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Raman Spectroscopic Investigation of Tetraethylammonium Polybromides

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A large number of polyhalides, especially polyiodides, have been discovered and studied, but definitive studies on polybromides remain scarce. Br$_3^-$ is the only monovalent polybromide with a known structure. Higher-order monovalent polybromide anions have been proposed but not structurally confirmed as discrete species. In this study tetraalkylammonium polybromides with molecular formulas R$_4$NBr$_{2x+1}$ (R = ethyl; $x = 1-4$) were prepared by reacting tetraalkylammonium monobromide or tribromide salts with gas-phase bromine. Distinct and characteristic Raman spectra were obtained from the solid polybromides in the spectral range between 100 and 400 cm^{-1}. Experimental Raman spectra were compared to ab initio calculations to propose the structure of these polybromide anions. A general agreement between the experimental and theoretical results was observed. This study demonstrates that Raman spectroscopy is a sensitive technique for probing the structure of discrete monovalent polybromides.

Introduction

Anionic polyhalides are an important class of inorganic ions that have found wide application in the field of supermolecular architecture design.[1] On the basis of conceptually simple Lewis acid−base interactions, polyhalides may adopt complex structures and serve as versatile building blocks. While extensive research has been carried out for polyiodides,[2] polybromide anions have received less attention, despite many practical applications of polybromides for water treatment,[3] battery applications,[4] selective bromination of alkenes,[5] and as a potential dopant for carbon nanotube property modification.[6]

The crystal structures of several polyvalent polybromides have been reported, including Br$_{10}^{2-}$,[7] (Br$^-$)$_2$(Br$_4^{2-}$),[8] and an infinite polybromide network.[9] Tribromide is the only monovalent polybromide that has been systematically studied by crystallographic and vibrational spectroscopic methods.[10] It has been demonstrated that the Raman spectrum of a tribromide salt can be correlated with its structure. The relative intensities of the symmetric and antisymmetric Br−Br stretching modes and their frequencies were shown to be highly sensitive to the bond angle and length. The existence of higher-order monovalent polybromides (with five or more bromine atoms per negative charge) was suggested based on traditional analytical techniques such as titration, melting point, and electrochemical methods.[11] However, they have not been confirmed as discrete species based on spectroscopic evidence nor was any structural information available for these monovalent polybromides. Raman bands around 230−250 cm^{-1} were only tentatively assigned to pentabromides or polybromides in a few publications.[6a,10,12] To the authors' knowledge, this paper is the first systematic investigation of polybromide anions. Tetraethylammonium was used as the cation in this study, and its tribromide, pentabromide, heptabromide, and nonabromide salts were prepared and characterized by Raman spectroscopy. In addition, ab initio calculations were carried out and compared to the experimental results. The most likely structure of each polybromide is proposed.

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Figure 1. Series of tetraethylammonium polybromide samples prepared via gas-phase reactions. The numbers below each sample refer to the molar ratios of Br_2 to Et_4NBr.

Experimental Section

Materials and Polybromide Synthesis. Bromine and tetraethylammonium bromide were obtained from Aldrich and used without further purification. Bromine and tetraethylammonium bromide were gravimetrically measured to prepare the samples with varied molar ratios of bromine to tetraethylammonium bromide. Liquid bromine was placed in a small glass dish at the bottom of a glass desiccator. Tetraethylammonium bromide was ground to a fine powder with a mortar and pestle and was placed in a glass dish on a porcelain tray in the desiccator above the bromine. The desiccator lid was attached (silicone grease was used as the sealant) to allow bromine vapors to contact the solid tetraethylammonium bromide. After standing for 1−4 days at ambient temperature, all liquid bromine in the bottom dish had evaporated. The resulting orange to orange-red solid was removed from the dish and ground to a finer powder consistency with a mortar and pestle before being placed in glass vial for Raman spectral collection.

Raman Spectroscopy Characterization. A Kaiser RXN1 Raman system was used for all Raman spectral characterization. Because of the potential hazards of bromine vapor, spectra were collected from polybromides in sealed glass vials in a backscattering geometry. Laser excitation at 785 nm with approximately 30 mW power was delivered using a PhAT probe (Kaiser Optical Systems, Inc.), which spread the laser power uniformly over a 6 mm spot area to minimize local sample heating. All studied polybromides had strong Raman signals, and care was taken to ensure that there was no detector saturation.

Neutron Activation Analysis (NAA). The total bromine was measured in tetraethylammonium polybromide samples by NAA. The samples were prepared by weighing aliquots of approximately 20 and 30 mg of the bromide salts into polyethylene vials, adding 5 mL of *N*,*N*-dimethylformamide (DMF), and heat-sealing the vials. Triplicate bromine standards were prepared by transferring aliquots of 4-bromobenzoic acid to 2 dram vials, adding 5 mL of DMF, and heat-sealing the vials. All vials were mixed on a vortex mixer until no visible solids were observed. The prepared samples and standards were irradiated for 10 min at a power level of 5 kW in the rotary specimen rack of The Dow TRIGA Research Nuclear Reactor. Spectra of the emitted γ radiation were acquired using two high-purity germanium detectors coupled to a ND/Canberra analyzer system (MCA). The 554, 698, and 777 keV γ-rays from 82-Br were used to quantify the bromine content using 4-bromobenzoic acid (Alfa Aesar lot 10003270) as the external standard.

Ab Initio Calculations. Calculations were performed with the *Gaussian03* software package.[13] Second-order Møller−Plesset perturbation theory (MP2)[14] was utilized with Pople's split-valence double-ζ basis set with d polarization functions [6-31G(d)][15] for geometry optimizations and frequency calculations. Calculations for Br_3^- and Br_5^- anions were carried out with the 6-31+G(d) basis set, which includes diffuse functions. Adding diffuse functions increased the computational requirements but did not improve the predicted harmonic frequencies (see the Supporting Information for details). Although computational requirements for the Br_3^- anion are low, MP2 Raman intensity calculations for the Br_9^- anion are prohibitively expensive with moderately large basis sets like 6-31+G(d). Therefore, MP2/6-31G(d) calculations were used for all polybromide anions.

Results

Polybromides have been demonstrated to form under various conditions including in the solid state, in suspension, and in solution.[11a] Free bromine was observed to be released from polybromides until the tribromide form was reached. The volatility and hazards of bromine make it difficult to study these species using traditional analytical techniques. The formation of polybromides with three, five, seven, and nine bromine atoms per anion has been systematically studied by our group. A series of polybromides with apparent molecular formulas $(CH_3CH_2)_4NBr_{2n+1}$ (n = 1−5) were prepared via gas-phase reactions between Br_2 and Et_4NBr based on procedures similar to those in a literature method.[11a] Polybromides with intermediate molar ratios of Br_2 to Et_4NBr were also prepared. The resulting polybromides changed color from orange to dark red as the Br_2 content increased (Figure 1). The sample with a 5:1 Br_2/Et_4NBr molar ratio was the only one with substantial bromine vapor in the vial headspace. The bromine content was independently verified with NAA (Table 1).

Raman Spectroscopy Characterization. Raman spectra of the polybromides listed in Table 1 are shown in Figure 2. The Raman spectrum from the sample with a 1:1 Br_2/Et_4NBr ratio is consistent with the literature results. It has a strong symmetric Br−Br stretching band at 163 cm^{-1} and a weak antisymmetric band at 198 cm^{-1}. Upon reaction with more Br_2, two new features are observed at 210 and 253 cm^{-1}. For the samples with 1.75 and 2:1 ratios, another band at 270 cm^{-1} appears. This band is the

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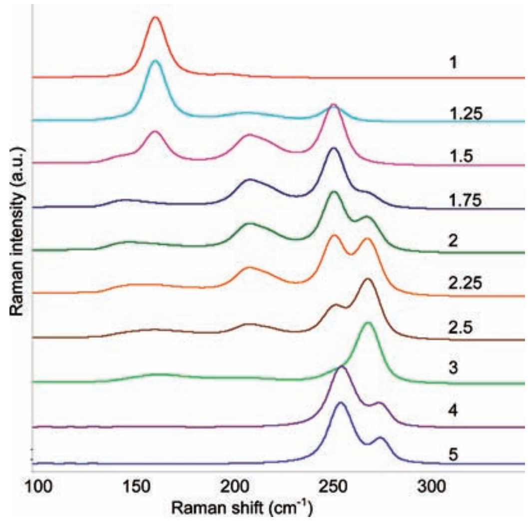


Figure 2. Raman spectra of the tetraethylammonium polybromide samples shown in Figure 1.

Table 1. Summary of the Sample Preparation and NAA Results

$Br_2/(CH_3CH_2)_4NBr$ molar ratio	Br wt % (by NAA)	x in $(CH_3CH_2)_4NBr_x$	
		expected	NAA results
1.00	65.6 ± 1.5	3.0	3.10 (2.91−3.32)
1.25	67.3 ± 1.5	3.5	3.35 (3.13−3.59)
1.50	70.7 ± 1.5	4.0	3.93 (3.66−4.23)
1.75	72.6 ± 1.5	4.5	4.31 (4.01−4.66)
2.00	72.8 ± 1.5	5.0	4.36 (4.04−4.71)
2.25	74.4 ± 1.5	5.5	4.73 (4.38−5.13)
2.50	78.5 ± 1.5	6.0	5.95 (5.45−6.52)
3.00	81.0 ± 1.5	7.0	6.94 (6.32−7.68)
4.00	83.0 ± 2.0	9.0	7.95 (6.94−9.23)

dominant feature for the sample with a 3:1 Br_2/Et_4NBr molar ratio. Two other weaker bands at 165 and 209 cm^{-1} are also discernible from that sample. Upon further incorporation of Br_2, the sample with a 4:1 Br_2/Et_4NBr molar ratio has two bands at 257 and 276 cm^{-1}, and they remain unchanged when the ratio is raised to 5:1.

The spectral changes in Figure 2 provide strong evidence that discrete polybromide species are sequentially formed as the Br_2/Et_4NBr molar ratio is changed from 1 to 4, with distinct and characteristic Raman features observed for samples with 1:1 (tribromide), 3:1 (heptabromide), and 4:1 (nonabromide) ratios. The samples with 1.75:1 and 2:1 ratios, however, have a band at 270 cm^{-1} that can be attributed to heptabromide. The fact that this band was absent from samples with 1.25:1 and 1.5:1 ratios further confirms that the 270 cm^{-1} band should be attributed to heptabromide instead of pentabromide. The presence of heptabromide in a sample with a 2:1 ratio could be a result of equilibrium between Br_2, tribromide, pentabromide, and heptabromide. It could also be a consequence of a heterogeneous reaction between tribromide and Br_2, leading to a mixture of pentabromide and heptabromide in the final sample.

To further investigate the sequential formation of these polybromides, *in situ* Raman spectra were also collected during the bromination and debromination processes. Although the Br_2 loading information from such *in situ* experiments was unavailable, the spectral changes can be explained based on the sequential formation of tribromide, pentabromide, heptabromide, and nonabromide. The spectral evolution observed *in situ* from a heptabromide to a nonabromide sample is shown in Figure 3 as an example. Ab initio calculations provide more insight into the structure of these polybromide anions.

Ab Initio Calculations. Several structures for each polybromide were optimized and are shown in Table 2. A summary of the corresponding calculation results is shown in Table 3. These structures were selected using the VSEPR model (see the Supporting Information for details) and known polyiodide structures.[2a] Closed-ring structures were not stable for any polybromide. Higher-level ab initio calculations at the MP2/6-31G(d) level were carried out for the lowest-energy structure of each polybromide, and Raman bands were assigned based on a comparison of the theoretically and experimentally observed frequencies (Table 4). Low-frequency bands below 100 cm^{-1}, which are generally deformations, were weak and are not listed in Table 4. Vibrational modes described as terminal stretches primarily involve the outer bromine atoms, and apex stretches involve the central bromine atom.

Discussion

Although it was difficult to prepare pure polybromides based on the gas-phase reaction approach used here, the Raman spectrum of pure polybromides could be obtained by spectral subtraction. Shown in Figure 4 are “pure” Raman spectra of all four polybromides after subtraction of neighboring polybromide contributions, based on the assumption that they share no common Raman bands. This assumption is supported by the results observed when the bromination process is monitored with *in situ* Raman spectroscopy (an example involving heptabromide and nonabromide is shown in Figure 3). It was found that, during a slow gas-phase bromination process, the monobromide was sequentially converted to tribromide, pentabromide, heptabromide, nonabromide, and then to some even higher-order bromides, which have not been successfully prepared via the batch-type reaction described in the Experimental Section. The “pure” spectra shown in Figure 4 are eigenspectra whose linear combination can be used to reconstruct most experimentally observed spectra. Normally only two neighboring polybromides coexist at any stage of the bromination process when bromine vapor is slowly exposed to the sample. The only exception was observed during the conversion from tribromide to pentabromide when the sample occasionally became liquid at room temperature before resolidifying. The liquid phase is likely a eutectic formed between tribromide and some intermediate species between tribromide and pentabromide (or pentabromide itself). Much broader bands were observed from the liquid polybromide material, and they could not be well characterized by Raman spectroscopy. Further study will be needed to understand this phenomenon.

All of the polybromide anions in Figure 4 have relatively simple Raman spectra, which indicates that these anions have high symmetry. A comparison between the theoretical and experimental results is summarized in Figure 4 and Table 4. Good agreement was found between the theoretical and experimental frequencies with the exception of heptabromide.

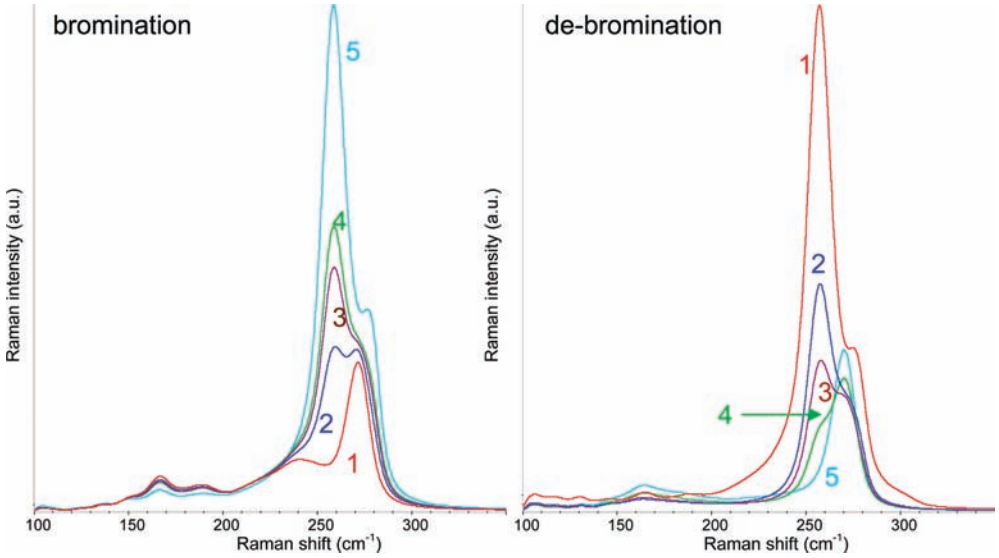


Figure 3. Representative Raman spectra collected during *in situ* bromination from heptabromide to nonabromide (left panel) and the corresponding debromination (right panel). Spectra 1−5 were collected sequentially.

Table 2. Potential Structures for the Polybromide Anions

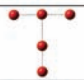
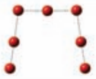
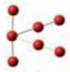
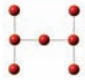
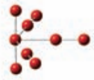
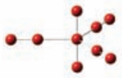
Molecule	Structure Label				
	1	2	3	4	5
Br$_3^-$					
Br$_5^-$					
Br$_7^-$					
Br$_9^-$					

Table 3. Theoretical Calculation Summary for the Polybromide Anions Listed in Table 2

molecule	label	method/ basis set	point group	relative energy (kJ/mol)	imaginary frequency
Br$_3^-$	1	MP2/6-31G(d)	$D_{\infty h}$		0
Br$_5^-$	1	MP2/6-31G(d)	C_{2v}	0.0	0
	2	MP2/6-31G(d)	$D_{\infty h}$	17.2	2
	3	MP2/6-31G(d)	C_{2v}	21.9	0
Br$_7^-$	1	MP2/6-31G(d)	C_{3v}	0.0	0
	2	MP2/6-31G(d)	C_{2h}	14.7	0
	3	MP2/6-31G(d)	C_{2v}	19.6	1
	4	MP2/6-31G(d)	C_{2v}	31.3	0
	5	MP2/6-31G(d)	D_{2h}	125.8	1
Br$_9^-$	1	HF/6-31G(d)	T_d	0.0	0
	2	HF/6-31G(d)	C_s	35.6	1
	3	HF/6-31G(d)	C_{2v}	45.1	0
	4	HF/6-31G(d)	D_{3h}	49.8	3
	5	HF/6-31G(d)	D_{4h}	240.1	2

The tribromide results agree with literature observations.[16] The pentabromide structure is proposed to be V-shaped with C_{2v} symmetry. The trigonal-pyramidal structure with C_{3v} symmetry for Br$_7^-$ provides acceptable agreement with the experimental results, but a better correlation may require the inclusion of the cation in the calculation. A tetrahedral structure with T_d symmetry is proposed for the Br$_9^-$ anion. These structures are similar to but not identical with their polyiodide counterparts.[2]

Many polyiodide structures can be described as iodide (I$^-$) or triiodide (I$_3^-$) coordinated with iodine (I$_2$).[2a] Likewise, the lowest-energy structures for Br$_5^-$, Br$_7^-$, and Br$_9^-$ have a central Br$^-$ coordinated with two or more Br$_2$ molecules. Calculated bond lengths for Br$_2$ and Br$_3^-$ to Br$_9^-$ are shown in Table 5. Bond lengths for the outer bromine atoms in Br$_5^-$, Br$_7^-$, and Br$_9^-$ are much shorter than the inner bond lengths and are similar to those of Br$_2$. As the series progresses from Br$_5^-$ to Br$_9^-$, the outer bonds grow shorter and the inner bonds grow longer.

While earlier papers postulate the existence of pentabromides, heptabromides, and nonabromides mainly based on the reactant composition, there was no experimental evidence regarding whether these polybromides were indeed discrete species or simply composed of monobromides/tribromides with loosely bound bromine. The Raman spectroscopic results presented above provide strong evidence that discrete monovalent polybromide anions exist and the transitions

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Table 4. Comparison between the Experimental and Theoretical Results for the Lowest-Energy Polybromide Anions[a]

			frequency		calcd intensity	
molecule	symmetry	band assignment	exptl	calcd	IR (km/mol)	Raman (Å^4/amu)
Br_3^-	Σ_g^+	sym. stretch	163	171		78.1
	Σ_u^+	asym. stretch	198	218	219.7	
Br_5^-	A_1	terminal sym. stretch	253	252	76.8	139.9
		apex sym. stretch		147	23.0	19.8
	B_2	terminal asym. stretch	210	217	211.5	136.8
		apex asym. stretch		136	172.3	1.2
Br_7^-	A_1	terminal sym. stretch	270	282	47.7	171.0
		apex sym. stretch		135	22.7	6.0
	E	terminal asym. stretch		250	123.2	245.5
		apex asym. stretch		109	70.7	25.8
Br_9^-	A_1	terminal sym. stretch	276	289		438.8
	T_2	terminal asym. stretch	257	265	140.6	425.3
		apex asym. stretch		121	69.5	82.2

[a] Only strong bands from the experimental results are listed.

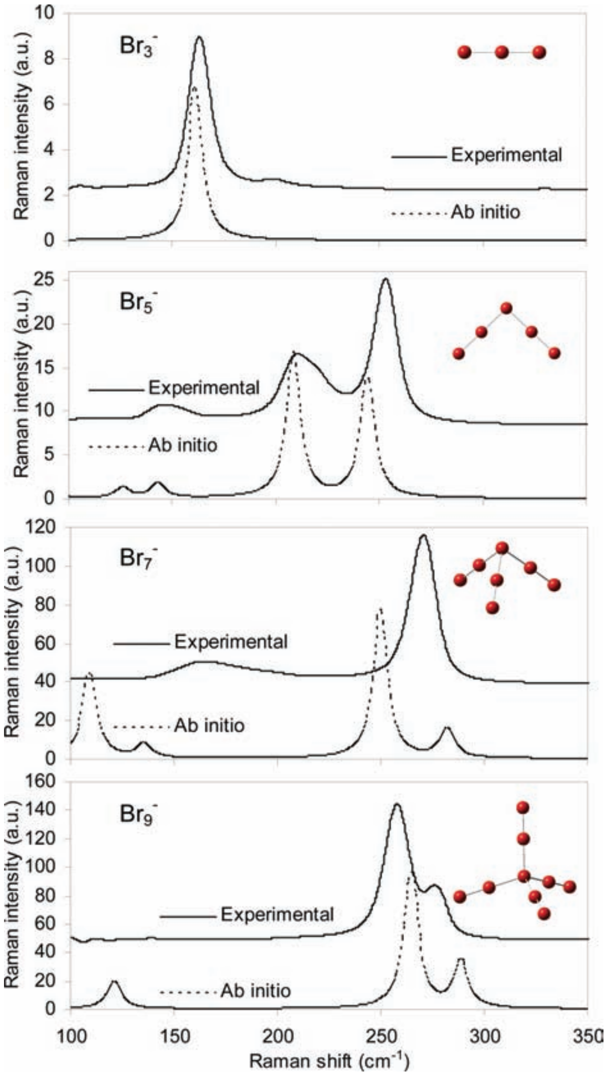

Figure 4. Comparison of the experimental Raman spectra (after subtraction of neighboring polybromides' contributions) and theoretical Raman spectra.

Table 5. Calculated Bond Lengths for Br_2 and Br_3^- to Br_9^-

	bond lengths (pm)[a]	
molecule	inner atoms	outer atoms
Br_2	231	
Br_3^-	258	
Br_5^-	271	246
Br_7^-	282	240
Br_9^-	285	239

[a] MP2/6-31G(d), from calculations in Table 4 except for Br_2.

between them are relatively sharp. Because of the high volatility of bromine, Raman spectroscopy with the PhAT probe's diffuse illumination was found to be the best characterization tool because it allows spectral collection from samples contained in sealed glass vials. Far-IR experiments were also attempted by pressing polybromide samples in a polyethylene powder. It was not possible to prevent bromine vapor evolution except for tribromides. Some examples of far-IR spectra are shown in the Supporting Information.

X-ray diffraction (both powder and single-crystal) experiments were attempted on these polybromide samples to obtain definitive structural information. However, the results were inconclusive because of the difficulty of the sample preparation and handling. Powder X-ray diffraction results indicate that all polybromides studied here were highly crystalline. It was difficult, however, to ascertain the true bromine loading in these samples because of the slow release of bromine. Differential scanning calorimetry (DSC) characterization was also attempted with polybromide samples in small flame-sealed ampoules. DSC results further confirmed the highly crystalline nature of these polybromides. Multiple sharp phase transitions were observed because most samples were a mixture of polybromides. This observation, combined with the possibility of eutectic formation between various polybromides, made it difficult to use DSC to gain further insights into these polybromides. Future X-ray diffraction and DSC studies of these polybromides may yield valuable structural information if these challenges are overcome.

Conclusion

In conclusion, we demonstrate for the first time that discrete monovalent pentabromides, heptabromides, and nonabromides exist based on their characteristic Raman spectra. These spectra were compared to theoretically calculated spectra to further acquire structural insights into these monovalent polybromide anions. Such results provide a framework for the future characterization of various polybromides in various environments and applications.

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Supporting Information Available: Far-IR spectra of tribromide, pentabromide, and heptabromide and ab initio calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.