentals.

	Observed	Calculated
32–14–32/34–14–34	1.005416	1.005327
32–14–32/32–15–32	1.02777	1.02839
32–15–32/34–15–34	1.005567	1.005636
34–14–34/34–15–34	1.02792	1.02870
76–14–76/80–14–80	1.002079	1.002122
76–14–76/76–15–76	1.03152	1.03184
76–15–76/80–15–80	1.002145	1.002260
80–14–80/80–15–80	1.03159	1.03199
76–12–76/80–12–80	1.00177	1.00184

The great reactivity of SNS^+ and $SeNSe^+$ on annealing follows that in preparative chemistry.[5,6] Three bands at 737.5, 617.2 and 528 cm^{-1} in the Se–N single-bond stretching region[6,17] increase on annealing. These bands are under analysis for possible identification as neutral or charged selenium–nitrogen ring species.

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Footnote

† The sharp 1254.5, 1253.4 cm^{-1} band and broad 1262 cm^{-1} bands are due to impurities in the discharge system that do not involve nitrogen based on the absence of a N-15 shift. Some of the 1253.3 cm^{-1} band in Fig. 1(*a*) is due to this impurity, possibly SeSiO, and some is due to the $SeNSe^+$ species identified here.

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