Resonance Raman Excitation Profiles of the Tetraisothiocyanatocobaltate(II) Ion[1]

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

The Raman band intensities of four of the fundamentals of the $[Co(NCS)_4]^{2-}$ ion have been investigated as a function of excitation frequency in the region of the $^4T_1(P) \leftarrow {}^4A_2$ ligand-field transition. All four Raman bands increase their intensities as the excitation frequency approaches the maximum in the ligand-field transition. In particular, the excitation profile of the most resonantly enhanced band, *viz.* that arising from the $\nu_{11}(t_2)$ Co–N stretching fundamental, has been studied in detail. The results suggest that it reaches a maximum *ca.* 250 cm^{-1} to the high-frequency side of the absorption maximum. This is discussed with reference to current theories of Raman scattering. The observed excitation profiles contrast with those recently observed for various centrosymmetric ions in the vicinity of their ligand-field transitions and reasons for this difference are discussed.

The pre-resonance Raman effect, whereby the intensities of certain fundamentals undergo enhancement as the exciting frequency (ν_0) approaches that of an electric-dipole-allowed electronic transition (ν_e), is now well known.[2] Indeed for several different molecular species, *viz.* tetrahedral MX_4 molecules,[3,4] octahedral $[MX_6]^{n-}$ ions,[5] and square-planar $[MX_4]^{n-}$ ions,[6,7] the effect has been studied in detail. Enhancement is observed not only for totally symmetric fundamentals but also (although usually to a lesser extent) for non-totally symmetric ones if they are vibronically active in the resonant electronic transition. However, very recent studies of Raman-active fundamentals of square-planar $[MX_4]^{n-}$ ions [6,7] have indicated surprisingly that, in the vicinity of ligand-field bands which are Laporte

---

[1] Presented at a meeting of the Societé de Chimie Belgique, Liège, Belgium, May 1975.

[2] A. C. Albrecht, *J. Chem. Phys.*, 1961, **34**, 1476; J. Tang and A. C. Albrecht in ' Raman Spectroscopy,' ed. H. A. Szymanski, Plenum Press, New York, 1970.

[3] R. J. H. Clark, B. K. Hunter, and P. D. Mitchell, *J.C.S. Faraday II*, 1972, 476.

[4] R. J. H. Clark and P. D. Mitchell, *J. Mol. Spectroscopy*, 1974, **51**, 458.

[5] Y. M. Bosworth and R. J. H. Clark, *J.C.S. Dalton*, 1974, 1749.

[6] Y. M. Bosworth and R. J. H. Clark, *Inorg. Chem.*, 1975, **14**, 170.

[7] V. Miskowski, W. H. Woodruff, J. P. Griffin, K. G. Werner, and T. G. Spiro, *J. Chem. Phys.*, submitted for publication. We are grateful to Professor T. G. Spiro for a preprint of this paper.

forbidden (albeit vibronically allowed), the intensities of the a_{1g} fundamentals are significantly reduced.

The present investigation was undertaken in order to establish the behaviour of the intensities of the Raman bands of a tetrahedral ion, $[Co(NCS)_4]^{2-}$, in the region of the ligand-field transition $^4T_1(P) \leftarrow {}^4A_2$ ($\nu_{max.}$ at 16 300 cm^{-1} in the solid state, 15 960 cm^{-1} in acetonitrile solution). This transition, which is formally *d–d*, obviously possesses some *d–p* character, as evident from the high absorption coefficient at the band maximum ($\varepsilon_{max.}$ 1 800 l mol^{-1} cm^{-1}).[8,9] It was thus not clear whether the a_1 bands of the $[Co(NCS)_4]^{2-}$ ion would display a pre-resonance enhancement or reduction in the vicinity of the $^4T_1(P) \leftarrow {}^4A_2$ transition. The nature of the pre-resonance Raman effect with respect to the intraligand charge-transfer transition of the thiocyanate group at 32 800 cm^{-1} ($\varepsilon_{max.}$ *ca.* 10 000 l mol^{-1} cm^{-1})[10] has also been investigated as far as is feasible with available laser-excitation lines.

EXPERIMENTAL

Samples.—The complex $[Et_4N]_2[Co(NCS)_4]$ was prepared according to literature methods,[11] and studied in solution in acetonitrile, the 918 cm^{-1} band of the latter being used as internal-intensity standard. Each solution was studied at two different relative concentrations of standard to solute; the approximate mol ratio (number of moles of solute : number of moles of acetonitrile) used was 0.0035 : 1. In the case of the studies involving the tunable dye laser, only one solution was studied with the optimum concentration of 1.5×10^{-4}M.*

Instrumental.—Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Radiation model 52 Ar$^+$ and Kr$^+$ lasers. The power available at the six exciting wavelengths used, *viz.* 676.4, 647.1, 568.2, 514.5, 488.0, and 457.9 nm, was *ca.* 30, 500, and 100 mW, 1.6 and 1.4 W, and 300 mW respectively. Other technical details were as reported previously.[3–5] Raman spectra were also recorded using a Coherent Radiation model 490 dye laser in conjunction with Rhodamine 6G. The exciting wavelengths used were 630.0, 626.0, 621.2, 618.1, 612.8, 608.9, 601.6, 597.5, 591.1, and 581.4 nm, for which the power lay in the 100—500 mW range. Peak areas were determined by the trace and weigh procedure.

Solutions were held in cylindrical cells (volume *ca.* 12 cm^3) which had flat bottoms and were sealed off *in vacuo*. These cells were rotated [12,13] in order to avoid problems associated with the thermal-lens effect and thermal decomposition of the sample. In all cases the exciting beam was kept as close as possible to the cell edge in order to minimise self absorption of the scattered radiation. The depolarisation ratios were measured using Ar$^+$ laser exciting lines, except for the $\nu_{11}(t_2)$ fundamental for which the 647.1 and 568.2 nm exciting lines were employed.

Electronic spectra were recorded using a Cary 14 spectrometer, and i.r. spectra using a Perkin-Elmer 225 spectrometer.

RESULTS AND DISCUSSION

Structure and Fundamental Frequencies of the $[Co(NCS)_4]^{2-}$ *Ion.*—*X*-Ray structural studies have shown [14] that, for both the hydrated and dehydrated potassium salt of the $[Co(NCS)_4]^{2-}$ ion, the cobalt atom is surrounded by a slightly distorted tetrahedron of nitrogen atoms [r(Co–N) 1.95 Å] and that the CoNCS linkages are bent at the nitrogen atom (Co–N–C 163°); this leads to approximately S_4 symmetry for the complex ion. Previous workers have, nevertheless, discussed the vibrational analysis of this and related ions in terms of T_d symmetry,[15] on which basis the vibrational representation of the ion is $3a_1 + 3e + 2t_1 + 6t_2$ (12 Raman-active fundamentals, six i.r.-active fundamentals, and six i.r.–Raman coincidences). The ion is not, however, a very good scatterer, and in consequence only five bands were observed in its Raman spectrum (acetonitrile solution). These were assigned (Herzberg's convention) [16] as follows:

ν_3	(a_1) Co–N symmetric stretch	247 ± 3 cm^{-1}	(ρ 0.0)
ν_{11}	(t_2) Co–N asymmetric stretch	306.5 ± 1 cm^{-1}	(ρ 0.68)
ν_2	(a_1) C–S symmetric stretch	832 ± 1 cm^{-1}	(ρ *ca.* 0.0)
ν_9	(t_2) C–N asymmetric stretch	2 068.5 ± 1 cm^{-1}	(dp)
ν_1	(a_1) C–N symmetric stretch	2 096 ± 1 cm^{-1}	(ρ *ca.* 0.0)

The ρ value for the 306.5 cm^{-1} band (0.68) is the average of five measurements with 568.2 nm and five with 647.1 nm excitation. Although this value is slightly less than that expected for a band arising from a non-totally symmetric fundamental, the assignment of this band to the $\nu_{11}(t_2)$ fundamental seems unambiguous. (The ρ value expected for an a_1 band of a molecule with T_d symmetry is zero under both resonance and non-resonance conditions.) [17] The slightly low ρ value of the 306.5 cm^{-1} band may be caused by a small unresolved splitting of the ion t_2 fundamental in the less than strictly tetrahedral geometry of the (*e.g.* to $a + e$ in the S_4 classification).

The result that the a_1 Co–N stretching fundamental is less intense than the corresponding t_2 fundamental is unexpected since, for simple tetrahedral MX_4 molecules and ions, the reverse is normally the case, *cf.* the situation for the $[Zn(NCS)_4]^{2-}$ ion [for which the Raman band arising from the $\nu_{11}(t_2)$ fundamental is negligibly weak by comparison with that arising from the $\nu_3(a_1)$ band],[15] and also that for the molecule $Si(NCO)_4$[18] (in which the Si–N–C angle is 146.3°).[19]

Intensities of the Five Observed Raman-active Fundamentals.—The intensities of the five observed Raman-active fundamentals of the $[Co(NCS)_4]^{2-}$ ion were

---

* 1M = 1 mol dm^{-3}.

[8] C. H. Brubaker and C. E. Johnson, *J. Amer. Chem. Soc.*, 1958, **80**, 5037.

[9] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157.

[10] C. K. Jorgensen, *Adv. Chem. Phys.*, 1963, **5**, 33.

[11] A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.

[12] W. Kiefer and H. J. Bernstein, *Appl. Spectroscopy*, 1971, **25**, 501.

[13] R. J. H. Clark, *Spex Speaker*, 1973, **18**, 1.

[14] G. S. Zhdanov and Z. V. Zvonkova, *Kristallografiya*, 1969, **14**, 691.

[15] D. Forster and W. D. Horrocks, *Inorg. Chem.*, 1967, **6**, 339; D. Forster and D. M. L. Goodgame, *ibid.*, 1965, **4**, 715.

[16] G. Herzberg, 'Infrared and Raman Spectra,' van Nostrand, New York, 1945.

[17] D. G. Rea, *J. Mol. Spectroscopy*, 1960, **4**, 499.

[18] F. A. Miller and A. M. Snider, *J. Raman Spectroscopy*, 1974, **2**, 377.

[19] K. E. Hjortaas, *Acta Chem. Scand.*, 1967, **21**, 1381.

measured relative to that of the 918 cm^{-1} band of acetonitrile as internal standard. The frequency-corrected relative molar intensities (relative scattering activities) of four of the bands at several exciting wavelengths, after correction for the spectral response of the instrument, are given in Tables 1 and 2. That of the fifth band, the $\nu_3(a_1)$ band, is very low and it could only be measured on resonance (615.0 nm excitation). At this exciting wavelength, and in acetonitrile solution, the intensity of this band relative to that of the $\nu_{11}(t_2)$ band [*i.e.* $I(\nu_3)/I(\nu_{11})$] is only 0.017 ± 0.004. The $\nu_3(a_1)$ band could therefore not be investigated in detail and will not be discussed further. The electronic-absorption spectrum of the complex in acetonitrile is shown in Figure 1, together with plots of the Raman intensities of two of the four observed fundamentals at each exciting frequency used (excitation profiles). It is clear that the excitation profile of each band closely parallels the absorption spectrum in the region of the $^4T_1(P) \leftarrow {}^4A_2$ transition. However, the factor by which the ν_{11} (t_2) fundamental, ν(CoN), is enhanced (*ca.* 600, even without any corrections for absorption having been made) is much greater than that for the other three fundamentals. This might have been expected because the resonant electronic transition is antibonding ← bonding with respect to the Co–N bonds.

TABLE 1

Frequency-corrected relative molar intensities, $(1/f)(I_2M_1/I_1M_2)$, of the ν_2 (a_1), ν_9 (t_2), and ν_1 (a_1) Raman-active fundamentals of the $[Co(NCS)_4]^{2-}$ ion in acetonitrile [a]

Wave-length/ nm	ν_i	$(1/f)$-(I_2M_1/I_1M_2) [b]	Wave-length/ nm	ν_i	$(1/f)$-(I_2M_1/I_1M_2) [b]
676.4	ν_2 (a_1)	51 ± 8	514.5	ν_2 (a_1)	16.6 ± 0.9
	ν_9 (t_2)			ν_9 (t_2)	25.6 ± 2.3
	ν_1 (a_1)			ν_1 (a_1)	16.5 ± 1.8
647.1	ν_2 (a_1)	113 ± 13	488.0	ν_2 (a_1)	20.6 ± 1.0
	ν_9 (t_2)	644 ± 100		ν_9 (t_2)	152 ± 14
	ν_1 (a_1)	505 ± 97		ν_1 (a_1)	92 ± 9
601.6 [c]	ν_2 (a_1)	184 ± 42			
568.2	ν_2 (a_1)	45 ± 5	457.9	ν_2 (a_1)	26.3 ± 1.8
	ν_9 (t_2)			ν_9 (t_2)	251 ± 23
	ν_1 (a_1)			ν_1 (a_1)	135 ± 9

[a] Intensities are given relative to that of the 918 cm^{-1} band of acetonitrile. The frequency factor f is given by the expression $\left(\frac{\nu_0 - \Delta\nu_2}{\nu_0 - \Delta\nu_1}\right)^4 \frac{\Delta\nu_1}{\Delta\nu_2}\left[\frac{1 - \exp(-hc\Delta\nu_1/kT)}{1 - \exp(-hc\Delta\nu_2/kT)}\right]$ where 1 refers to the 918 cm^{-1} band of acetonitrile and 2 to a band of the $[Co(NCS)_4]^{2-}$ ion. [b] The error limits refer to the scatter between 10 different measurements of each datum (five of which were carried out at one concentration of the anion and five at a different one). [c] Dye laser wavelength.

TABLE 2

Frequency-corrected relative molar intensities, $(1/f)(I_2M_1/I_1M_2)$, of the ν_{11} (t_2)(Co–N stretch) fundamental of the $[Co(NCS)_4]^{2-}$ ion in acetonitrile [a]

Ion-laser lines		Tunable dye-laser lines	
Wavelength/ nm	$(1/f)(I_2M_1/I_1M_2)$ [b]	Wavelength/ nm	$(1/f)(I_2M_1/I_1M_2)$ [c]
457.9	1.4 ± 0.2	581.4	343 ± 36
488.0	1.1 ± 0.1	591.1	381 ± 19
514.5	1.7 ± 0.2	597.5	408 ± 12
568.2	46 ± 3	601.6	406 ± 18
647.1	224 ± 17	608.9	513 ± 25
676.4	69 ± 8	612.8	586 ± 45
		618.1	625 ± 37
		621.2	565 ± 36
		626.0	555 ± 58
		630.0	490 ± 50

[a] See footnote *a* to Table 1. [b] See footnote *b* to Table 1. [c] The error limits refer to the scatter between five different measurements of each datum.

In recent papers it has been shown both theoretically[20] as well as experimentally[21,22] that, for non-totally symmetric fundamentals, the frequency at which maximum enhancement occurs may correspond to either ν_{00} or ν_{01}. However, in the case of totally symmetric fundamentals this maximum need not coincide with either.[20,23] In the present case, the excitation profile of the ν_{11} (t_2) band was the only one (because of its large enhancement under resonance Raman conditions) which could be studied in detail with the dye laser. The excitation profile reached a maximum at 617 nm, *i.e.* at 250 ± 75 cm^{-1} from the ν_{00} transition at 626.5 nm [*cf.* the frequency of the ν_{11} (t_2) vibration in the ground electronic state is 305 cm^{-1}]. The maximum thus lies between ν_{00} and ν_{01}, but is probably very close to ν_{01}. The maximum in the excitation profile of the ν_2 (a_1) fundamental was shifted from ν_{00} by a comparable amount. These results are consistent with the theoretical work of Koningstein and Jakubinek.[20]

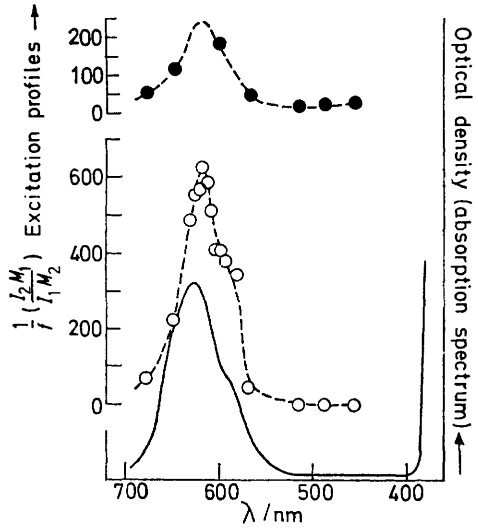

FIGURE 1 Electronic-absorption spectrum (——) of the complex $[Et_4N]_2[Co(NCS)_4]$ in acetonitrile solution together with the excitation profiles (– – – –) of the ν_{11} (t_2) (○) and ν_2 (a_1) (●) fundamentals of the anion

The selection rules proposed by Mingardi and Siebrand[24] predict that, on the assumption of a T_1 intermediate state, the bands arising from the non-totally symmetric

---

[20] J. A. Koningstein and B. G. Jakubinek, *J. Raman Spectroscopy*, 1974, **2**, 317.

[21] T. C. Strekas, A. J. Packer, and T. G. Spiro, *J. Raman Spectroscopy*, 1973, **1**, 197.

[22] T. C. Strekas and T. G. Spiro, *J. Raman Spectroscopy*, 1973, **1**, 387.

[23] H. Hamaguchi, I. Harada, and T. Shimanouchi, *J. Raman Spectroscopy*, 1974, **2**, 517.

[24] M. Mingardi and W. Siebrand, *J. Chem. Phys.*, 1975, **62**, 1074.

fundamentals e and t_2 would each show pre-resonance enhancement. The intensity-gaining mechanism is considered to be that of vibronic coupling between the $^4T_1$ states associated with the ligand-field and the charge-transfer transitions. Although bands arising from the e fundamentals were not observed, the obvious enhancement to the intensity of the $\nu_{11}(t_2)$ fundamental is consistent with the above predictions.

Albrecht's theory of the pre-resonance Raman effect predicts [2] that if an electronic transition is electric-dipole forbidden it should make no observable contribution to band enhancement as ν_0 approaches ν_e. Hence the observation above of resonance enhancement for four fundamentals of the $[Co(NCS)_4]^{2-}$ ion provides clear evidence for d–p mixing (d_{xy}, d_{yx}, d_{zx} and p_x, p_y, p_z) in tetrahedral complexes, and thus confirms the allowed character of the ligand-field transition under discussion. This is also evident from the high absorption coefficients for the transition.

TABLE 3

Electronic spectral data for various $[MX_6]^{n-}$ ions

Anion	Ref.	Band maxima (nm) and absorption coefficients (in parentheses)			
		Ligand field		Charge transfer	
$[PdCl_6]^{2-}$	*a, b*	480 (700)	$^1T_{1g} \leftarrow {}^1A_{1g}$	340 (14 000)	$\gamma_3 \leftarrow \pi$
$[PtBr_6]^{2-}$	*b, c*	525 (140)	$^3T_{1g}, {}^3T_{2g} \leftarrow {}^1A_{1g}$	315 (18 000)	$\gamma_3 \leftarrow \pi$
		435 (1 500)	$^1T_{1g} \leftarrow {}^1A_{1g}$		
$[RhCl_6]^{3-}$	*a, d*	518 (102)	$^1T_{1g} \leftarrow {}^1A_{1g}$	255 (30 000)	$\gamma_3 \leftarrow \pi$
		412 (82)	$^1T_{2g} \leftarrow {}^1A_{1g}$		
$[IrCl_6]^{2-}$	*a*	590 (410)	?	487 (3 200)	$\gamma_5 \leftarrow \pi$

[a] C. K. Jørgensen, *Mol. Phys.*, 1959, **2**, 309. [b] A. J. Cohen and N. Davidson, *J. Amer. Chem. Soc.*, 1951, **73**, 1955. [c] C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 518. [d] C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 500.

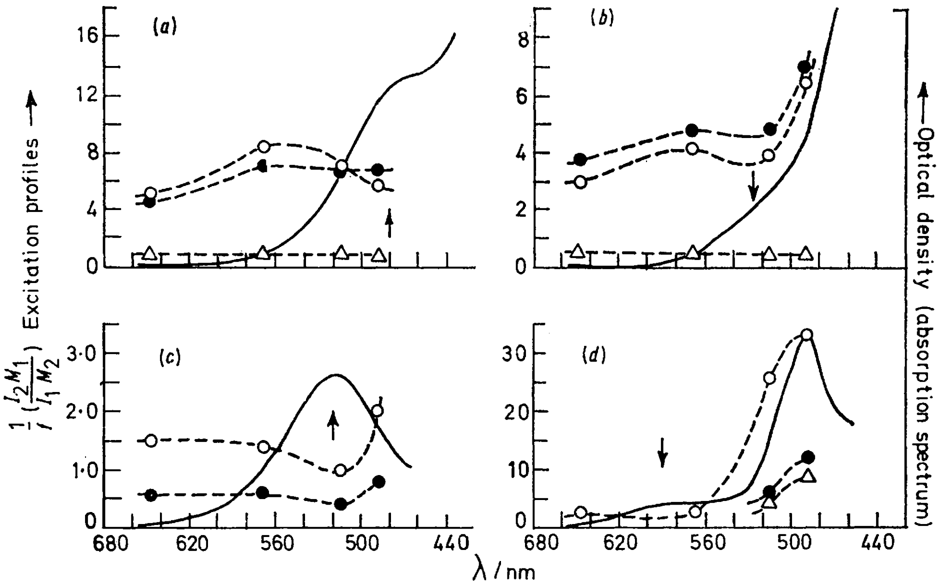

FIGURE 2 Electronic-absorption spectra (——) of the complex ions $[PdCl_6]^{2-}$ (*a*), $[PtBr_6]^{2-}$ (*b*), $[RhCl_6]^{3-}$ (*c*), and $[IrCl_6]^{2-}$ (*d*) in aqueous solution, together with the excitation profiles (– – – –) of the ν_1 (a_{1g}) (○), ν_2 (e_g) (●), and ν_5 (t_{2g}) fundamentals (△) of each anion. The arrows mark positions of ligand-field band maxima

As ν_0 approaches the frequency of the intraligand charge-transfer transition at 32 800 cm^{-1}, both CN as well as (to a much lesser extent) the CS stretching fundamental again display the pre-resonance Raman effect. However, ν(CoN) does not. This selectivity [(CoN) preferentially enhanced by approach of ν_0 to the ligand-field transition and ν(CN) and ν(CS) by approach to the charge-transfer transition] might have been expected intuitively since for the former transition the electrons remain (essentially) localised on the metal atom, whereas for the latter they remain (essentially) localised within the thiocyanate groups. Thus in resonance spectroscopy vibrational modes which exhibit enhancement are localised on the groups of atoms most closely associated with the electronic transition. No overtones of either of the CoN stretching fundamentals were observed under resonance conditions, *cf.* other tetrahedral molecules [25] and ions.[26]

Comparison of the Present Results with Those observed for Centrosymmetric Ions.—The present results differ in certain respects from those very recently found for the $[PdX_4]^{2-}$ (X = Cl, Br, or I) [6,7] and the $[Co(en)_3]^{3+}$ (en = ethylenediamine) ions, for which reduction of the intensity of the totally symmetric fundamental occurs

---

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

[26] W. Kiefer and H. J. Bernstein, *Mol. Phys.*, 1972, **23**, 815.

in the vicinity of vibronically allowed ligand-field transitions. This effect, which is not predicted by the Albrecht theory,[2] is thought to arise from interference between two terms in the dispersion equation.[7,27] Similar effects are evident from the intensity studies recently published for certain transition metal $[MX_6]^{n-}$ ions.[5] These effects are illustrated in Figure 2. The ν_1 (a_{1g}) bands of the $[PdCl_6]^{2-}$, $[PtCl_6]^{2-}$, and $[RhCl_6]^{3-}$ ions display marked, and for the $[IrCl_6]^{2-}$ ion a slight, loss of intensity in the vicinity of the indicated ligand-field transitions (Table 3); indeed the excitation profiles in these regions look like the inverse of the absorption bands. This is possibly also true of the ν_2 (e_g) bands, but only to a very much lesser extent. The ν_5 (t_{2g}) fundamental of these $[MX_6]^{n-}$ ions (with the exception of the $[IrCl_6]^{2-}$ ion) did not display any pre-resonance Raman effects with any of the exciting lines used. It is thus evident that the pre-resonance Raman effects displayed by the ν_1 (a_{1g}) fundamental of these octahedral $[MX_6]^{n-}$ ions in the vicinity of ligand-field transitions are the same as those displayed by the ν_1 (a_{1g}) fundamental of square-planar $[MX_4]^{n-}$ ions under these circumstances, namely a fairly selective intensity reduction. It seems significant that all these ions are centrosymmetric and thus they differ fundamentally from the $[Co(NCS)_4]^{2-}$ ion, which is not. For the latter the partly allowed character of the resonant ligand-field transition is such as to ensure pre-resonance enhancement to Raman bands in its vicinity and not de-enhancement as evident for the centrosymmetric ions (whose ligand-field transitions are only vibronically allowed).

Further studies along these lines, particularly with tunable dye lasers, will enable more detailed excitation profiles to be plotted for ions in the vicinity of their ligand-field transitions, and thus permit a better understanding of pre-resonance Raman effects.

We thank the S.R.C. (Y. M. B. and P. C. T.) and the Thomas Witherton Batt foundation (Y. M. B.) for the award of maintenance grants, and the Central Research Fund of the University of London for an equipment grant.

[5/482 *Received*, 11*th March*, 1975]

---

[27] J. Friedman and R. M. Hochstrasser, *Chem. Phys. Letters*, 1975, **32**, 414.