

Matrix Isolation Study of the Dissociation and Isomerization Pathways of Benzene following Corona Discharge Excitation

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Reactions of C_6H_6 and C_6D_6 after exposure to a corona-excited discharge have been studied by the trapping of products into an argon matrix at 14 K. Infrared spectroscopy was employed to identify product species; most were known species and identified by comparison to literature spectra. Tentative assignments for several previously unreported deuterated products are made. The product distribution included species from both rearrangement and dissociation processes. In general, the product distribution differed from previous UV irradiation studies; a mechanism for product formation is proposed. The effectiveness of the corona excitation discharge as a simple source for the generation of transient organic species for matrix spectroscopic study was confirmed.

Introduction

Free jet expansions have proven useful both in producing interesting species and in simplifying the analysis of their spectra.^{1,2} A number of both pulsed and continuous discharge sources have been coupled to free jet expansions.^{2,3} Among these, the corona-excited supersonic expansion (CESE) has been demonstrated to be an effective tool to prepare ions and radicals for spectroscopic study.⁴ Several polyatomic organic radicals, including CH_3O and CH_3N , have been generated by CESE and characterized by emission spectroscopy.^{5–10}

The matrix isolation (MI) technique was developed for the isolation and characterization of a range of reactive intermediates, including neutral radicals and molecular cations.^{11–14} Spectroscopic probes can include vibrational and electronic absorption and emission. Coupling of CESE with MI has the potential to merge an effective technique for the production of short-lived species with a well-known technique for the isolation and study of these interesting species. An apparatus for this coupling has been designed, and test results were reported recently.¹⁵ It was noted that the relative yield of radical and charged products depended on the mode of deposition; the mechanism of product formation was not determined.

Isomerization and dissociation reactions of aromatic compounds represent a fascinating area for mechanistic and theoretical study and have received extensive attention. Aromatic rings are known to isomerize to both cyclic and open-chain isomers following UV irradiation in the gas and liquid phases. The mechanism of the isomerization process has been reviewed and discussed by Bryce-Smith and Gilbert.¹⁶ Two matrix isolation studies of the photochemistry of C_6H_6 using different UV sources revealed in several new products that did not appear in the early gas-phase studies.^{17,18} Recent molecular beam studies of the photodissociation of benzene at 193 and 248 nm revealed new channels under collision-free conditions.¹⁹ In contrast, little is known about the products arising from irradiation of C_6D_6 . The study reported here had as goals to (1) trap and characterize new intermediate species and to (2) investigate the mechanism of product formation in CESE–MI studies.

Experimental Section

The apparatus designed to couple a CESE to a conventional matrix isolation system has been described.¹⁵ In the present study only the twin-jet mode was employed; in a single-jet mode the aromatic compounds produced heavy soot deposits inside the nozzle, clogging the orifice and preventing gas flow. In the twin-jet mode, argon was passed through the nozzle and the corona-excited discharge, while a mixture of Ar/C_6H_6 was introduced into the vacuum vessel from a second line. This gas mixture was subjected to the argon discharge downstream from the nozzle at roughly a 90° angle, then rapidly condensed on the cold window. All of the geometric and discharge parameters influencing the operation

of the discharge, production of species, and optical quality of the matrix were examined and optimized. Generally, the back pressure on the nozzle was 400–700 Torr, with an argon flow rate of about 6 mmol/h. Typical discharge currents ranged from 450 to 500 μA at voltages between 12.5 and 15.0 kV. When this potential was applied to the electrodes, a small bright violet glow was noted at the nozzle tip. A green jet formed when an Ar/C_6H_6 mixture was exposed to this discharge.

Benzene (Baker and Adamson) and benzene- d_6 (Aldrich) were degassed by freeze–thaw cycles at 77 K prior to sample preparation. Samples with Ar/C_6H_6 ratios (M/R) of either 200 or 500 were discharged and deposited for about 6 h. Final spectra were recorded from 4000 to 400 cm^{-1} at 1- cm^{-1} resolution on an IBM 98 Fourier-transform infrared spectrometer.

Results

Prior to any discharge experiments, blank spectra were run with both C_6H_6 and C_6D_6 in solid argon. In all of the blank spectra, good agreement with literature spectra was noted. Exposure of a sample of $Ar/C_6H_6 = 500$ to a CESE followed by matrix trapping led to a large number of new infrared absorptions, some of which were quite intense. These are listed in Table I. These product bands were reproducible over a range of experiments employing the same concentrations. When M/R was increased to 200, an overall higher yield of product was noted, as described in Table I and shown in Figures 1 and 2. In general, new products were not observed as a result of the increase in concentration. When the excitation voltage was increased from 12.5 to 15 kV, the product absorption at 3312 cm^{-1} was seen to increase significantly (from 0.4 to 0.17 OD) as seen in Figure 3, while parent absorptions, and the product absorptions at 736, 913, and 1001 cm^{-1} , markedly decreased.

Similar experiments were conducted employing samples of $Ar/C_6D_6 = 200$, and a number of new absorptions were noted. These are shown in Figure 4 and listed in Table II. In general, fewer product bands were seen with C_6D_6 than with C_6H_6 , and those that were observed had lower intensities, although they were still distinct and reproducible.

Discussion

Numerous new absorptions were seen in the spectra of matrices after exposure of Ar/C_6H_6 samples to the CESE. Many of the product absorbers may be identified as known chemical species on the basis of comparison of spectra to the literature. As noted in Table I, the two major products are fulvene²⁰ and 1,3-hexadien-5-yne.²¹ Less intense absorptions were noted for benzvalene, benzyne,²² triacetylene,²³ ethyne,²⁴ ethene,²⁵ and the phenyl radical,²⁶ $C_6H_5^{\cdot}$. While a few weak bands remain unassigned, these species account for nearly all of the product absorptions.

Product identification is somewhat more difficult with C_6D_6 , since little data are available on the infrared spectra of inter-

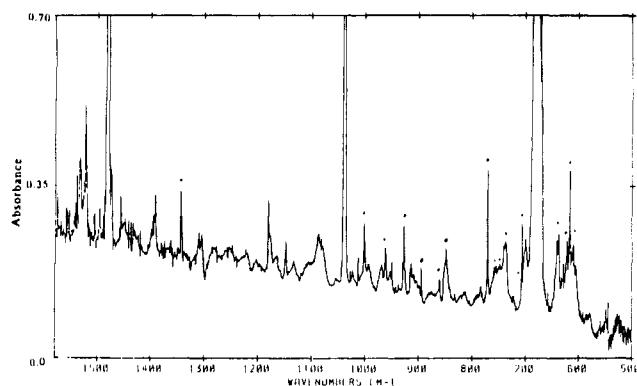


Figure 1. Infrared spectrum from 500 to 1600 cm^{-1} of the products of the corona-excited discharge of a sample of $\text{Ar}/\text{C}_6\text{H}_6 = 200$ followed by trapping at 14 K, with a discharge voltage of 12.5 kV. The dots denote product absorptions.

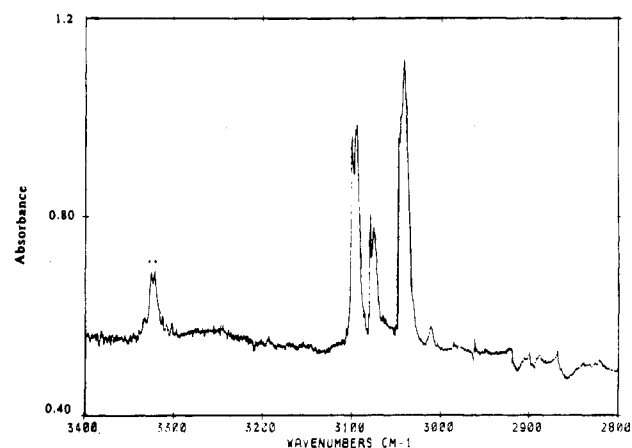


Figure 2. Infrared spectrum from 2800 to 3400 cm^{-1} of the products of the corona-excited discharge of a sample of $\text{Ar}/\text{C}_6\text{H}_6 = 200$ followed by trapping at 14 K, with a discharge voltage of 12.5 kV. The dots denote product absorptions.

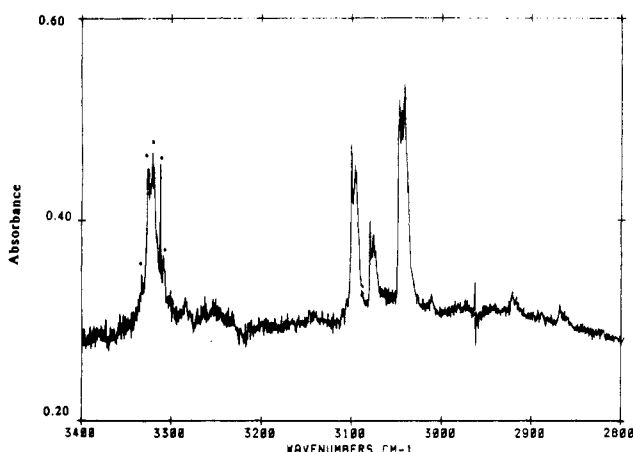


Figure 3. Infrared spectrum from 2800 to 3400 cm^{-1} of the products of the corona-excited discharge of a sample of $\text{Ar}/\text{C}_6\text{H}_6 = 200$ followed by trapping at 14 K, with a discharge voltage of 15 kV. The total amount and concentration of sample was the same as in Figure 2. The dots denote product absorptions.

mediate isomers of the deuterated species. A few bands can be assigned on the basis of band position and comparison to the C_6H_6 experiments. The alkynic C-D stretching modes of triacetylene- d_6 and 1,3-hexadien-5-yne- d_6 should be located near 2600 cm^{-1} , by analogy to a number of deuterated alkynes. Product bands were observed at 2594, 2597, and 2601 cm^{-1} with band profiles that were very similar to the C-H stretching modes of triacetylene and 1,3-hexadien-5-yne between 3320 and 3330 cm^{-1} . They are appropriate for assignment to the corresponding C-D stretching modes. Since triacetylene was higher in frequency than 1,3-

TABLE I: Product Band Positions,^a Intensities, and Assignments after Twin-Jet Corona Discharge Excitation of C_6H_6 and Argon Matrix Trapping

position	absorbances		assignment	ref
	$M/R = 200$	$M/R = 500$		
3327	0.12	0.12	triacetylene	23
3324	0.06		triacetylene	23
3320	0.12	0.12	1,3-hexadien-5-yne	21
3312	0.04		triacetylene	23
1343	0.14	0.07	fulvene	18, 20
1232	0.02		triacetylene	23
1080	0.01		fulvene	18, 20
1001	0.12	0.04	1,3-hexadien-5-yne	21
961	0.08			
952	0.05		fulvene	18, 20
949	0.05		ethene	24, 25
927	0.12	0.14	fulvene	18, 20
913	0.06	0.03	1,3-hexadien-5-yne	21
896	0.06		fulvene	18, 20
849	0.10		benzynes	22
771	0.24	0.14	fulvene	18, 20
762	0.08		benzvalene	20
756	0.07			
742, 739	0.12		benzvalene	20
737	0.11	0.08	ethyne	24, 25
736	0.10		benzynes	22
708	0.05		phenyl, C_6H_5^+	26, 27
706	0.16	0.05	phenyl, C_5H_5^+	26, 27
644	0.15	0.07		
639	0.16	0.12	1,3-hexadien-5-yne	21
637	0.10	0.10	1,3-hexadien-5-yne	21
627	0.09	0.08	triacetylene	23
621	0.16	0.10	triacetylene	23
616	0.26	0.15	fulvene	18, 20
469	0.06		benzynes	22

^a Band positions in cm^{-1} . Experimental conditions: 12.5 kV; 450 μA ; $M/R = 200$, 10.3 mmol of sample and 40.2 mmol of Ar deposited in 6 h.

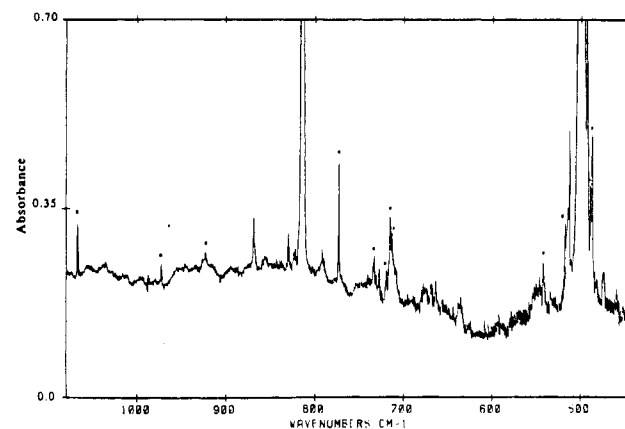


Figure 4. Infrared spectrum from 400 to 1100 cm^{-1} of the products of the corona-excited discharge of a sample of $\text{Ar}/\text{C}_6\text{D}_6 = 200$ followed by trapping at 14 K, with a voltage of 12.5 kV. The dots denote product absorptions.

hexadien-5-yne, the same assignments are made for the deuterated species. The alkynic C-H bending modes were observed near 620 cm^{-1} ; the deuterium counterparts would be expected in the region 480–515 cm^{-1} . A product doublet was noted at 488, 489 cm^{-1} and is likely assigned to one of the deuterated product alkynes. However, there are insufficient data to choose between assignment to 1,3-hexadien-5-yne- d_6 and triacetylene- d_6 .

A sharp, moderately intense product absorption was observed at 773 cm^{-1} in the C_6D_6 experiments. The hydrogen counterpart should lie at higher energies, up to 40% higher for a pure hydrogenic motion (although with anharmonicity and carbon participation in the vibration, the shift should be less than this limiting value). Since this was one of the most intense product bands observed in the deuterium experiments, it likely corresponds to

TABLE II: Band Positions, Absorances, and Tentative Assignments for Products of the Corona Discharge Excitation of C_6D_6 ^a

position ^b	absorbance	tentative assignment	ref
2601	0.08	triacyetylene- d_2	c
2597, 2593	0.12	1,3-hexadien-5-yne- d_6	c
2469	0.05	ethyne- d_2	24, 25
2458	0.03	benzyne- d_4	19
1067	0.08		
987	0.01		
913	0.03		
829	0.06	benzyne- d_4	19
792	0.05	benzyne- d_4	19
773	0.18	fulvene- d_6	c
733	0.06	benzyne- d_4	19
719	0.04		
716	0.12		
713	0.10		
543	0.08	ethyne- d_2	24, 25
518	0.14	phenyl, $C_6D_5^*$	27
489, 488	0.27	1,3-hexadien-5-yne- d_6 or triacyetylene- d_6	c
475	0.07	benzyne- d_4	19

^a Experimental parameters: 12.5 kV, 450 μ A, 11 mmol of sample and 27.5 mmol of argon deposited for 8 h, twin-jet mode, $M/R = 200$.

^b Band positions in cm^{-1} . ^c Tentative assignment, this work.

one of the most intense products in the C_6H_6 experiments. Candidates, then, include the deuterium counterpart of either the 927- cm^{-1} band of fulvene or the 1001- cm^{-1} band of 1,3-hexadien-5-yne. The fulvene band is assigned^{18,20} to an out-of-plane bending mode, while the 1001- cm^{-1} band of 1,3-hexadien-5-yne has not been assigned to a specific mode.^{21a} Thus, one predicts a significant deuterium shift for the former, while no prediction can be made for the latter. Overall, based on magnitude of shift and band profile, tentative assignment to fulvene- d_6 is made, although assignment to 1,3-hexadien-5-yne- d_6 cannot be ruled out.

Additional product bands were observed, which can be assigned to the known benzyne- d_4 , ethyne- d_2 , and $C_6D_5^*$ species by comparison to literature spectra.^{19,24,25,27} All assignments are listed in Table II. A number of quite weak bands remain unassigned, and, since literature spectra are not available for many of the possible deuterated products, assignments cannot be made at this time.

Photochemical rearrangements of benzene have been studied many times and there are similarities between photochemical processes and those occurring here. The major products obtained here at lower voltage and current (fulvene and 1,3-hexadien-5-yne) are quite similar to those obtained after irradiation of C_6H_6 vapor at low pressure with 185-nm light. The major products noted at higher discharge voltage and current (triacyetylene and fulvene) are quite similar to those obtained after prolonged 160-nm irradiation of argon matrices containing C_6H_6 .

Differences between photochemical processes and those occurring here are also apparent. The minor products in these different experiments are not all the same; in particular, the earlier studies made no report of formation of the phenyl radical, $C_6H_5^*$. A distinct band was observed here at 706 cm^{-1} , with a shoulder at 708 cm^{-1} . This matches well the most intense band of $C_6H_5^*$, a species that has been isolated in argon matrices after either microwave discharge of Ar/ C_6H_6 samples²⁶ or reaction²⁷ of F atoms with C_6H_6 . Although Sodeau and co-workers¹⁸ report a band of Dewar benzene at 706 cm^{-1} , other strong bands known to be due to Dewar benzene (for example, at 793 cm^{-1}) were not observed. This rules out assignment of the absorption seen here to Dewar benzene and supports assignment to $C_6H_5^*$. Also, observation of a new band at 518 cm^{-1} when C_6D_6 was employed slightly higher in energy than the analogous mode in parent C_6D_6 supports assignment to C_6D_5 .

When benzene was excited to the $^1B_{1u}$ state (S_2) by absorption at 193 nm under collision-free conditions, dissociation of the excited benzene occurred¹⁹ through three primary channels: $C_6H_5 + H$ (80%), $C_6H_4 + H_2$ (16%), and $C_5H_3 + CH_3$ (4%). While the experiments conducted here are not in a collision-free regime,

they are at quite low pressure, and one might expect a similar product distribution. Thus, formation of $C_6H_5^*$ is quite reasonable. Moreover, by analogy to the earlier studies, production of the open-chain isomer and triacyetylene suggests that the energy imparted to the C_6H_6 precursor (whether photochemically or through argon metastables, see below) is equivalent to a photon of 160 nm or shorter. Under these conditions, the C-H bond dissociation channels should be open. Thus, one might well expect to see C_6H_5 as well as C_6H_4 , as was observed.

Triacyetylene was observed as the dominant product (in terms of band intensity, not absolute yield) at higher discharge voltage and current. This is in agreement with the results of Greenburg,¹⁷ who exposed argon matrices containing benzene to prolonged 160-nm irradiation. The decreased yield of 1,3-hexadien-5-yne and benzyne suggests that they may be the precursor species to triacyetylene via H_2 loss. Higher photon energy or longer irradiation time leads to secondary processes and to triacyetylene in this case.

While H atom and H_2 elimination products were observed, at a lower discharge voltage rearrangement products dominated. The relevant excited electronic states are 4.72, 6.20, and 7.0 eV above the ground state and correspond to $^1B_{2u}$ (S_1), $^1B_{1u}$ (S_2) and $^1E_{1u}$ (S_3).²⁸ In the present studies, then, sufficient energy is available to populate S_3 , or higher, levels. In earlier studies, deactivation of upper electronic states led to a highly vibrationally excited ground state S_0^* or S_1 (B_{2u}). Nakashima and co-workers²⁹ have studied this process and suggest that the cooling process competes with the chemical reaction and rearrangement processes. Several vibrationally hot isomers can be produced from benzene in S_0^* or S_1 in competition with collisional deactivation. These isomers can then be collisionally stabilized and trapped in the cryogenic matrix. This mechanism provides a rationale for the formation and subsequent detection of several different isomers of C_6H_6 .

The mechanism of product formation in the present experiments with corona discharge excitation is of interest as well. The previous report from this laboratory on corona discharge of CCl_4 left this question unanswered.¹⁵ Baldwin et al.³⁰ have reported a nozzle beam source incorporating a DC discharge a high voltage and a cooled nozzle that can be used to prepare relatively high populations of rare gas excimers, such as Ar_2^* . The emission spectrum of the argon excimer near 105 and 107 nm showed that vacuum ultraviolet radiation from argon excimers can be comparable to that of the atomic resonance lines under these conditions. Argon excimers may be formed when a metastable monomer, formed by electron impact, undergoes a soft collision with a second monomer in its ground electronic state. The experimental conditions in the present study are quite similar to those employed by Baldwin. Consequently, it is likely that radiation from argon excimers as well as from the atomic resonance lines are present during the corona discharge process. Of course, metastable argon atoms may also be present, as well as argon ions. Whether benzene excitation occurs through the absorption or one or more vacuum ultraviolet photons or through collision with an argon metastable is not readily determined. Excitation through collision with an argon ion is less likely, in that no evidence of $C_6H_6^+$ or daughter ions was observed. The reaction of Ar^+ with C_6H_6 would be expected to lead to charge transfer and polyatomic cation formation. In effect, the CESE apparatus used here serves as a windowless argon resonance lamp with high energy and low current. Earlier studies of windowless argon lamps excited with microwave energy led to an extensive debate about the role of argon metastables versus irradiation in product formation.³¹⁻³⁴ While significant evidence in support of photons, not metastables, initiating product formation was produced, it is difficult to directly transfer that evidence to the corona-excited discharge used here. What can be concluded is that the coupling of a relatively inexpensive CESE with matrix isolation has significant potential for the formation and isolation of polyatomic organic radicals if experimental parameters are carefully optimized.

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Infrared and Visible Spectra of Small Selenium Clusters ($n = 2, 3, 4$) in Solid Argon

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Se_2 , generated by thermal decomposition of selenium vapor, was condensed with argon at 12 K; in concentrated samples, both Se_2 and Se_4 were isolated in good yield. The forbidden transition between the fine structure components of the $X^3\Sigma_g^-$ state of Se_2 was observed directly: $\Delta\nu_{10} = 513.9 \pm 0.1 \text{ cm}^{-1}$. Two different Se_4 isomers were observed: One isomer is characterized by an IR band at 345 cm^{-1} and a near-IR (710–850 nm) electronic absorption consisting of a progression in the symmetric stretching mode. The other Se_4 isomer has an IR band at 370 cm^{-1} and a broad, featureless electronic absorption with a maximum at 632 nm. When the products of a microwave discharge in argon seeded with either selenium vapor or H_2Se were condensed, spectra of Se_3 were observed in addition to all the Se_4 bands. The ν_3 fundamental for Se_3 was observed at 350 cm^{-1} , and an electronic absorption with 11 peaks assignable to a progression in the symmetric stretching mode extended from 480 to 575 nm.

Introduction

When sulfur, selenium, or tellurium vapors are superheated and codeposited with a large excess of argon on a cold substrate, the diatomic molecule is readily isolated. The ultraviolet-visible spectrum of S_2 was studied in frozen inert gas matrices nearly 30 years ago;^{1,2} Bondybey and English extended the spectroscopy of matrix-isolated S_2 in two seminal papers.^{3,4} More recently, the matrix isolation technique has been extended to the examination of Se_2 ,^{5,6} Te_2 ,^{6,7} and the three mixed diatomic molecules TeSe , TeS , and SeS .⁷ In typical experiments, the concentration of diatomic molecules is much less than one molecule per thousand argon atoms.

To study larger aggregates, it is necessary to increase the concentration of chalcogen species by at least an order of magnitude. Under these circumstances, the diatomic molecules may react to form tetratomic molecules, and in the presence of atoms, triatomic molecules may also be formed. Early experimental work on S_3 and S_4 was published by Meyer and coworkers,^{8–11} pursued by several others in intervening years, and reexamined in our own laboratories using separated isotopes.^{12,13} On the basis of the accumulated evidence it is concluded that the S_3 molecule trapped in the matrix has C_{2v} geometry and that two different isomers of S_4 are trapped.^{10–13} It was, therefore, of interest to discover

whether the behavior of selenium parallels that of sulfur.

The resonance Raman spectrum of Se_3 isolated in argon and nitrogen matrices has been studied in detail.¹⁴ In that work, Se atoms, generated by superheating selenium vapor to 1100°C , reacted with Se_2 (the dominant species in the vapor at this temperature) on the surface of the matrix to give Se_3 . Schnöchel et al. also observed 10 fluorescence bands and estimated the origin of the transition at about $17\,000 \text{ cm}^{-1}$.

Theoretical insight into possible structures for the Se_3 and Se_4 molecules can be gained both from comparisons with S_3 and S_4 , for which high-level calculations have been done,^{15–18} and from molecular dynamics and density functional (MD/DF) calculations for Se_3 and Se_4 .¹⁹ The MD/DF calculations suggest that Se_3 is characterized by two nearly degenerate singlet structures—a D_{3h} ring and an open C_{2v} structure—and that the open structure lies about 0.3 eV below the ring structure. The MD/DF calculations found two low-lying singlet states of very similar energies for Se_4 : a cis ground state and a planar, trans, excited state. The first triplet state and a rectangular D_{2h} configuration were found to lie about 0.3 eV higher.

Given the paucity of information on these systems, it was decided to examine the matrix isolation spectroscopy of selenium species at concentrations of selenium which favor production of