Resonance Raman and Electronic Spectra of Different Salts of the $[AuBr_4]^-$ Ion[1]

By **Yvonne M. Bosworth** and **Robin J. H. Clark**,* Christopher Ingold Laboratories, University College, 20 Gordon Street, London WC1H 0AJ

Three different salts of the $[AuBr_4]^-$ ion display the resonance Raman effect when irradiated in the solid state with any one of several different exciting lines (frequency ν_0). For 457·9 nm excitation, which approximately coincides in frequency with that of an intense electronic band maximum (ν_e) of the anion, the resonance is most effective, with high-intensity overtone progressions in the $\nu_1(a_{1g})$ fundamental extending as far as the ninth harmonic. For each salt, two other progressions in the $\nu_1(a_{1g})$ fundamental have also been observed, *viz.* $\nu_2 + n\nu_1$ and $\nu_4 + n\nu_1$, where $\nu_2(b_{1g})$ is an AuBr stretching fundamental, and $\nu_4(b_{2g})$ is a BrAuBr bending fundamental. The members of each overtone progression decrease in intensity and increase in half-bandwidth with increase in the vibrational quantum number. The relationship between the overtone intensities and $\nu_e - \nu_0$ is detailed. The observation of various overtone progressions has permitted the determination of the spectroscopic constants ω_1 and x_{11} for the $[AuBr_4]^-$ ion in each crystalline environment.

WHEN a molecule in the gaseous state under high pressure or in a condensed state is excited with a laser beam whose wavenumber corresponds or closely corresponds with the band maximum of a strongly allowed electronic transition of the molecule, then a rigorous resonance Raman (r.r.) spectrum may be obtained. Such spectra are normally characterised by an enormous increase in the intensity of a totally symmetric fundamental of the molecule together with the appearance of long overtone progressions in this same fundamental.[2-6]

Previous resonance Raman studies of the $[AuBr_4]^-$ ion have been confined to aqueous solutions. For these it has been demonstrated[7] that both the $\nu_1(a_{1g})$ and $\nu_2(b_{1g})$ as well as (to a lesser extent) the $\nu_4(b_{2g})$ fundamentals display the so-called pre-resonance Raman effect, whereby certain fundamentals show a selective (small) increase in their intensities as ν_0, the exciting frequency, is made to approach ν_e, the frequency of the first allowed electronic transition of the molecule.[8,9] No r.r. spectra have been observed for aqueous solutions of the $[AuBr_4]^-$ ion. There are, however, both shifts (500—2300 cm^{-1}) in the frequencies and changes in the relative intensities of the allowed transitions of the $[AuBr_4]^-$ ion on change from solution to the solid state,[10] and accordingly we have closely investigated the Raman spectra of the $[AuBr_4]^-$ ion in the solid state. The ion has been found, for all the salts investigated, to display the r.r. effect, three overtone progressions in the $\nu_1(a_{1g})$ fundamental being observed in each case. These have been found to reach, at most, $9\nu_1$ for the $n\nu_1$ progression on excitation of the ion with the 457·9 nm Ar^+ line.

The change in the appearance of the solid-state Raman spectra of the three salts of the $[AuBr_4]^-$ ion with change in exciting frequency has been investigated in detail, in particular to establish the relationship between the overtone intensities relative to that of the fundamental as a function of $\nu_e - \nu_0$. Moreover, the observation of these overtone progressions has made possible the determination of the spectroscopic constants ω_1 and x_{11} for the $[AuBr_4]^-$ ion, and hence an assessment of the influence of the ionic lattice on the $\nu_1(a_{1g})$ fundamental.

EXPERIMENTAL

Preparation of Samples.—The complex $K[AuBr_4]\cdot2H_2O$ was obtained from Johnson Matthey and Co. Ltd. The complex $[Et_4N][AuBr_4]$ was prepared by literature methods.[11] The complex $[Bu^n{}_4N][AuBr_4]$ was prepared by treating $K[AuBr_4]\cdot2H_2O$ with tetra-n-butylammonium bromide in aqueous hydrobromic acid (Found: C, 25·4; H, 4·75; Br, 42·8; N, 1·7. $C_{16}H_{36}AuBr_4N$ requires C, 25·3; H, 4·75; Br, 42·1; N, 1·85%). All the salts of the $[AuBr_4]^-$ ion are deep red-brown in colour.

The caesium salts of the $[AuBr_4]^-$ ion have also been investigated by the addition of aqueous solutions of CsBr to a solution of $K[AuBr_4]\cdot2H_2O$ in aqueous hydrobromic acid. With a CsBr : $K[AuBr_4]\cdot2H_2O$ mole ratio of *ca.* 1, the red-brown salt $Cs[AuBr_4]$ is formed.[12] This gave low-intensity overtones of $\nu_1(a_{1g})$ only as far as the fourth harmonic with 514·5, 488·0, or 457·9 nm excitation, and in consequence its spectra were not investigated in detail. With higher CsBr : $K[AuBr_4]\cdot2H_2O$ mole ratios, the jet black mixed-valence compound[13] $Cs_2[Au^IAu^{III}Br_6]$ is formed. Surprisingly, Raman spectra could be obtained from this compound with all five exciting lines used (see below), strong bands being observed at 200 and 184 cm^{-1} with a further band of variable intensity at *ca.* 190 cm^{-1}. No overtones of these fundamentals were observed, so the spectra of the compound were not investigated further.

Instrumental Details.—The Raman spectra were recorded by use of a Spex 1401 spectrometer in conjunction with

---

[1] Presented in part at the 16th International Conference on Co-ordination Chemistry, Dublin, August 1974: preliminary report, Y. M. Bosworth and R. J. H. Clark, *Chem. Phys. Letters*, 1974, **28**, 611.

[2] W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, 1970, **52**, 399.

[3] J. Behringer, in 'Raman Spectroscopy,' ed. H. A. Szymanski, Plenum Press, New York, 1967.

[4] W. Kiefer and H. J. Bernstein, *Mol. Phys.*, 1972, **23**, 835.

[5] R. J. H. Clark and P. D. Mitchell, *J. Amer. Chem. Soc.*, 1973, **95**, 8300.

[6] W. Kiefer and H. J. Bernstein, *J. Raman Spectroscopy*, 1973, **1**, 417.

[7] Y. M. Bosworth and R. J. H. Clark, *Inorg. Chem.*, in the press.

[8] A. C. Albrecht, *J. Chem. Phys.*, 1961, **34**, 1476.

[9] A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, 1971, **55**, 4438.

[10] J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2058.

[11] P. Braunstein and R. J. H. Clark, *J.C.S. Dalton*, 1973, 1845.

[12] A. Sabatini, L. Sacconi, and V. Schettino, *Inorg. Chem.*, 1964, **3**, 1775.

[13] A. Ferrari and R. Cecconi, *Gazzetta*, 1942, **72**, 170.

Coherent Radiation model 52 Ar^+ and Kr^+ lasers. The scattered radiation was collected at 90° and focussed by a $f/0{\cdot}95$ lens onto the entrance slit of the monochromator after having been passed through a polarisation scrambler.[7] The spectra were calibrated by reference to the emission lines of neon which were superimposed directly onto the spectra themselves during their recording. The rotating sample technique was employed. Other details were as described elsewhere.[7]

Band areas were determined by the cut-and-weigh procedure and then corrected for the relative spectral response of the instrument as described previously.[7, 14]

The diffuse-reflectance spectra of the powdered solids were recorded by use of a Cary 14 spectrometer.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer (to 200 cm^{-1}) as Nujol mulls, and on a R.I.I.C. interferometer (200—20 cm^{-1}) as paraffin wax discs (P.C.M.U. Service, Harwell). In the latter case, spectra were recorded for 10—17 mg of compound to 150—300 mg paraffin wax in 13 or 25 mm discs.

RESULTS AND DISCUSSION

Fundamental Frequencies.—In the complex $K[AuBr_4]{\cdot}2H_2O$, the $[AuBr_4]^-$ ion has the square planar stereochemistry with the water molecules being present as water of crystallisation.[15] The $[AuBr_4]^-$ ion is undoubtedly square planar in each of the other complexes and it thus belongs to the D_{4h} symmetry point group. The ion therefore possesses three Raman-active fundamentals, $\nu_1(a_{1g})$, $\nu_2(b_{1g})$, and $\nu_4(b_{2g})$, three infrared-active fundamentals $\nu_3(a_{2u})$, $\nu_6(e_u)$, and $\nu_7(e_u)$, with $\nu_5(b_{2u})$ being inactive. Values found for the active fundamentals are summarised in Table 1.

No problem arises in the assignment of the Raman-active fundamentals; ν_1 and ν_2 are both pure stretching vibrations distinguished by the low depolarisation ratio of the former in aqueous solution (*ca.* 0·1),[7] while ν_4 must occur at much lower wavenumbers on account of its being a pure in-plane bending mode. The i.r.-active stretching fundamental, ν_6, is likewise clearly identifiable as the very intense band at the relatively high frequency of 250—252 cm^{-1}. However, the assignment of ν_3 and ν_7 is not certain. Force constant calculations and other studies on some tetrachlorometallates and related ions have been interpreted [16-18] to suggest that $\nu_7 > \nu_3$, and this suggestion is adopted herein. It thus appears that ν_7 is considerably weaker, and only *ca.* 10 cm^{-1} higher in frequency than ν_3. Such a small frequency difference between two bands could suggest that both arise from solid-state splittings of ν_7, which is doubly degenerate. However, this interpretation of the results seems improbable, first because the band separation is very comparable for all four salts studied, and secondly because no such splitting is evident in the i.r. spectra of any of the complexes studied herein for the ν_6 band, which is likewise doubly degenerate.

TABLE 1

Fundamental frequencies of the $[AuBr_4]^-$ ion in crystalline solids and in aqueous solution (cm^{-1}) [a]

Complex	$\nu_1(a_{1g})$ R	$\nu_2(b_{1g})$ R	$\nu_3(a_{2u})$ i.r.	$\nu_4(b_{2g})$ R	$\nu_6(e_u)$ i.r.	$\nu_7(e_u)$ i.r.	Ref.
$[Et_4N][AuBr_4]$	213·3	197·0	104wm	106·9	252vs	117vw?	*b*
$[Bu^n{}_4N][AuBr_4]$	212·4	195·1	99w	106·7	252vs	108vw	*b*
$K[AuBr_4]{\cdot}2H_2O$	210·3	194·7	103w		250vs	118vw	*b, c*
$Cs[AuBr_4]$	214·5	194·3	101m		252vs	110vw, sh	*b*
$K[AuBr_4]$	214	196		102	260/249	134?	*d*
Aqueous soln.	214·4	196·5		103·5			*e*

[a] Estimated wavenumber accuracies: ν_1 and ν_2 $\pm 0{\cdot}5$ – $\pm 1{\cdot}0$ cm^{-1}; other bands $\pm 1{\cdot}5$ cm^{-1}. [b] This work. [c] Additional unassigned bands appear in the i.r. spectrum of this complex at 137m, 94s, 86vs, 77s, and 58wm cm^{-1}; these may be librational modes of the water molecules or lattice modes. The infrared spectral assignments for ν_3 and ν_7 of this salt (D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, 1963, **19**, 925) are considered to be incorrect. Their assignments were made without the benefit of studies on anhydrous derivatives of the $[AuBr_4]^-$ ion, which give much simpler and more certainly interpretable spectra. [d] P. J. Hendra, *J. Chem. Soc.*, 1967, 1298 (Raman results); the i.r. results quoted in this paper are those of D. P. Athens, but it does not appear certain that they pertain to the anhydrous material. [e] Y. M. Bosworth and R. J. H. Clark, *Inorg. Chem.*, in the press.

Features of the Observed Overtone Progressions.—The appearance of the Raman spectrum of solid complexes of the $[AuBr_4]^-$ ion is found to depend markedly on the exciting line used to gather the data, and in particular on the energy gap between the exciting frequency (ν_0) and the frequency of the lowest electronic band maximum (ν_e) of the ion at *ca.* 22 500 cm^{-1}, and assigned to the superposition of two electric-dipole allowed transitions ${}^1A_{2u}$, ${}^1E_u \leftarrow {}^1A_{1g}$.[19] In Figure 1 are shown the diffuse-reflectance spectra of each of the three salts studied, together with an indication of the wavelengths of the five lines used to excite the Raman spectra. In each case, 647·1 nm excitation is seen to be well removed from the maximum of the lowest intense absorption band of the ion (which is very broad) but 457·9 nm excitation corresponds closely to the frequency of the electronic band maximum.

With 647·1 nm excitation, only the first overtone of the $\nu_1(a_{1g})$ fundamental could be detected for each salt, but with higher frequency exciting lines (lower $\nu_e - \nu_0$) both this fundamental as well as its overtones increase in intensity in the manner characteristic of the r.r. effect. The overtone progressions were observed to

---

[14] R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, 1971, **10**, 1118.

[15] E. G. Cox and K. C. Webster, *J. Chem. Soc.*, 1936, 1635.

[16] H. Poulet, P. Delorme, and J. P. Mathieu, *Spectrochim. Acta*, 1964, **20**, 1855.

[17] L. H. Jones, *Co-ordination Chem. Rev.*, 1966, **1**, 351.

[18] P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1298.

[19] H. B. Gray, in 'Transition Metal Chemistry,' ed. R. L. Carlin, Dekker, 1965, vol. 1, p. 239.

reach $9\nu_1$, $7\nu_1$, and $5\nu_1$, for the tetraethylammonium, tetra-n-butylammonium, and potassium salts respectively. The r.r. spectrum of the complex $[Et_4N][AuBr_4]$ with 488·0 nm excitation is shown in Figure 2. Owing to the difficulty of removing plasma lines the spectrum obtained with 457·9 excitation is unsuitable for display purposes.

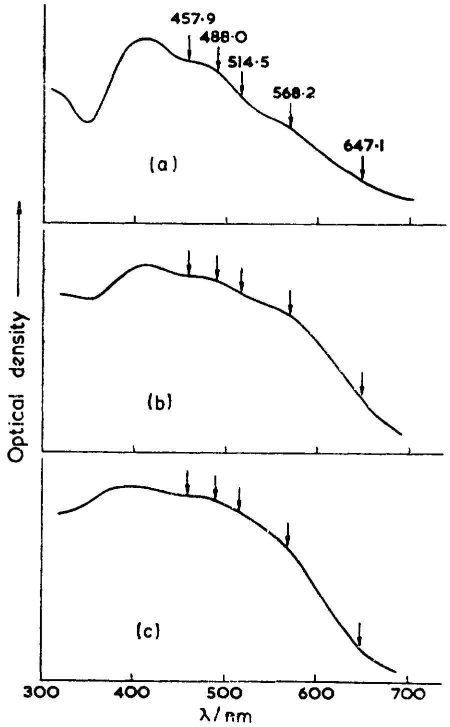

FIGURE 1 Diffuse reflectance spectra of the complexes (a) $[Bu_4N][AuBr_4]$, (b) $[Et_4N][AuBr_4]$, and (c) $K[AuBr_4]\cdot 2H_2O$ in relationship to the exciting lines used in the Raman study

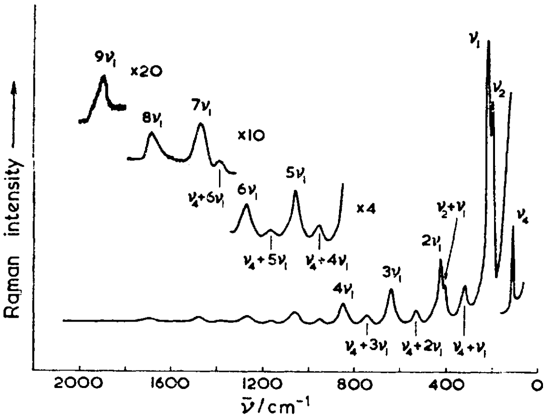

FIGURE 2 Resonance Raman spectrum of the complex $[Et_4N]$-$[AuBr_4]$ obtained with 488·0 nm excitation. Instrumental settings: slit widths 330/400/330 μm (spectral slit width 7 cm^{-1}), gain 20K (inset 5K, 2K, 1K), time constant 2 s, scanning speed 50 cm^{-1}/min (1K = 1000 counts/s^{-1})

The wavenumbers of the $\nu_1(a_{1g})$ fundamental and its overtones for each salt of the $[AuBr_4]^-$ ion are listed in Table 2, together with the half-bandwidths for each band. The overtones show a continuous increase in half-bandwidth and a continuous decrease in both peak height and band area as the vibrational quantum number (n) increases. These are known to be characteristic features of the r.r. effect. Moreover, it is significant that, in agreement with the theory of Peticolas *et al.*,[20] only the totally symmetric mode exhibits the r.r. effect.

From Figure 2, it is also apparent that two other progressions in the $\nu_1(a_{1g})$ fundamental occur *viz.* $\nu_2 + n\nu_1$ and $\nu_4 + n\nu_1$. The appearance of a second progression in a totally symmetric fundamental in addition to the main $n\nu_1$ progression has also been observed for the r.r. spectra of the $[MnO_4]^-$ ion $[\nu_3(t_2) + n\nu_1(a_1)$ as far as $n = 5]$,[4] the $[MoS_4]^{2-}$ ion $[\nu_3(t_2) + n\nu_1(a_1)$ as far as $n = 2]$ [21] and the $[Mo_2Cl_8]^{4-}$ ion $[\nu_4(a_{1g}, b_{1g}$, or $e_g) + n\nu_1(a_{1g})$ as far as $n = 4]$.[22] In no previous case, however, have three progressions been observed. It can be seen from Figure 2 that the $\nu_2 + n\nu_1$ progression is much weaker than the $\nu_4 + n\nu_1$ progression, which in turn is much weaker than the $n\nu_1$ progression. These two additional overtone series were observed for all three complexes, and the wavenumbers and half-bandwidths for each member of these series are given in Table 3.

TABLE 2

Wavenumbers and half-bandwidths of the ν(Au–Br), $\nu_1(a_{1g})$ fundamental and its overtones for the $[AuBr_4]^-$ ion in different crystal lattices obtained by use of 488·0 and 514·5 nm excitation

Band assignment	$[Bu_4N][AuBr_4]$ Max.	$\Delta\nu_{\frac{1}{2}}$	$[Et_4N][AuBr_4]$ Max.	$\Delta\nu_{\frac{1}{2}}$	$K[AuBr_4]\cdot 2H_2O$ Max.	$\Delta\nu_{\frac{1}{2}}$
ν_1	212·4	11·5	213·3	10·8	210·3	7·7
$2\nu_1$	424·9	16	425·6	15	420·4	11·5
$3\nu_1$	636·5	21	637·4	23	630·4	18
$4\nu_1$	846	28	849	28	840	29
$5\nu_1$	1057	40	1060	37	1050	49
$6\nu_1$	1266	50	1270	49		
$7\nu_1$	1475	62	1480	56		
$8\nu_1$			1690	74		
$9\nu_1$			1899			

TABLE 3

Wavenumbers and half-bandwidths of the $\nu_2 + n\nu_1$ and $\nu_4 + n\nu_1$ progressions for the $[AuBr_4]^-$ ion in different crystal lattices obtained by use of 488·0 and 514·5 nm excitation

Band assignment	$[Bu_4N][AuBr_4]$ Max.	$\Delta\nu_{\frac{1}{2}}$	$[Et_4N][AuBr_4]$ Max.	$\Delta\nu_{\frac{1}{2}}$	$K[AuBr_4]\cdot 2H_2O$ Max.	$\Delta\nu_{\frac{1}{2}}$
			$\nu_2 + n\nu_1$ progression			
$\nu_2 + \nu_1$	408·5		409·7		403·7	
$\nu_2 + 2\nu_1$					611·3	
			$\nu_4 + n\nu_1$ progression			
$\nu_4 + \nu_1$	318·3	18·7	318·4	20·1	315·3	28
$\nu_4 + 2\nu_1$	530	23	530	24		
$\nu_4 + 3\nu_1$	740	29	743	30		
$\nu_4 + 4\nu_1$	951	33	953	36		
$\nu_4 + 5\nu_1$	1161	41	1162	44		

---

[20] L. A. Nafie, P. Stein, and W. L. Peticolas, *Chem. Phys. Letters*, 1971, **12**, 131.

[21] A. Ranade and M. Stockburger, *Chem. Phys. Letters*, 1973, **22**, 257.

[22] R. J. H. Clark and M. L. Franks, *J.C.S. Chem. Comm.*, 1974, 316.

The $\nu_2 + n\nu_1$ progression extends clearly as far as $n = 2$, and as unresolved shoulders as far as $n = 5$, while the $\nu_4 + n\nu_1$ progression extends at most as far as $n = 6$. These overtones display the same trends in half-bandwidths, peak heights, and band areas as were observed and outlined above for the $n\nu_1$ progression.

TABLE 4

Relative intensities [a] of the overtones to the fundamental ν(Au–Br), $\nu_1(a_{1g})$ of the $[AuBr_4]^-$ ion in different crystal lattices as a function of the exciting wavelength (nm)

	$[Bu_4N][AuBr_4]$					$[Et_4N][AuBr_4]$					$K[AuBr_4]\cdot2H_2O$				
Band	457·9	488·0	514·5	568·2	647·1	457·9	488·0	514·5	568·2	647·1	457·9	488·0	514·5	568·2	647·1
ν_1	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
$2\nu_1$	0·92	0·35	0·18	0·060	0·017	0·84	0·43	0·22	0·059	0·028	0·14	0·087	0·062	0·024	0·017
$3\nu_1$	0·70	0·25	0·12	0·045		0·64	0·33	0·15	0·028		0·10	0·066	0·031	0·019	
$4\nu_1$	0·42	0·18	0·074	0·019		0·48	0·23	0·093	0·019		0·078	0·042	0·025		
$5\nu_1$	0·27	0·13	0·049	0·013		0·28	0·15	0·064	0·016		0·060	0·029			
$6\nu_1$	0·17	0·077	0·036			0·17	0·099	0·034							
$7\nu_1$	0·11	0·051				0·13	0·068	0·015							
$8\nu_1$						0·090	0·056	0·012							
$9\nu_1$						0·064	0·038	0·009							

[a] Determined from band areas and corrected for the spectral response of the instrument.

TABLE 5

Relative intensities [a] of the $\nu_4 + n\nu_1$ and $\nu_2 + \nu_1$ overtones to the ν(Au–Br), $\nu_1(a_{1g})$ fundamental for the $[AuBr_4]^-$ ion in different crystal lattices as a function of the exciting wavelength (nm)

	$[Bu_4N][AuBr_4]$					$[Et_4N][AuBr_4]$					$K[AuBr_4]\cdot2H_2O$				
Band	457·9	488·0	514·5	568·2	647·1	457·9	488·0	514·5	568·2	647·1	457·9	488·0	514·5	568·2	647·1
$\nu_2 + \nu_1$	0·11	0·096	0·050	0·015	0·005	0·15	0·070	0·053	0·024	0·015	0·078	0·073	0·044	0·019	0·009
$\nu_4 + \nu_1$	0·33	0·41	0·18	0·015	0·006	0·24	0·18	0·10	0·036			0·050	0·029		
$\nu_4 + 2\nu_1$	0·28	0·24	0·093	0·010		0·17	0·10	0·046	0·020						
$\nu_4 + 3\nu_1$	0·21	0·19	0·062			0·11	0·080	0·022	0·014						
$\nu_4 + 4\nu_1$	0·15	0·11	0·035			0·061	0·047	0·015							
$\nu_4 + 5\nu_1$	0·12	0·062	0·028			0·050	0·030	0·011							
$\nu_4 + 6\nu_1$	0·079	0·050													

[a] Determined from band areas and corrected for the spectral response of the instrument.

Figure 3 illustrates the relationship between the half-bandwidths and n for the $n\nu_1$ and $\nu_4 + n\nu_1$ overtone progressions as observed for the tetraethylammonium salt.

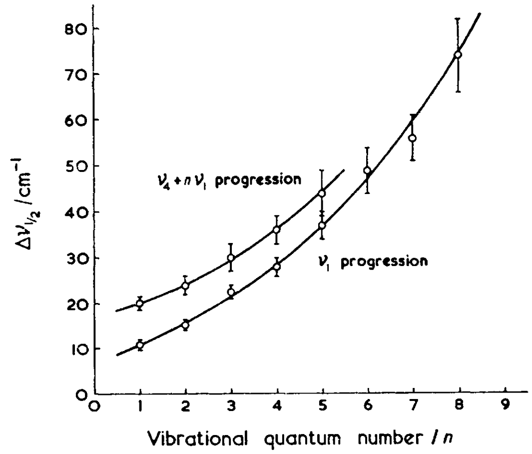

FIGURE 3 The half-bandwidths for the $\nu_1(a_{1g})$ fundamental and for the members of the $n\nu_1$ and $\nu_4 + n\nu_1$ progressions observed in the resonance Raman spectrum of the complex $[Et_4N][AuBr_4]$

The intensities of the overtones observed in the three progressions, $n\nu_1$, $\nu_2 + n\nu_1$, and $\nu_4 + n\nu_1$, were determined relative to that of the $\nu_1(a_{1g})$ fundamental of the $[AuBr_4]^-$ ion for each complex and for each of five different exciting wavelengths. The results for the $n\nu_1$ progression are listed in Table 4, and for the $\nu_2 + n\nu_1$ and $\nu_4 + n\nu_1$ progressions in Table 5. In all cases it was observed that not only did the number of observed overtones in the three progressions increase, but also their intensities relative to that of the fundamental, as the wavelength was changed in the order 647·1 < 568·2 < 514·5 < 488·0 < 457·9 nm, *i.e.* in the order of decreasing values for $\nu_e - \nu_0$. This result is in accord with theoretical predictions for the r.r. effect.[23] The maximum observed value of the intensity of the first overtone of ν_1 to that of the fundamental was 0·92.

Calculation of Harmonic Frequencies and Anharmonicity Constants.—The observation of a large number of overtones of the $\nu_1(a_{1g})$ fundamental of the $[AuBr_4]^-$ ion allows the accurate determination of the harmonic frequency (ω_1) and anharmonicity constant (x_{11}) for this fundamental in each complex salt. The observed wavenumber, $\nu(n)$, of any overtone of an anharmonic oscillator is given by the expression [24]

$$\nu(n) = G(n) - G(0)$$
$$= n\omega_1 - (n^2 + n)x_{11} + \text{higher terms}$$

where G(n) is the term value of the nth vibrational level. The higher terms are considered to be partly responsible for the increase in half-bandwidth with

---

[23] S. Kobinata, *Bull. Chem. Soc. Japan*, 1973, **46**, 3636.

[24] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' van Nostrand, Princeton, N.J., U.S.A., p. 205.

increase in n.[5] A plot of $\nu(n)/n$ *versus* n should therefore be a straight line, the slope of which gives x_{11} immediately, and the intercept of which gives $\omega_1 - x_{11}$ and hence ω_1. Such plots are shown in Figure 4 for the three complexes studied. Values for ω_1 and x_{11} may also be deduced from the frequencies of the members of the $\nu_4 + n\nu_1$ progression by plotting $[(\nu_4 + n\nu_1) - \nu_4]/n$ *versus* n. For all three salts a value for $\nu_4(b_{2g})$ of 106 cm^{-1} was used (*cf.* Table 1) for these plots, which also are included in Figure 4.

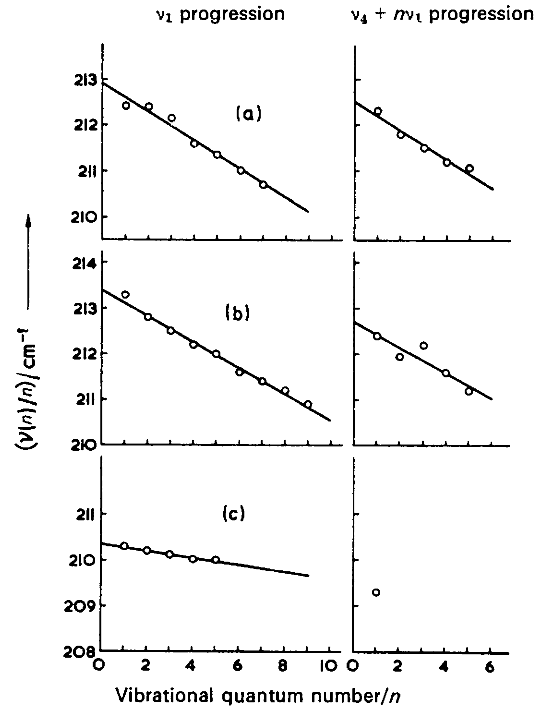

FIGURE 4 Plots of $\nu(n)/n$ *versus* n for the $n\nu_1$ and $\nu_4 + n\nu_1$ progressions of each salt; (a) $[Bu_4N][AuBr_4]$, (b) $[Et_4N][AuBr_4]$, and (c) $K[AuBr_4]\cdot 2H_2O$

The results of these analyses are summarised in Table 6. The value for ω_1 from the $n\nu_1$ progression falls slightly in the order $[Et_4N][AuBr_4] > [Bu_4N][AuBr_4] > K[AuBr_4]\cdot 2H_2O$, presumably on account of decreasing lattice-energy effects in this order. Such observations are reasonably well established features of i.r.-active stretching fundamentals of inorganic ions.[25-27] The value of ω_1 determined from the $\nu_4 + n\nu_1$ progression is slightly less for each complex than that obtained from the $n\nu_1$ progression. This difference is a direct measure of the cross-term x_{14} in the expression for the energy. Thus x_{14} is *ca.* 0·5 cm^{-1}; however, it is unlikely that the data are sufficiently good for the second progression to permit an accuracy claim of better than ±0·5 cm^{-1} for this anharmonicity constant.

TABLE 6

Harmonic frequencies (ω_1) and anharmonicity constants (x_{11}) for the different salts of the $[AuBr_4]^-$ ion (cm^{-1})

Complex	$n\nu_1$ progression		$\nu_4 + n\nu_1$ progression	
	ω_1	x_{11}	ω_1	x_{11}
$[Et_4N][AuBr_4]$	213·7 ±0·2	0·29 ±0·03	213·0 ±0·2	0·27 ±0·03
$[Bu_4N][AuBr_4]$	213·2 ±0·2	0·31 ±0·03	212·8 ±0·2	0·31 ±0·03
$K[AuBr_4]\cdot 2H_2O$	210·4 ±0·3	0·08 ±0·05	209·3 ±0·5	

The anharmonicity constant, x_{11}, is very small and not significantly different for the tetra-alkylammonium salts, the average value being 0·30 ± 0·03. The x_{11} value for complex $K[AuBr_4]\cdot 2H_2O$ is significantly smaller (0·08 ± 0·05), but the reason for this is not known. However it is clear that resonance is much less effective for this salt than for the others, as evidenced by the smaller $I(2\nu_1)/I(\nu_1)$ values and the fewer observed overtones (Table 4); the results are therefore not so accurate in this case.

In conclusion, it is clear that in common with previous results on the r.r. effect, the totally symmetric fundamental displaying the overtone progressions is highly harmonic. The technique of r.r. spectroscopy is thus very valuable as a means of establishing accurate spectroscopic constants of totally symmetric vibrations of molecules in any phase for which the molecule is stable under resonance conditions.

The authors are indebted to the Central Research Fund of the University of London for financial support. One of us (Y. M. B.) thanks the S.R.C. for a maintenance grant.

[4/1377 *Received, 8th July,* 1974]

---

[25] W. C. Price, W. F. Sherman, and G. R. Wilkinson, *Proc. Roy. Soc.*, 1960, **A255**, 5.

[26] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1963, 1198.

[27] A. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.