

On the Constituents of Aqueous Polyselenide Electrolytes: A Combined Theoretical and Raman Spectroscopic Study

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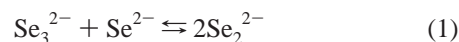
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Received October 14, 1998

Abstract: The speciation of aqueous polyselenide solutions at high pH values has been investigated by Raman and UV/vis absorption spectroscopy. Complementary, ab initio molecular orbital calculations at the HF/6-31+G* level of theory have been carried out on the vibrational frequencies of polyselenide dianions Se_x^{2-} ($x = 2-4$), polyselenide radical anions Se_x^- ($x = 2, 3$), and protonated polyselenides HSe_x^- ($x = 1-3$) in order to substantiate the assignment of the experimental Raman spectra. Although the optical spectra suggest the successive formation of Se_2^{2-} , Se_3^{2-} , and Se_4^{2-} with progressive oxidation of the solutions, only two characteristic Raman bands are observed at 269 and 324 cm^{-1} . A sequence of overtones of the 269 cm^{-1} band is observed after excitation with blue light. Likewise strong overtones of the 324 cm^{-1} band appear after excitation with green light. The 269 cm^{-1} feature is assigned to Se_4^{2-} while the 324 cm^{-1} band is attributed to the radical anion Se_2^- . The occurrence of polyselenide radicals in aqueous solution is without precedent, and the formation of Se_2^- is ascribed to a photolytic process in the electrolyte. The only protonated species observed in this study is HSe^- , which is characterized by a Raman band at 2303 cm^{-1} .

Introduction

Aqueous polyselenide solutions are frequently used as electrolytes in high-efficiency photoelectrochemical cells with photoanodes made of cadmium chalcogenides or gallium arsenide.¹⁻³ Despite the technical interest, these polyselenide electrolytes are relatively poorly characterized. Fairly complicated equilibria⁴⁻⁷ have been reported between various protonated and deprotonated polyselenides, but so far, the actual composition of the solutions is still open to question. Lyons and Young⁴ carried out the most comprehensive investigation, but no distinction between protonated and deprotonated Se_x^{2-} was made. They reported a mean oxidation state of the Se-saturated solution equivalent to that of $\text{Se}_{3.8}^{2-}$ in good agreement with earlier work,⁵ but their ⁷⁷Se NMR experiments required highly concentrated solutions and yielded only one broad signal for electrolytes in different oxidation states while their ESR results did not reveal any paramagnetic species.⁴ However, the optical absorption curves and the results of potentiometric titrations were analyzed independently assuming the formation of four single species Se_x^{2-} with $x = 1-4$ characterized by formal redox potentials.⁴ Licht and Forouzan⁶ performed a subsequent spectrophotometric study taking into account the equilibrium between HSe^- and Se^{2-} and determined the equilibrium constants, $\text{p}K_{23} = -0.7$ and $\text{p}K_{34} = -4$, for:



These values are in fair agreement with those by Lyons and Young,⁴ $\text{p}K_{23} = -0.3$ and $\text{p}K_{34} = -3.5$. A recent electrospray mass spectroscopy (ESMS) study by Raymond et al.⁷ (i) indicated the presence of Se_3^{2-} and protonated polyselenides that have not been taken into consideration in earlier studies and (ii) found Se_4^{2-} to be predominant at high pH regardless of the nature of the cation in the solution. In stark contrast to the earlier spectrophotometric studies,^{4,6} Raymond et al. conclude that both equilibrium constants K_{23} and K_{34} are <1 for $\text{pH} > 9$.⁷ A recent ⁷⁷Se NMR study on Se_x^{2-} in various solvents by Cusick and Dance⁸ identified oxidized Se species with $x = 3-6$, but no evidence was found for the existence of Se_2^{2-} in water.

Here we use Raman spectroscopy for the structural identification of Se_x^{2-} in aqueous solution. Lyons and Young dismissed this optical technique in their investigation on account of the intense color of concentrated polyselenide solutions.⁴ However, the well-separated optical transitions of Se_x^{2-} with $x = 2-4$ in the visible region^{4,6} provide in principle a very selective detection method which can be exploited by adjusting the excitation wavelength to produce resonance. To consolidate the assignment of the experimental Raman spectra, we have performed ab initio molecular orbital calculations on the structure and vibrational spectra of polyselenide species in various states of oxidation and protonation.

Experimental Section

Preparation of Polyselenides. We used aqueous solutions of H_2Se at high pH and added calculated amounts of H_2O_2 to generate polyselenide solutions of varying mean oxidation state. All solutions were prepared in a glovebox under nitrogen atmosphere. A typical

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Table 1. Composition of the Polyselenide Solutions Used in the Present Study^a

mean Se oxidation level	equivalent polyselenide	0.08 M H ₂ Se soln, mL	0.10 M H ₂ O ₂ soln, mL	2 M KOH soln, mL	H ₂ O, mL
-2	Se ²⁻	12.5	0	25	62.5
-1	Se ₂ ²⁻	25	10	25	40
-2/3	Se ₃ ²⁻	37.5	20	25	17.5
-1/2	Se ₄ ²⁻	50	30	25	0

^a The solutions were designed to give optimum concentrations of the respective polyselenide.

preparation is described below. Stock solutions of 2 M KOH and 0.1 M H₂O₂ were deoxygenated by bubbling Ar gas through them for 15–20 min. Saturated H₂Se solutions were prepared by bubbling the gas into deoxygenated water in a septum sealed flask. At 28 °C and under atmospheric H₂Se pressure the concentration of this solution is 8.4×10^{-2} M.⁹ Then, appropriate amounts of these solutions (Table 1) were combined to obtain 0.01 M Se_x²⁻ with nominal mean selenium oxidation states of -2, -1, -0.67, and -0.5 (i.e. $x = 1, 2, 3, 4$), respectively, in 0.5 M OH⁻ solution (pH 13.7).

For the spectroscopy measurements the polyselenide solutions were filled under N₂ atmosphere in sealed quartz cuvettes. Prior to the Raman measurement an absorption spectrum of each solution was recorded with a Varian Cary 5 spectrophotometer. The setup for the Raman measurement consisted of a triple Jobin Yvon T64000 spectrometer equipped with an optical multichannel analyzer.¹⁰ Multiple lines in the visible range of the emission spectrum of an argon and a krypton ion laser were used for excitation: 457.1, 476.2, 488.0, 514.5, 530.9, 568.2, 647.1, and 676.4 nm. The resolution of the instrument was set to 3 cm⁻¹. Due to the strong coloration of the solutions, the penetration depth of the excitation light was very small and the Raman spectra had to be recorded in 45° backscattering geometry.

Computational Methods. *Ab initio* molecular orbital calculations were performed using the Gaussian 94 computer program.¹¹ The Hartree–Fock (HF) method with the 6-31+G* basis set¹² was used in the determination of the structures and harmonic vibrational frequencies of all clusters. The frequencies presented here are scaled by the factor 0.893.¹³

Theoretical Frequencies

Optimized geometries of polyselenides Se_x⁻ ($x = 2, 3$), Se_x²⁻ ($x = 2-4$), and HSe_x⁻ ($x = 2, 3$) are shown in Figures 1 and 2 while their relative stabilities and vibrational frequencies are grouped in Tables 2 and 3. We are aware of only one earlier theoretical investigation dealing with the radical anion Se₂⁻. Heinemann et al.¹⁴ calculated the structure of the X²Π_g ground state at the MRCI and the CCSD(T) level of approximation and reported bond distances of 2.306 (MRCI) and 2.290 Å (CCSD(T)), slightly larger than our value of 2.260 Å which is in good agreement with the experimental bond distances deduced from photoluminescence spectra of Se₂⁻ implanted into KI ($r = 2.25$ Å)¹⁵ and sodalite ($r = 2.26$ Å).¹⁶ The scaled HF/6-31+G* vibrational frequency of 326 cm⁻¹ compares favorably with

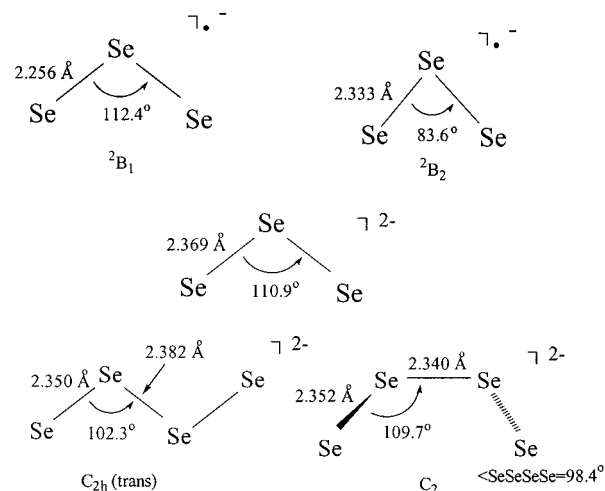


Figure 1. HF/6-31+G* optimized geometries of Se₃⁻, Se₃²⁻, and Se₄²⁻. The bond lengths of Se₂⁻ and Se₂²⁻ are 2.260 and 2.415 Å, respectively.

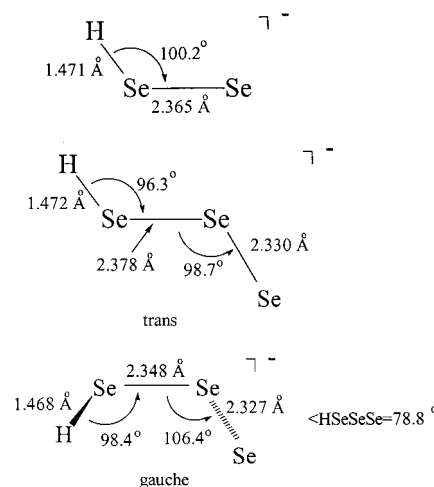


Figure 2. HF/6-31+G* optimized geometries of HSe₂⁻ and HSe₃⁻. The bond lengths of HSe⁻ is 1.475 Å.

experimental values: 329 and 328.5 cm⁻¹ for Se₂⁻ implanted in zeolite Y^{10,17} and KI,¹⁵ respectively.

The triselenide radical anion Se₃⁻ has been studied in a couple of earlier computational investigations.^{14,18} In agreement with Heinemann et al.¹⁴ we find a C_{2v} geometry and a ²B₁ ground state with a bond distance of 2.256 Å, slightly shorter than the CCSD(T) value of 2.284 Å¹⁴ and a bond angle of 112.4° close to their value of 113.5°. Basch performed complete active space multi-configuration self-consistent field (CAS-MCSCF) *ab initio* calculations¹⁸ which yielded two low-lying states of C_{2v} geometry with the ²B₂ state ($r = 2.35$ Å, $\alpha = 115.8^\circ$) favored by 16.6 kcal/mol over the ²B₁ state ($r = 2.39$ Å, $\alpha = 84.1^\circ$). At the HF/6-31G* level, the ²B₂ state ($r = 2.333$ Å, $\alpha = 83.6^\circ$) lies 12.4 kcal/mol above the ²B₁ state. No experimental data are available on the geometry of Se₃⁻, but a Raman band has been reported at 405 cm⁻¹ for Se₃⁻ generated from Se₆²⁻ in acetone solution.¹⁹ This frequency is notably larger than the highest value of the three scaled HF/6-31+G* vibrational modes of the ²B₁ state (107, 235, and 293 cm⁻¹) and different from any of the ²B₂ state vibrational modes at 152, 267, and 471 cm⁻¹.

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Table 2. Calculated HF/6-31+G(d) Frequencies for Se_x^{2-} and Se_x^{2-} Anions

	relative energy ^a	ω_{calc} (cm ⁻¹)	raman activity	IR activity
Se_2^{2-}		365	s	
Se_3^{2-} (² B ₁)	0.0	120	s	w
		263	vs	vs
		328	vs	w
Se_3^{2-} (² B ₂)	12.4	171	s	vw
		300	s	vw
		530	vs	vs
		273	m	
Se_2^{2-} Se_3^{2-} (<i>C</i> _{2v})		103	m	ia
		276	s	ia
		303	s	w
Se_4^{2-} (<i>C</i> ₂)	0.0	50	m	m
		93	m	w
		115	w	m
		277	s	w
		293	s	s
		312	m	m
		32	ia	m
		67	ia	m
		106	m	ia
Se_4^{2-} (trans)	1.3	299	m	s
		303	ia	ia
		305	ia	ia
		55i		
		51		
		134		
		246		
304				
305				

^a Relative energy for different species with more than one structure reported. In kcal/mol.

Table 3. Calculated HF/6-31+G(d) Frequencies for HSe_x^{2-} Anions

	rel energy ^a	ω_{calc} (cm ⁻¹)	raman activity	IR activity
HSe^{2-}		2474		
HSe_2^{2-}		293	s	w
		768	w	m
		2514	vs	s
HSe_3^{2-} (trans)	3.0	85	w	m
		93	w	w
		292	s	m
		300	s	w
		767	m	m
		2528	vs	vs
HSe_3^{2-} (gauche)	0.0	103	w	w
		222	w	m
		291	s	m
		300	m	m
		785	w	m
		2544	vs	s

^a Relative energy for different species with more than one structure reported. In kcal/mol.

We are not aware of any theoretical studies of polyselenide dianions, but experimental structural parameters are available for various bulk compounds featuring polyselenide chains Se_x^{2-} in the range $2 \leq x \leq 6$. Our calculated Se_2^{2-} bond distance of 2.415 Å agrees well with the values reported for Na_2Se_2 (2.43 Å)²⁰ and K_2Se_2 (2.40 Å)²⁰ while the calculated frequency of 244 cm⁻¹ is slightly smaller than the measured value of 253 cm⁻¹ for the bulk K_2Se_2 but in remarkable agreement with Se_2^{2-} confined in the channels of the zeolite cancrinite.²¹ To

assess the influence of the aqueous environment, the complex of the diselenide dianion with one water molecule was studied and found to have a *C*_{2v} structure with the two hydrogen atoms interacting with the two selenium atoms at a Se–H distance of 3.34 Å. Changes in the Se–Se bond length and the stretching frequencies were negligible.

We have here considered a *C*_{2v} and two ring geometries for the triselenide dianion Se_3^{2-} . Both ring variants (*D*_{3h} and one with a double bond) are approximately 60 kcal/mol higher in energy than the open *C*_{2v} structure and can be thus dismissed. The calculated bond distance for Se_3^{2-} (*C*_{2v}) is 2.369 Å, which is in good agreement with the experimental values for the bulk triselenides K_2Se_3 (2.382 Å), Rb_2Se_3 (2.383 Å), and Cs_2Se_3 (2.358 Å).²² However, the calculated angle of Se_3^{2-} (*C*_{2v}) of 110.9° is considerably less compressed than in the condensed phases: K_2Se_3 (102.5°), Rb_2Se_3 (103.1°), and Cs_2Se_3 (103.6°).²² All three computed vibrational modes (scaled: 92 cm⁻¹, 247 cm⁻¹, 271 cm⁻¹) of the *C*_{2v} geometry are Raman active with the two high-frequency vibrations forming a characteristic double band of equal intensity.

Two HF/6-31+G* structures of Se_4^{2-} are separated by about 1 kcal/mol, a *C*₂ conformer being energetically slightly more favorable than the *C*_{2h} trans conformer. The cis structure is more than 12 kcal/mol higher in energy than the *C*₂ conformer and it is only a saddle point on the potential energy surface as indicated by an imaginary frequency. Most notably for the *C*₂ structure the terminal bonds are slightly longer (*r*_t = 2.352 Å) than the center distance (*r*_c = 2.340 Å). The bond angle α of this conformer comes to 109.7° and the dihedral angle γ amounts to 98.4°. These geometrical parameters compare reasonably with a Se_4^{2-} (*C*₂) molecule identified in the ethylenediamine (en) stabilized barium salt [Ba-4en][Se₄]: *r*_t = 2.329 Å, *r*_c = 2.342 Å, α = 112.1°, and γ = 98.4°.²³ Experimental vibrational spectra of this compound have not been measured, but the theoretical calculations indicate three fairly intense Raman bands between 246 and 278 cm⁻¹ (Table 2). A crystal structure containing the *trans*- Se_4^{2-} molecule has been synthesized yielding²⁴ *r*_t = 2.312 Å, *r*_c = 2.397 Å, and α = 103.4° in good agreement with the calculated values for the Se_4^{2-} (*C*_{2h}) isomer: *r*_t = 2.350 Å, *r*_c = 2.382 Å, and α = 102.3°. While experimental data on the vibrational spectra are not available, our calculations indicate a single high-frequency Raman band around 267 cm⁻¹ for this highly symmetric structure.

No structural information is available on protonated polyselenides HSe_x^{2-} , $x > 1$, but our calculations indicate that the bonding of a hydrogen atom to a terminal Se atom is hardly affected by the length of the chain. The H–Se bond length is virtually constant for all structures considered (Figure 2), and accordingly the frequencies for the stretching mode vary by less than 3% from 2209 cm⁻¹ for HSe^{2-} to 2265 cm⁻¹ for the gauche form of HSe_3^{2-} and are smaller than the stretching modes of H_2Se in the gas phase: ν_1 = 2345 cm⁻¹ and ν_3 = 2358 cm⁻¹.²⁵ The stretching mode should be dominant in the Raman spectrum of any HSe_x^{2-} species (Table 3). A second characteristic Raman active mode of the higher polyselenides HSe_x^{2-} , $x > 1$, should appear around 700 cm⁻¹ (Table 3). The calculated vibrational spectra of the two HSe_3^{2-} geometries considered here are virtually identical, the gauche form being more stable than the trans isomer by approximately 3 kcal/mol.

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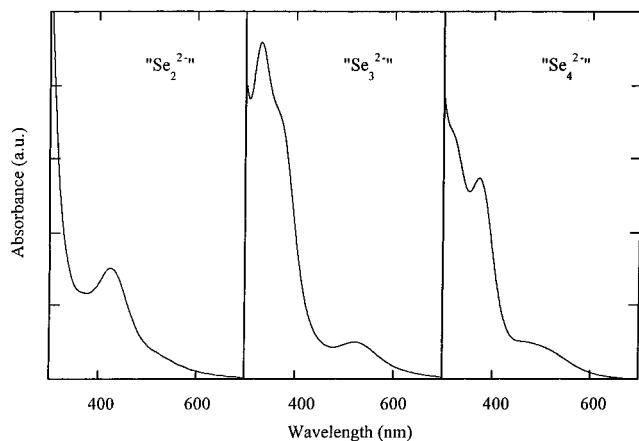


Figure 3. UV/vis spectra of the polyselenide solutions with the degree of oxidation increasing from left to right. The spectra are dominated by the 430 nm band of Se_2^{2-} (left), the 330, 380, and 530 nm transitions of Se_3^{2-} (middle), and the two bands of Se_4^{2-} at 380 and 470 nm (right), respectively.

Experimental Results

Figure 3 shows optoelectronic spectra of typical polyselenide solutions used in this investigation. From left to right the mean oxidation state of the solutions increases. At first as expected, the UV/vis spectrum is dominated by the 430 nm band of the diselenide dianion Se_2^{2-} (left).^{4,6} With increasing oxidation level the three bands attributed to Se_3^{2-} become prominent at 330, 380, and 530 nm (middle).^{4,6} Finally, the highest oxidation level bands at 380 and 470 nm which have been previously assigned to Se_4^{2-} (right)^{4,6} prevail. Thus, by scanning the Raman excitation energy through the visible range of the spectrum, we can resonantly excite the triselenide dianion with green light (530 nm band) and the tetraselenide dianion with blue light (470 nm band). Unfortunately, we have not been able to excite the diselenide dianion (430 nm band) in the same way in the UV range near 400 nm since the laser emission lines at 407 and 413 nm of the Ar ion laser could not be sufficiently stabilized.

Raman measurements on species in solution face the particular problem of the overriding light scattering by the solvent. Due to the hindered motion of molecules in the liquid, the translational and rotational degrees of freedom of gas-phase molecules become restricted translations and librational modes, respectively, which contribute to the Raman spectra. In liquid water very intense Raman bands related to the restricted translations are centered in the vicinity of 65 and 160 cm^{-1} and the librational modes cause very broad Raman scattering between 300 and 900 cm^{-1} .²⁶ The intrinsic modes of the water molecules give rise to broad bands around 1600 cm^{-1} (bending vibrations) and between 3000 and 3800 cm^{-1} (stretching vibrations).²⁶ In practice, this means that Raman bands of the solute unless very intense are completely hidden below 200 cm^{-1} and in the regions of the intrinsic water Raman bands.

Figures 4 and 5 show Raman spectra of polyselenide solutions excited at 530.9 and 476.2 nm, respectively; both spectra include bands at 269, 324, 645, 965, and 1287 cm^{-1} which are not due to water scattering. In Figure 5, the strong fluorescence above 800 cm^{-1} is probably related to the formation of colloidal selenium at the highest levels of oxidation; the two additional relatively broad bands at 538 and 810 cm^{-1} are not due to water scattering and can be readily attributed to overtones of the 269 cm^{-1} band. Likewise, the 645, 965, and 1287 cm^{-1} bands are

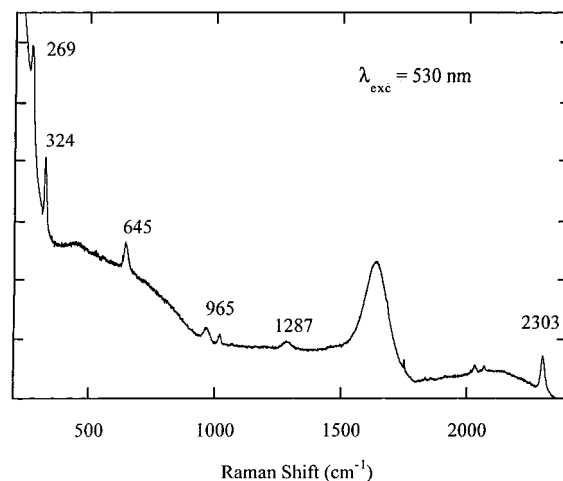


Figure 4. Raman spectrum of a polyselenide solution with mean Se oxidation state -0.67 , i.e., Se_3^{2-} is predominant. At an excitation energy of 530 nm three overtones of the 324 cm^{-1} band are observed at 645, 965, and 1287 cm^{-1} .

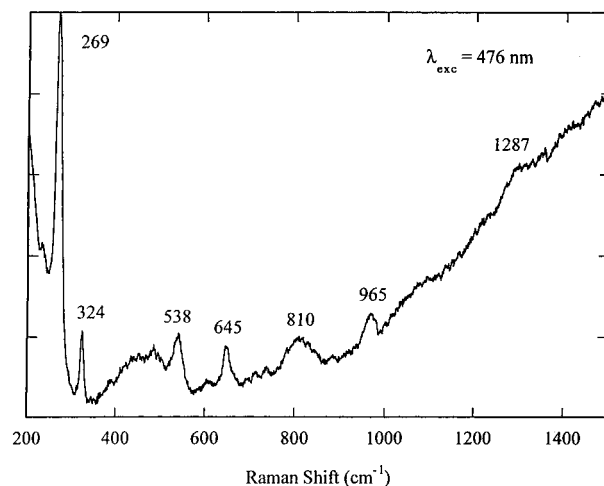


Figure 5. Raman spectrum of a polyselenide solution with mean Se oxidation state -0.5 , i.e., Se_4^{2-} is predominant. At an excitation energy of 476 nm two broad overtones of the 269 cm^{-1} band are observed at 538 and 810 cm^{-1} .

overtones of the 324 cm^{-1} band. The markedly different broadening of the overtones is especially noteworthy. Since natural selenium consists of six isotopes with the fraction of the most abundant ^{80}Se amounting to only 0.50, the energy spread of vibrational levels due to isotopic substitution of the polyselenides increases rapidly with the vibrational excitation giving rise to the observed broadening of the overtones. In addition, this energy spread increases with the number of selenium atoms in the polyselenide species. The broader overtones of the 269 cm^{-1} band compared to the 324 cm^{-1} band indicate a larger number of selenium atoms in the responsible polyselenide species: *the 269 cm^{-1} band originates from a species that includes at least three Se atoms.*

Another remarkable feature in Figure 4 is the well-defined band at 2303 cm^{-1} close to the gas-phase stretching frequencies of H_2Se ($\nu_1 = 2345 \text{ cm}^{-1}$, $\nu_3 = 2358 \text{ cm}^{-1}$)²⁵ and the calculated H–Se stretching modes of HSe_x^- species (Table 3). For clarification, we measured Raman spectra of H_2Se in aqueous solution and in a highly basic solution (Figure 6). While the aqueous solution becomes acidic upon dissolution of H_2Se ($\text{p}K_{a1} = 3.8$),^{27–29} even at pH 14 HSe^- still exists ($\text{p}K_{a2} = 15.0$).^{28,29}

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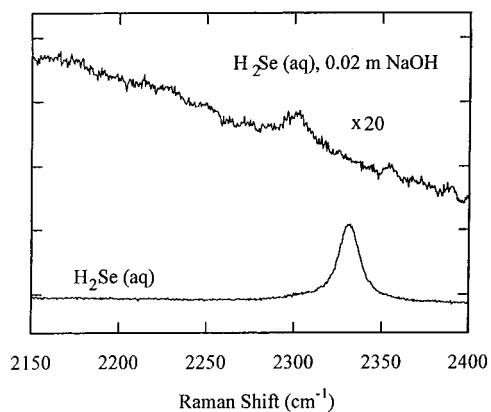


Figure 6. Raman spectra of aqueous solutions of H_2Se (pH 4) and HSe^- (pH 12.3). While one broad stretching mode of H_2Se is found at 2330 cm^{-1} , the corresponding vibrational mode of HSe^- is slightly red-shifted to 2303 cm^{-1} .

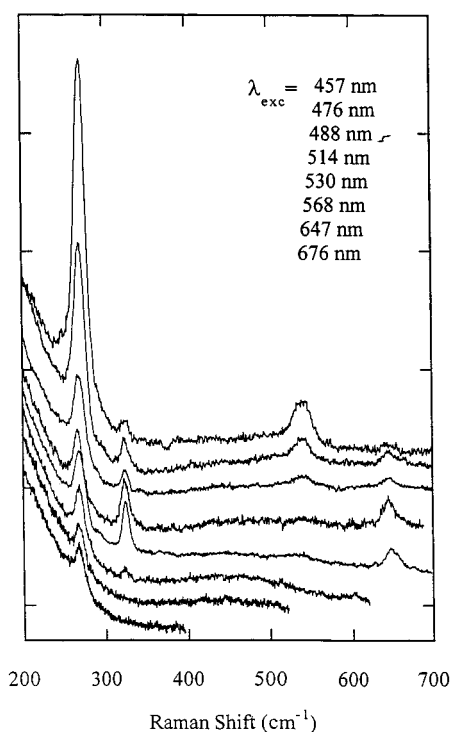


Figure 7. Raman spectra of a polyselenide solution with mean Se oxidation state -0.67 at various excitation energies. The order of the excitation energies from the bottom (676 nm) to the top trace (457 nm) is indicated. The 269 and 324 cm^{-1} bands are resonantly enhanced in the blue and green regions of the spectrum, respectively.

According to Figure 6, H_2Se in aqueous solution is characterized by a Raman band at 2330 cm^{-1} whereas the HSe^- band shifts to 2303 cm^{-1} in perfect agreement with the Raman band displayed in Figure 4.

The bands at 269 and 324 cm^{-1} originate from two different polyselenide species, which can be resonantly excited in different regions of the visible range of the spectrum. To outline the excitation profiles of both species, we repeated the measurements at all excitation energies provided by the argon and krypton ion lasers. The corresponding low-frequency-range spectra are assembled in Figure 7. The band around 269 cm^{-1} is evident at all excitation energies and its intensity increases with the frequency of the excitation radiation above 500 nm .

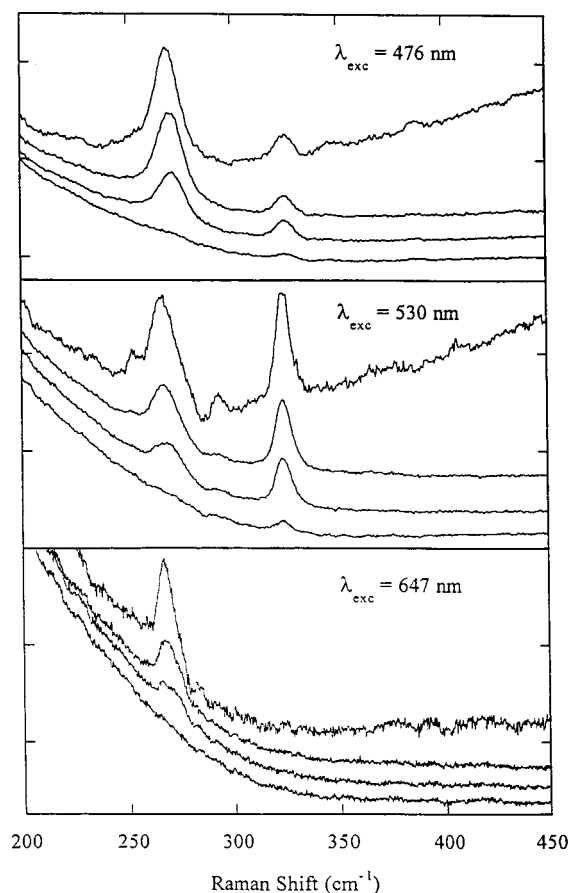


Figure 8. Raman spectra of polyselenide solutions with varying mean oxidation state at excitation energies 476 , 530 , and 647 nm . The bottom traces result from H_2Se solutions with no H_2O_2 added, i.e., Se oxidation state -2 . The remaining traces from bottom to top correspond to solutions with a mean Se oxidation state of -1 , -0.67 , and -0.5 , respectively.

Below 500 nm , the intensity of this band increases at a faster pace and the first overtone becomes visible at 538 cm^{-1} with a maximum in intensity at 457.1 nm . Even though the excitation band for the resonant amplification of the 269 cm^{-1} band is not fully determined, it is clear that the corresponding polyselenide is resonantly excited in the blue region of the spectrum. In contrast, the 324 cm^{-1} band and its first overtone at 645 cm^{-1} becomes weakly perceptible only at 568 nm , reaches a maximum intensity around 530 nm , and then fades when the excitation energy is shifted to the blue. Therefore, the second polyselenide has an absorption band in the green region of the spectrum with a maximum around 530 nm .

Results shown in Figure 3 provide additional support to the earlier spectrophotometric studies suggesting that Se_2^{2-} , Se_3^{2-} , and Se_4^{2-} are successively generated as majority polyselenides in solution by the gradual additions of the oxidizing agent. Figure 8 shows Raman spectra of these polyselenide solutions at increasing oxidation levels recorded at 647.1 , 530.9 , and 476.2 nm , respectively. Unfortunately, even in the absence of H_2O_2 , our selenide solutions have already a weak yellow color indicating the formation of traces of polyselenides generated by residual oxygen in the starting solution. Despite this, no polyselenide Raman band is observed in the starting solution at 647.1 nm excitation (Figure 8), but the 324 cm^{-1} band is already noticeable at 530.9 and 476.2 nm . Upon addition of a small amount of H_2O_2 , a shoulder emerges at 269 cm^{-1} at 647.1 nm excitation and the 324 cm^{-1} band gains intensity at 530.9 and 476.2 nm . Further addition of H_2O_2 leads to

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continuous enhancement of both bands except that the 324 cm^{-1} band is noticeably absent from the spectra excited with red light. The absence of this band at 647.1 nm excitation even at the highest oxidation levels implies a very low concentration of the responsible polyselenide relative to that responsible for the 269 cm^{-1} band. On the other hand, the simultaneous growth of both bands upon progressive oxidation suggests an interactive link between the two species.

Discussion

The assignment of the two overtone sequences starting with the 269 and the 324 cm^{-1} bands is straightforward from the evidence obtained here. The band at 269 cm^{-1} could not be attributed to either Se_2^{2-} or HSe_2^- because of the overtone broadening mentioned above. The triselenide Se_3^{2-} is an unlikely candidate since the only probable Se_3^{2-} geometry C_{2v} is expected to give rise to two Raman bands of fairly equal intensities near 250 and 270 cm^{-1} (Table 2). In addition, one expects the maximum of the excitation profile of Se_3^{2-} around 530 nm following from the reported absorption spectra^{4,6} while the 269 cm^{-1} band is resonantly enhanced in the blue region of the spectrum (Figure 7). Similarly to Se_3^{2-} both conformers of HSe_3^- are expected to exhibit two Raman bands between 260 and 270 cm^{-1} (Table 3) which is not the case here. The occurrence of high concentrations of protonated polyselenides is rather unlikely considering the $\text{p}K_a$ values of H_2Se and H_2Se_2 (vide infra). These considerations lead to Se_4^{2-} as the only deprotonated polyselenide species under consideration. The C_2 conformer is expected to have two or three Raman active modes between 250 and 280 cm^{-1} (Table 2). On the other hand, the computed trans isomer has only one Raman band at 267 cm^{-1} , which is in excellent agreement with the 269 cm^{-1} band: this assignment is supported by the excitation profile mapped out in Figure 5, which indicates a nonlinear enhancement in the blue region of the spectrum. The absorption band of the Se_4^{2-} dianion centered around 470 nm is well established from earlier spectrophotometric studies.^{4,6}

The excitation profile of the 324 cm^{-1} band (Figure 7) matches the lowest energy absorption band attributed to Se_3^{2-} .^{4,6} However, this vibrational frequency is much too high to originate from any polyselenide dianions or protonated polyselenides listed in Tables 2 and 3. But it is well in the range of frequencies observed for the Se_2^- radical anion in various solid-state matrices.^{10,15–17,30} This is rather unexpected since the earlier ESR studies⁴ did not reveal any paramagnetic species in the polyselenide electrolytes. Nevertheless, the lowest lying electronic transition of Se_2^- in solid-state matrices occurs around 500 nm as well.^{15,16,30,31} The actual center of the absorption band depends on the host matrix and is 515 nm in KI,^{15,31} for instance. Therefore, the 324 cm^{-1} band is assigned as the sole vibrational mode of this radical anion.

Protonated species were never considered to play a major role in basic polyselenide solutions. Recently, Levy and Myers²⁹ examined the dissociation of H_2Se in water by UV spectroscopy and established $K_{a2} = (8.8 \pm 0.4) \times 10^{-16}$ in agreement with the value of $10^{-(15.0 \pm 0.6)}$ by Wood²⁸ and much smaller than the value of 10^{-11} reported by Hagisawa.²⁷ Thus, in aqueous environment, fully reduced Se will mostly exist as HSe^- anion and not as naked Se^{2-} dianion. In the early studies, the formation

of HSe^- was deduced from titration curves, while the more recent studies identified it by its UV spectrum. The 2303 cm^{-1} Raman band (Figure 7) is the first structural manifestation of HSe^- in aqueous solution. Among the polyselenides only the dissociation constants of H_2Se_2 are known:³² $K_{a1} = 2 \times 10^{-2}\text{ mol L}^{-1}$ and $K_{a2} = 5 \times 10^{-10}\text{ mol L}^{-1}$. The corresponding dissociation constants of H_2Se_3 and larger hydrogenated polyselenides are expected to be in the same range or even larger. It is reasonable to assume then that only fully ionized polyselenides will exist at pH 13.7. Notwithstanding, Raymond et al.⁷ observed small amounts of HSe_3^- by mass spectroscopy in aqueous solutions, particularly in the presence of NH_4^+ : this is not in contradiction with the above assumption since the ammonium ions neutralize some of the base and lead to the formation of a buffered solution at pH 10. At such low pH values, the polyselenide equilibria may still sustain noticeable concentrations of the hydrogenated forms. However, since we observe only a single Raman band in the vicinity of 2303 cm^{-1} that originates from HSe^- it should be emphasized that the hydrogenated polyselenides do not play a significant role in the electrolytes investigated here.

It is unexpected that Se_4^{2-} is the only polyselenide dianion clearly identified from our Raman results since according to the absorption spectra (Figure 3) Se_2^{2-} and Se_3^{2-} should be the predominant polyselenides.^{4,6} However, Raymond et al.⁷ indicate a predominance of Se_4^{2-} for pH >9 particularly in the presence of K^+ cations. In fact, the mass spectrum obtained for K_2Se_4 dissolved in 0.1 M KOH shows the tetraselenide as the only major component in this electrolyte, whereas the dissolution of Na_2Se_4 in 0.1 M NaOH results in significant amounts of Se_3^{2-} and Se_5^{2-} besides the predominant Se_4^{2-} .⁷ Thus the preeminence of the latter dianion in polyselenide electrolytes containing KOH is not without precedent. It should be noted that the Raman spectra do not completely rule out the occurrence of the di- and triselenide dianions in these solutions. The calculated vibrational spectra indicate that most of the Raman bands of the polyselenides considered fall into a narrow range between 240 and 270 cm^{-1} . Some of these polyselenides may have overlapping vibrational bands and be difficult to distinguish. The intense scattering due to the restricted translation of the solvent (water) complicates the detection of the solute bands and may simply blur minute differences in band positions. Furthermore, the Raman spectroscopic identification of Se_4^{2-} in these electrolytes does not merely rely upon the coincidence between the experimental and the calculated position of the Raman band of the Se_4^{2-} trans isomer. *It is both the resonance enhancement below 500 nm (Figure 7) and the large energy spread of the vibrational overtones due to isotopically substituted molecules (Figure 5) that are pivotal in our assignment of the 269 cm^{-1} band to Se_4^{2-} .*

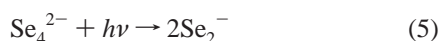
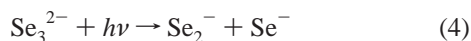
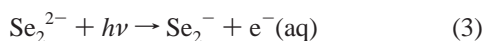
The identification of the Se_2^- radical anion in aqueous solution establishes a new component of polyselenide electrolytes. So far attempts to trace polyselenide radicals in an aqueous environment have not been successful,⁴ although such radicals are suspected to play an important role in photoelectrochemical cells utilizing polyselenide electrolytes. The redox reactions at the surfaces of electrodes in such cells are likely to be one-electron processes involving intermediate paramagnetic species. The one-electron oxidation products of selenide ions, the Se^- , its acid form HSe , and its complexed form HSe_2^{2-} have been identified by pulse radiolysis.³² Nevertheless, experiments show that the formation of polyselenides in the electrolyte is

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prerequisite for sustained photocurrents in the above-described electrochemical cells.¹ Therefore paramagnetic polyselenide species may be crucial in these electrode reactions. The occurrence of the Se_2^- in aqueous solution is not completely unexpected since the complementary S_2^- and S_3^- radicals are known to form in aqueous electrolytes at elevated temperatures.³³ Also, it should be pointed out that in nonaqueous polar solvents such as dimethylformamide (DMF), radical species (e.g., Se_2^- , Se_3^-) have been postulated to exist in high concentrations.³⁴ Because the fundamental 324 cm^{-1} mode is always accompanied by overtones, the Se_2^- bands are due to resonance enhancement and the actual concentration of the radicals may be many orders of magnitude smaller than that of the dianions Se_4^{2-} . It is surprising that the radicals have not been previously found by ESR spectroscopy⁴ which is an extremely sensitive technique for paramagnetic species unless Se_2^- forms in situ during the Raman measurements. Because the polyselenides Se_x^{2-} are all strongly absorbing in the visible region of the spectrum, it is possible that the intense laser radiation used for excitation breaks up one of these dianions to form the radical. Since Se_2^- is detected even in the least oxidized selenide solutions (Figure 8) any polyselenide dianion has to be taken into consideration for a parent molecule:



Se_2^{2-} is the most improbable progenitor because the formation of the radical dianion would require the release of an electron (eq 3). Such a photoionization is highly unlikely in an aqueous environment. In addition, the lowest energy absorption band of Se_2^{2-} is found in the violet around 430 nm .^{4,6} The formation of Se_2^- from Se_2^{2-} under 568.2 nm irradiation will hardly be very efficient even if the onset of the 430 nm transition extends that far into the yellow. The formation of Se_2^- from Se_3^{2-} seems a more plausible route (eq 4), especially when the 530 nm absorption band attributed to this polyselenide is taken into account. It involves the formation of the Se^- radical ion which has been previously obtained in aqueous solution by pulse radiolysis.³² The latter is not a very stable species and dimerizes very fast to form Se_2^{2-} .³² Likewise the Se_2^- radicals are prone to dimerization to form the omnipresent tetraselenide dianion. As such this scenario is quite attractive since it neatly accounts for the seemingly absent Se_3^{2-} . However, at this stage the most probable precursor for Se_2^- appears to be the tetraselenide Se_4^{2-} . It is the only clearly identified dianion here and its 470 nm absorption band extends far enough into the green region of the spectrum to support a photolytic decomposition. The formation of Se_2^- can be simply achieved by symmetrical bond cleavage of the tetraselenide with no need to invoke another energetically less favorable species (eq 5).

Conclusion

The structures and vibrational frequencies of polyselenide dianions Se_x^{2-} ($x = 2-4$), polyselenide radical anions Se_x^-

($x = 2, 3$), and protonated polyselenides HSe_x^- ($x = 1-3$) have been calculated using ab initio molecular orbital theory at the HF/6-31+G* level of theory. The computed geometries and vibrational spectra of Se_x^{2-} and Se_x^- molecules are in satisfactory agreement with the available experimental data. In particular, the vibrational frequencies of the Se_x^{2-} dianions do not exceed 300 cm^{-1} while the radical anions Se_2^- and Se_3^- have higher characteristic modes. The computed Raman spectra of all protonated polyselenides have an intense H–Se stretching vibration around 2250 cm^{-1} . The characteristic band of HSe_x^- molecules with $x \geq 2$ lies in the vicinity of 700 cm^{-1} .

The UV/vis absorption spectra of polyselenide solutions at various mean oxidation levels are in good agreement with optical spectra published by other groups.^{4,6} However, we have observed only two Raman bands at 269 and 324 cm^{-1} which can be ascribed to polyselenide species. The low-frequency mode is assigned to Se_4^{2-} on account of its resonance enhancement below 500 nm (Figure 5) and the large energy spread of the vibrational overtones which is the result of the large number of isotopically different molecules. The high-frequency band does not correspond to any calculated or observed experimental vibrational mode of a polyselenide dianion but is in excellent agreement with the theoretical and measured values of the Se_2^- stretching vibration. This assignment is corroborated by the excitation profile, which indicates an absorption band in the green region of the visible spectrum, where the lowest lying optical transition is known to occur. The lack of Raman spectroscopic evidence in the present work for the previously postulated^{4,6} Se_2^{2-} and Se_3^{2-} is consistent with the conclusions reached from a mass spectroscopic investigation⁷ showing that Se_4^{2-} is the prevalent species at high pH (>9) and especially in the presence of K^+ cations, i.e., the conditions under which the polyselenides were generated here. Also, the initially present triselenide dianions may have been removed by a photolytically induced decomposition leading to the formation of the paramagnetic Se_2^- anion.

The Raman spectroscopic identification of the Se_2^- radical anion in aqueous solution is significant for the understanding of the (electrode) processes that occur in photoelectrochemical cells with polyselenide electrolytes. Previous attempts to locate it in aqueous solution have been unsuccessful⁴ and the exclusive observation of the 324 cm^{-1} band in combination with its overtones after excitation in the (blue-)green spectral range suggests a very low actual concentration of this radical anion. It may form either under the intense laser radiation from Se_4^{2-} or from Se_3^{2-} . Finally, it has been established by Raman spectroscopy that protonated polyselenides apart from HSe^- do not play a significant role in aqueous solutions at pH 13. Furthermore, the observation of the Raman band at 2303 cm^{-1} , even at the highest pH values in aqueous solution, lends further support to the existence of HSe^- as already suggested from the earlier UV-spectroscopic study.²⁹

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. A. Goldbach gratefully acknowledges support from the Deutsche Forschungsgemeinschaft and thanks Dr. M. Grimsditch for generous access to the Raman spectrometer and valuable advice during the collection of the Raman spectra.

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