Resonance-Enhanced Raman Spectra of Iodine Complexes with Amylose and Polyvinyl Alcohol, and of Some Iodine-Containing Trihalides

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Abstract: Resonance-enhanced Raman (RR) spectra of the trihalide ions I_3^-, I_2Br^-, IBr_2^- and their complexes with amylose were obtained by laser excitation at 5680 Å. Iodine complexed with polyvinyl alcohol exhibited a RR spectrum similar to that of the amylose complex. By means of the theory of vibrations of a monatomic, infinite chain, the iodine chain length was calculated to be 28 atoms in both the amylose and PVA complexes. Significantly, different boundary conditions for the iodine chain had to be invoked for the two systems. The Raman spectra of iodine complexed with amylose of various DP (100, 300, and 800) were identical. The incorporation of iodine into a gel-forming solution of PVA or into an oriented PVA film (Polaroid HN-22) yielded Raman spectra which did not differ from those of aqueous iodine–PVA. The Raman spectrum of iodine complexed with a gel-forming solution of agarose coincided with that of iodine–amylose. The Raman spectra of all the halogen-polymer complexes studied, including [iodine + ethanol]–amylose, contained a mode at approximately one-third of the $q = \pi/a$ Brillouin zone, possibly indicating the presence of repeating I_3 units in these polymer complexes.

The resonance Raman effect (RRE), which is characterized by an intensity enhancement of the normal Raman spectrum, is observed when the frequency of the exciting radiation approaches an electronic absorption band of the scatterer.[2] In recently reported studies of the Raman spectra of molecular iodine in the crystalline[3a] and vapor phases[3b] and in liquids,[4,5] the phenomenon of RR was suggested. Consequently, it was anticipated that the trihalide ions I_3^-, I_2Br^-, and IBr_2^-, which absorb strongly in the region of 355–460 nm, would exhibit resonance-enhanced Raman spectra upon excitation in the visible. The RRE was also expected for the inclusion compounds of iodine and iodine bromide with several organic high polymers, such as amylose, amylopectin, agarose, and polyvinyl alcohol. Incorporation of I_2 or IBr into the aforementioned polymers gives rise to a new, very intense absorption band in the visible, as evidenced by the well-known starch–iodine reaction. The structure of the iodine complex with amylose has been determined by X-ray diffraction;[6] the accepted model is that of a linear chain of approximately equidistant (3.10 Å) iodine atoms, in which two iodine atoms are centered inside each gyre (6 glucose units) of the amylose helix. Electrons are able to move substantial distances along the iodine chain in the amylose complex, thus accounting for the bathochromic shift in λ_{max} of the complex as compared with λ_{max} of I_2 or I_3^-. The host polymer in these complexes is transparent to incident radiation in the visible and, therefore, only the included halogen chromophore is excited by irradiation near its electronic transition.

The expectation of obtaining resonance-enhanced Raman spectra of the halogen arrays was fully substantiated. However, in the halogen–polymer complexes the observed spectral lines were accountable in terms of the halogen chromophore; the nature of the polymer was manifest only in affecting the frequency of the length-dependent modes of the halogen array. Therefore, the hope of employing this technique for general structural studies of polysaccharides in iodine-stained tissues was not fulfilled.

Experimental Procedures

In order to obtain the inclusion compounds, the trihalides were prepared by the addition of reagent grade potassium iodide or potassium bromide in excess (~0.1 *M*) to hot aqueous suspensions of 0.1 *M* iodine or iodine bromide (Alfa Inorganics). The cooled trihalide solutions were then mixed to a paste-like consistency with commercial amylose (DP ~300) and amylopectin obtained from Nutritional Biochemicals, and with synthetic amylose (DP 100 and 800) graciously provided by Dr. Robert Ullman. The iodine–PVA complex was formed by addition of aqueous KI + I_2 to a saturated solution of polyvinyl alcohol (Du Pont, grade 72-60) in hot water. A second iodine–PVA complex was obtained by incorporation KI + I_2 into a gel-forming mixture of 5% PVA, 70% H_2O, and 25% ethylene glycol. The iodine–agarose complex was prepared by the addition of KI + I_2 to a hot aqueous solution of 0.50 g of agarose (Aldrich)/50 ml. All the trihalide solutions and the halogen–polymer complexes were allowed to cool a few hours before their spectra were taken. The HN-22 Polaroid sheet, which consists of an oriented polyvinyl alcohol film containing iodine, was generously supplied by C. Moriarty of the Polaroid Corp. Most of the Raman spectra of the starch inclusion compounds were taken with Krypton plasma radiation (568 and 647.1 nm). The spectra of the trihalides were surveyed with several Ar and Kr laser radiations ranging from red to blue for the reason that the relative intensities of the Raman lines depended on the excitation frequency (see below). The scattered radiation was analyzed and detected with a previously described spectrophotometric system.[7]

Results and Discussion

The resonance-enhanced Raman spectra of aqueous solutions of various trihalides and the corresponding polyhalide–polymer complexes are shown in Figures 1–3; the frequencies and polarizations are listed in Table I. The far-infrared and Raman spectra of several trihalides

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Table I. Frequencies of Raman Active Modes in Some Trihalide Ions and Some of Their Inclusion Compounds

	KI + I_2				KBr + I_2				KBr + JBr			
λ_{max} of trihalide ions, nm	355				457				377			
	Raman-active vibrations, cm^{-1} [a]											
Trihalide ion			113	158			112	180			167	
Amylose complex	27	57	107	158	25	54	110	167	27	51	152	181
Aqueous PVA complex	13	49	112	161								
HN-22 Polaroid sheet		48	108	156								
Agarose complex	27		112	156								

[a] All the lines are strongly polarized.

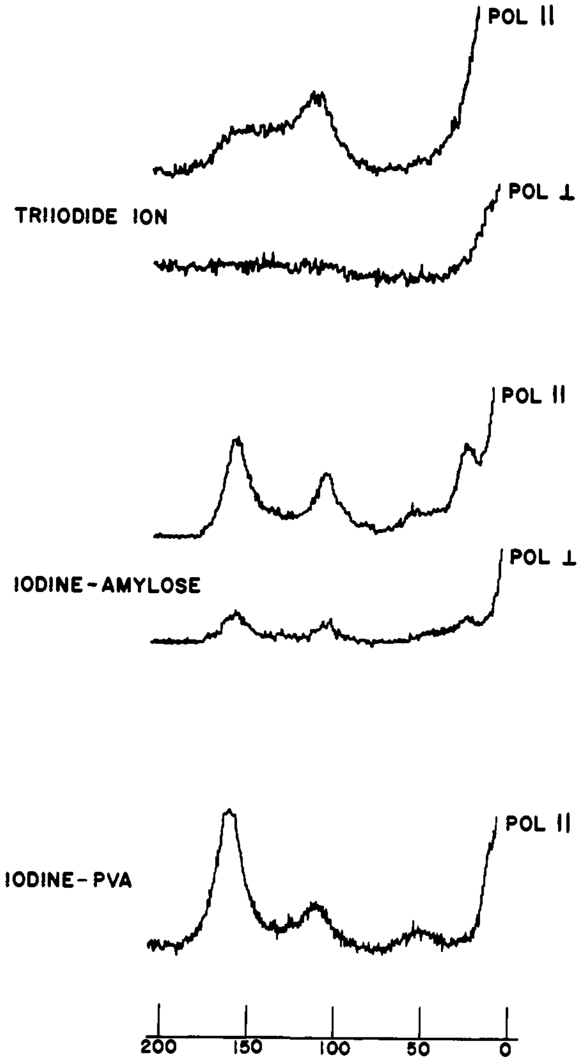

Figure 1. Recorder tracings of the Raman spectra of aqueous KI_3 and its complexes with amylose and polyvinyl alcohol (PVA): excitation at 647.1 nm (Krypton); spectral resolution, 2 cm^{-1}; integration time, less than 1 sec. Polarizations of the scattered radiation with respect to that of the exciting radiation are shown. The mode at lowest frequency, fully resolved in the iodine–amylose spectrum and partly resolved in the iodine–PVA spectrum, is assigned to the lowest frequency, length-dependent mode of the iodine chain.

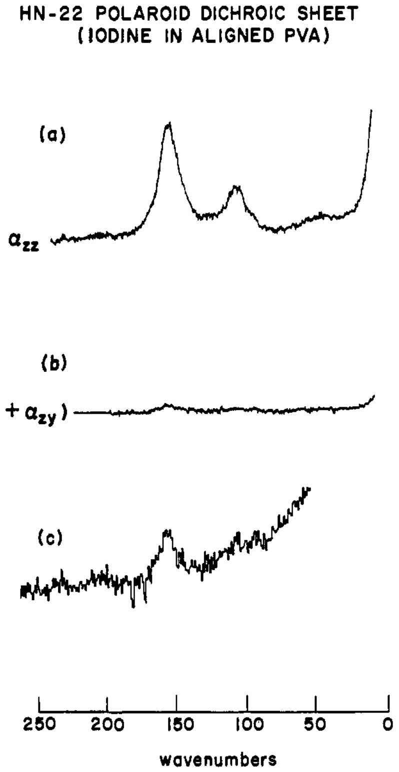

Figure 2. Laser excited (568.0 nm) Raman spectra of polyiodide in a commercial HN-22 Polaroid dichroic sheet. The Polaroid consists of stretched fibers of the iodine-polyvinyl alcohol (PVA) complex. The long axes of the iodine chains (z) are aligned along the axis of maximum attenuation of the sheet. The Raman scattering tensor elements α_{ik} contributing to the spectra are selected as follows. (a) The electric vector E of the laser radiation is *parallel* to z, and the *parallel* (z) component of scattered radiation is detected. The lowest frequency length-dependent mode, discernible as a shoulder in the iodine-PVA solution spectrum (Figure 1), is absent from the Polaroid spectrum (Figure 2a). (b) E is *parallel* to z, and the perpendicular component of the scattered radiation is detected. The dominance of the α_{zz} tensor element and the high degree of chromophore alignment in the Polaroid are evident. (c) E is perpendicular to z, and the polarization of the weakly scattered radiation is not analyzed.

have been reported,[8-10] but no Raman polarization data could be found in the literature. Our Raman data for the triiodide ion are in essential agreement with the earlier results;[8,9] the interesting new feature is the dependence of the intensity distribution in the spectrum on the excitation frequency. As the laser is tuned to shorter wavelengths (red to blue) the relative intensity of the higher frequency mode decreases; in spectra excited at 488.0 nm this subdued mode is evidenced in the strong asymmetry of the 112-cm^{-1} line and it can be located by line shape analysis.

Structural parameters for the triiodide ion,[11,12] obtained by X-ray diffraction, are as follows.

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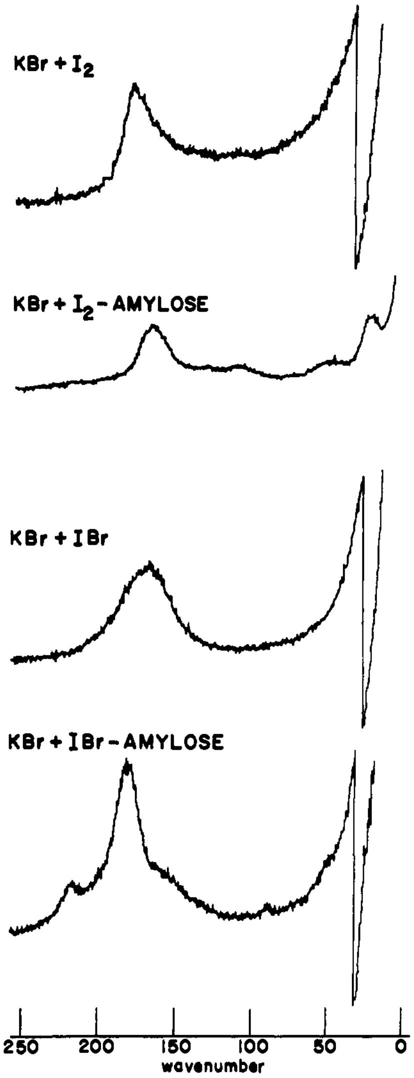

Figure 3. Recorder tracings of the laser (568.0 nm) excited Raman spectra (parallel polarization) of aqueous KBr + I_2 and KBr + IBr and of their respective amylose complexes. The amplitudes near the Rayleigh line fold over due to recycling in the digital system. The KBr + I_2 + amylose spectrum is similar to, but not identical with, the spectrum of KI + I_2 + amylose (Figure 1). The peculiar KBr + IBr + amylose spectrum is characteristic of this particular interhalogen system and is reproducible.

	Distance, Å		Angle, deg	
	I_1–I	I–I_2	I_1–I–I_2	Ref
$(CH_3)_4NI_3$	2.75	2.75	180	11
CsI_3	3.04	2.83	176	12

These X-ray data depict the iodide ion as a linear molecule. The assignment of the trihalide modes involves the following considerations. (a) For a triatomic, linear, symmetric molecule, only one polarized Raman active fundamental is expected. The observation of two Raman active transitions with corresponding fundamentals in the infrared[8,9] may thus be attributed to the asymmetry of the triiodide ion in the aqueous solution of the potassium salt. (b) Assuming a linear, nonsymmetric, triatomic molecule, the polarized Raman lines at 113 and 158 cm^{-1} are assigned to ν_1 (symmetric stretch) and ν_3 (asymmetric stretch), respectively. The absence in the Raman spectrum of the third low frequency fundamental, the perpendicular vibration ν_2, does not contradict the assumed structure, because generally a nontotally symmetric fundamental is weak in Raman spectra.[13] (c) An alternative possibility of a symmetric, nonlinear structure is ruled out because then the ν_3 fundamental (highest frequency) would be depolarized,[13] contrary to the observed polarization of the line at 158 cm^{-1}. (d) An asymmetric, nonlinear structure for I_3^- is another possibility. However, the absence of the third Raman fundamental (the bending mode), which should be strong for this model, indicates that any deviation from linearity is negligible. In any event the 158-cm^{-1} line is relatively weaker than the normally Raman-allowed symmetric mode at 113 cm^{-1}, especially when excited at lower wavelengths. The difference in excitation spectrum is probably related to the fact that vibrations of different symmetry couple to different electronic excited states. For sufficiently small asymmetry of a linear triatomic (case b), the eigenfrequencies are still given to a good approximation by eq 1 and 2.[13] Here a_{11} is the stretching force constant

$$4\pi^2\nu_1^2 = (a_{11} + a_{12})/m \qquad (1)$$

$$4\pi^2\nu_3^2 = 3(a_{11} - a_{12})/m \qquad (2)$$

of the I–I bond, a_{12} is the force constant representing the interaction of the two I–I bonds, and m is the atomic weight. Using the KI_3 frequencies of Table I, eq 1 and 2 yield $a_{12}/a_{11} \simeq 0.2$. It has indeed been noted[10] that the present assignments require abnormally high values for the bond–bond interaction force constant a_{12}.

The triiodide has been shown to be necessary for the formation of colored starch–iodine complexes in aqueous solution.[14] Comparison of the Raman spectra of the triiodide ion or molecular iodine[2–5] with the iodine–amylose complex indicates that the complex is a distinct molecular species. Assuming that the chromophore of the complex is a linear chain of equidistant iodine atoms, an application of the theory of vibrations of a monatomic, infinite linear chain[15–17] yields useful information about the iodine chain length. In the following discussion only the longitudinal waves are considered. The transverse (perpendicular) modes, which are generally weak in Raman spectra, are ignored here because the observed lines in the iodine–amylose spectrum are polarized and have comparable intensities. Thus, considering only nearest-neighbor interactions, the potential energy is given by

$$\begin{aligned}2V = \sum_{n=1}^{N} \{a_{11}(x_n - x_{n-1})^2 + 2a_{12}[(x_{n-1} - x_{n-2}) \times \\ (x_n - x_{n-1}) + (x_{n+1} - x_n)(x_{n+2} - x_{n+1}) + \\ (x_n - x_{n-1})(x_{n+1} - x_n)] + a_{11}(x_{n+1} - x_n)^2\} \qquad (3)\end{aligned}$$

where a_{11} and a_{12} are defined as in eq 1 and 2 and x_n denotes the longitudinal displacement of the nth atom from its equilibrium position. On substitution of a trial traveling wave function $x_n = \xi e^{i(\nu t - qna)}$ into the equation of motion of the nth atom, one has a solution of

$$\begin{aligned}\nu_1^2 = 1/m\{4(a_{11} - a_{12}) \sin^2 (qa/2) + \\ 2a_{12}(\cos (qa) - \cos (2qa))\} \qquad (4)\end{aligned}$$

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q is the wave vector, $q = 2\pi/\lambda$ where λ is the wavelength, a is the interatomic distance, and n is the running index. The dependence of ν_l on q for the positive branch of the curve is shown in Figure 4, where the force constants derived from the triiodide spectrum have been substituted into eq 4. Out of the continuum of modes for the infinite chain, we select those which are congruent with the modes of a finite chain by imposing suitable boundary conditions at two points separated by the length of the finite chain. In conjunction with current models of helical amylose segments interrupted by more randomly coiled segments about which rotation can occur,[18,19] a reasonable initial assumption is one of clamped boundary conditions for the included iodine chains. Since the Raman scattering cross section increases rather rapidly with the spatial wavelength $\lambda = 2\pi/q$ of the vibration,[20] it is reasonable to assume that the mode corresponding to the longest wavelength will give rise to the strongest Raman line,[16,17] provided all the chains are uniform in length. If, as discussed previously, the iodine chain in the amylose complex is considered to have N atoms with an interatomic distance a and the terminal atoms clamped, the first Raman active (inversion symmetric) mode corresponds to $q = 2\pi/L$, $L = (N - 1)a$. For the sine modes (clamped end points) only the even modes $q = 2n\pi/L$ are inversion symmetric and hence Raman active. Therefore, inserting $\nu_l = 27$ cm^{-1} for $q = 2\pi/L$ into eq 4, we obtain $L = 27a$ and $N = 28$. The second Raman active mode ($q = 4\pi/L$), as shown in Figure 1, coincides with the second observed Raman frequency at 57 cm^{-1}. The high frequency mode ($q = \pi/a$) is expected to yield a sharp Raman vibration because it is relatively independent of chain length and hence all the iodine chains, irrespective of length, contribute to the same high frequency mode. Referring to the iodine–amylose spectra, the high frequency line at 158 cm^{-1} is assigned to the longitudinal mode for $q = \pi/a$. The observed value compares well with the calculated value of 157 cm^{-1} (Figure 4). Although the Raman line at 107 cm^{-1} fits the value of the fourth Raman active sine mode (Figure 4), the third mode is absent from all the observed spectra. The presence of the 107-cm^{-1} mode in all the complexes studied by us and the simultaneous absence of the third mode, as well as other spectrophotometric measurements that indicate the presence of I_3^- units in the amylose complex,[21] lend support to the following interpretation. If the polymer-complexed iodine chain consists of I_3 units, then $q' = \pi/3a$ now becomes the edge of a new zone. Therefore, one expects a discontinuity at one-third of the π/a zone, with the two branches of the $\nu_l = \nu(q)$ plot approaching this point with horizontal tangents. The corresponding frequency would again be independent of length. In this model another new zone boundary is predicted at $q'' = 2\pi/3a$. The corresponding vibration, however, essentially coincides with that at $q = \pi/a$ because in this range the dispersion curve (Figure 4) is horizontal. The line at 107 cm^{-1} corresponds reasonably well to $q = \pi/3a$ (dotted line, Figure 4) and its presence is thus interpreted as evidence for repeating I_3 units in the aqueous iodine–amylose complex. A variation of the KI concentration in the KI + I_2 solution had no effect on the iodine–amylose spectrum, indicating the presence of I_3 units even at lower iodide concentrations. The Raman spectrum of [I_2 + ethanol]–amylose was also idential with the aqueous [KI + I_2]–amylose spectrum. No triiodide ions are formed *a priori* in the ethanol solution; yet the present interpretation implies that even in this case repeating I_3 units are formed in the amylose complex. With regard to the X-ray analysis, it is noted that only a slight perturbation of the interatomic distance is necessary for a discontinuity in the zone to occur. The fact that the intensity of the $q = \pi/3a$ (also that of the $q = \pi/a$ mode) mode is greater than that of the $q = 2\pi/L$ mode can be taken as an indication that there is a distribution in iodine chain lengths which broadens and, therefore, weakens the lower length-dependent modes, whereas the length-independent mode corresponding to the zone edge tends to be sharp and intense despite the distribution in chain lengths.

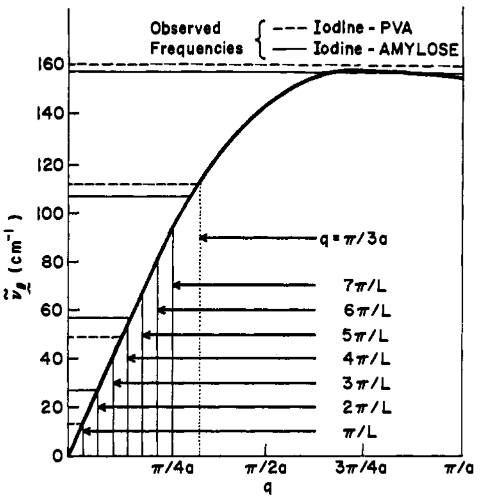

Figure 4. Plot of the longitudinal frequency ν_l *vs.* the wave vector q for a linear chain of equidistant iodine atoms. The stretching force constant and the bond interaction constant were derived from the triiodide spectra. The horizontal lines designate the Raman frequencies observed in the complexes of amylose and PVA with iodine. The vertical lines indicate some of the allowed values of q in an iodine chain of length L carrying N particles at separation a. $L = (N - 1)a$.

In order to study the effect of the degree of amylose polymerization on the iodine chain length, the Raman spectra of iodine complexed with synthetic amylose (DP = 100 and 800) and with amylopectin were taken. The spectra did not differ from those of iodine in starch amylose (DP ~ 300). Earlier investigations of the iodine–amylose complex are in agreement with this observation and with the calculated value of the most probable iodine chain length. For example, in the work of Bailey and Whelan[22] it was found that the "blue value" (optical density at 680 nm) and the absorption maximum increase rapidly and linearly with the amylose chain length between DP 12 and 70. The rate of increase then falls abruptly and attains a new steady value (<10% of the initial value). On the basis of these results it was postulated that there is a buildup of a stable linear iodine complex through successive addition of

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iodine atoms until a chain of optimal stability is reached. Thus a DP of 72, corresponding to approximately 24 iodine atoms, represents the minimal degree of polymerization for optimal complex stability. A second study[19] of iodine binding to synthetic amyloses, using potentiometric titration, qualitatively confirmed the results of the light absorption measurements. The amount of bound iodine in the complex increased rapidly in the range $\bar{P}_n$[19] 25 to $\sim$80, then reached a value of one iodine molecule per 7.65 glucose residues, and remained constant up to $\bar{P}_n$ 15,000. The sudden change at $\bar{P}_n$ 80 was interpreted as evidence for a preferred length of the iodine chain (20–22 iodine atoms) enclosed in the amylose helix. Two current concepts of the amylose conformation in aqueous solution, the model of a broken helical chain (*i.e.*, alternating rigid helical segments and random coil regions) and the model of a wormlike helical chain, offer feasible explanations for these experimental results. Regarding such models, it is significant that the outlined analysis of the Raman spectra yields a direct measure of the iodine chain, which is independent of the degree of amylose polymerization for DP $>$ 100 and is in reasonable agreement with the aforementioned estimates.

Analogously to the iodine–amylose color reaction, the formation of an adduct between iodine and polyvinyl alcohol (PVA) is accompanied by intense blue coloration. The mechanism of the iodine–PVA reaction is understood to a lesser extent than that of iodine–starch. It has been suggested that the ordered shape of the PVA chain is helical,[23] but no solid evidence has been presented thus far. In an X-ray diffraction study of halogen–polymer complexes, West[24] found reflections characteristic of a one-dimensional iodine lattice with a period of 3.10 Å, which was essentially independent of the polymer. He interpreted these spacings as interatomic distances in linear polyhalogen chains. A more recent work,[25] however, reports a new diffuse layer corresponding to 5.4-Å spacing for iodine complexes of aqueous PVA or freshly spun PVA fibers. Despite the incomplete description of the iodine–PVA structure, there is evidence that the PVA complex, like the iodine–amylose complex, is an addition compound rather than a solid solution or the product of adsorption. The Raman spectrum of an aqueous solution of KI + I_2 and PVA, displayed in Figure 2, indeed resembles that of the iodine–amylose complex. If one interprets the spectra by assuming clamped boundary conditions, as was done for iodine–amylose, the lowest observed frequency at 13 cm^{-1} yields $L = 54a$ and $N = 55$. If, however, the terminal atoms are considered to be unclamped, the first Raman-active mode corresponds to $q = \pi/L$ and hence $L = 27a$ and $N = 28$. This would be a cosine mode, having amplitude maxima at the boundaries of the segment. The center of gravity would not move, as required for vibrational normal modes. The $\lambda_{\max}$ of the iodine–PVA complex has variously been reported as 595–620 nm,[23] while $\lambda_{\max}$ of iodine in native amylose (DP $\simeq$ 300) is 630 nm.[22] Since $\lambda_{\max}$ is a unique function of the chain length, we are forced to conclude that the lengths of the conjugated iodine segments are near equal in amylose and PVA. Thus the observed differences in the vibrational frequencies of the two systems are assigned to different boundary conditions at the extremities of the conjugated segments: clamped in amylose and unclamped (free) in PVA. These boundary conditions yield values of chain lengths in agreement with those obtained from the optical absorption data. The near coincidence of the high frequency modes $\nu_1 = 161$ and 158 cm^{-1} in the PVA and amylose complexes, respectively, indicates that iodine spacing is similar in both. As was mentioned previously, the PVA sample also has a peak at 112 cm^{-1} for $q = \pi/3a$.

The iodine–PVA complex is of further interest, because iodine can be incorporated into well-oriented uniaxial preparations of PVA, as employed in the H-type Polaroid dichroic sheets.[24,26] When the halogen is incorporated into such polymer preparations, strong uniaxial positive dichroism (*i.e.*, the incident electric vector is most strongly absorbed and scattered when polarized parallel to the axis of alignment) accompanies the enhanced light absorption. The anisotropy of these samples makes possible the isolation of some of the contributing Raman tensor components α_{ij},[27] which are given together with the corresponding spectra in Figure 2. The spectrum is again similar to that of the aqueous solutions of KI + I_2 with amylose and PVA. The higher frequency lines at 156 and 108 cm^{-1} are assigned to $q = \pi/a$ and $q = \pi/3a$, respectively. As in aqueous PVA–iodine, the line at 48 cm^{-1} is attributed to $q = 3\pi/L$. The low-frequency vibration $q = \pi/L$ is probably obscured by the intense Rayleigh tail.

Agarose, the main constituent of agar, is composed of the alternating copolymers of 3,6-anhydro-α-L-galactopyranosyl and β-D-galactopyranosyl. A double helix conformation has been proposed for agarose on the basis of model building in the computer.[28] Agarose is known to form a colorless gel in aqueous solutions which upon addition of KI_3 turns blue. An iodine–agarose complex was prepared to study the effects of the matrix on the iodine complex. The Raman spectra of the iodine–agarose complex contained three peaks at 27 ($q = 2\pi/L$), 112 ($q = \pi/3a$), and 156 cm^{-1} ($q = \pi/a$). The second Raman-active mode was not observed, possibly because of a broader distribution of lengths in the agarose. The weakening of the 27-cm^{-1} mode was concomitant with the general broadening observed in the agarose spectrum as compared with that of the amylose. As the given assignments indicate, the iodine spectrum was essentially unaltered by the substitution of amylose by agarose.

The Raman spectra of various interhalogens and their adducts with amylose are presented in Figure 3 (to be compared with the iodine complex). The polarized Raman-active mode in IBr_2^- (KBr + IBr) at 167 cm^{-1} has been tentatively assigned to ν_1 (symmetric stretch). The Raman spectrum of I_2Br^- (KBr + I_2) has not been previously reported. In accord with infrared measurements on CsI_2Br, the 112- and 180-cm^{-1} lines are assigned to ν_1 and ν_3, respectively. In the absence of further evidence, these assignments are tentative. Similar to the [KI + I_2]-amylose adduct, the Raman spectrum of KBr + I_2 complexed with amylose contains four polar-

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ized lines at 167 ($q = \pi/a$), 110 ($q = \pi/3a$), 54 ($q = 4\pi/L$), and 25 cm^{-1} ($q = 2\pi/L$). From the similarity of the spectra, it seems probable that the chromophores in the [KBr + I_2]-amylose complex consist of a linear chain of iodine atoms randomly interspersed by a small number of bromine atoms. The Raman spectrum of [KBr + IBr]-amylose also contains four polarized lines at 181, 152, 54, and 27 cm^{-1}, with probable assignments as in the KI + I_2 sample. In that case the larger frequency shifts for the $q = \pi/a$ and $q = \pi/3a$ in the KBr + IBr adduct compared with the KBr + I_2 complex reflect an increased bromine distribution in the former. However, it is possible that the 181 cm^{-1} in [KBr + IBr]-amylose is a local Br mode and that the $q = \pi/3a$ mode is not visible.

In conclusion, resonance-enhanced Raman spectra of the trihalide ions I_3^-, I_2Br^-, and IBr_2^- are presented. Although a complete excitation profile (Raman line intensity *vs.* exciting frequency) was not obtained, the relative intensity of ν_3 was found to decrease with respect to that of ν_1 as the excitation was tuned from the red (6328 Å) toward the blue (5308 Å). The length of the iodine chain in both amylose and PVA was calculated to be approximately 28 atoms. In the amylose complex, however, it appears that the iodine chain has clamped end points, whereas in the PVA complex the terminal iodine atoms are unclamped. In the natural organic polymers (amylose, agarose, and amylopectin) and the synthetic amylose polymers (DP = 100 and 800) studies, the inclusion matrix of the iodine chain had no observable effect on the Raman spectra. It was, therefore, concluded that there is a preferred iodine chain length of approximately 28 atoms in all these iodine–complexing polymers. The Raman spectra of the iodine–amylose complex in ethanol and of the iodine–polymer complexes in water (independent of KI concentration) displayed a line at approximately one-third of the π/a zone. The $q = \pi/3a$ line is interpreted as an indication of the presence of I_3 units in these complexes. The incorporation of iodine into gel-forming solutions of PVA and agarose and into oriented PVA films had no effect on the iodine chain length.

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X-Ray Photoelectron Spectroscopic Study of Some Bis(triphenylphosphine)iminium Salts

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Abstract: X-Ray photoelectron spectroscopy (ESCA) has been used to measure the phosphorus 2p and nitrogen 1s electron binding energies in the bis(triphenylphosphine)iminium cation (abbreviated, PPN). The magnitudes of the binding energies, *ca.* 133 eV for the P(2p) electrons and *ca.* 397 eV for the N(1s) electrons, imply that the phosphorus atoms in the PPN cation bear some degree of positive charge while the nitrogen atom has some negative character. Variation of the anion in the lattice is found to have little or no effect on the binding energies in the PPN cation.

The bis(triphenylphosphine)iminium cation, $\{[(C_6H_5)_3P]_2N\}^+$ (hereafter abbreviated PPN), was first synthesized by Appel and Hauss[1] as a bromide salt. More recently, Ruff and Schlientz[2] prepared the chloride salt by a much simpler method in close to quantitative yield. They were then able to convert the chloride salt in a straightforward manner to salts containing other simple inorganic anions such as bromide, iodide, cyanate, thiocyanate, azide, and nitrate. Ruff[3–6] has shown that the PPN cation imparts a remarkable degree of stability to mono- and polynuclear metal carbonyl anions. Handy, *et al.*,[7] have reported the structure of the PPN cation as determined by X-ray crystallographic analysis for $\{[(C_6H_5)_3P]_2N\}^+$ $\{Cr_2(CO)_{10}\cdot CH_2Cl_2\}^-$ and related polynuclear metal carbonyl salts.

Aside from carbon and sulfur, the most extensive X-ray photoelectron spectroscopic (ESCA) studies have been reported on nitrogen[8–10] and phosphorus[11,12] compounds. Since the PPN salts were suggested to contain a quaternary nitrogen atom and two P–N double bonds, ESCA studies, of the P(2p) and N(1s) electron binding energies, were undertaken with the aim of elucidating bonding characteristics in the simple salts PPN(X) (where X = F^-, Cl^-, Br^-, I^-, SCN^-, N_3^-, NO_3^-, OCN^-, and $V(CO)_6^-$).

The magnitudes of the binding energies, *ca.* 133 eV for the P(2p) electrons and *ca.* 397 eV for the N(1s) electrons, imply that the phosphorus atoms in the PPN

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