Resonance-Raman Spectra of Nitro Cobalt(III) Complexes: $K_3[Co(NO_2)_6]$, $Na_3[Co(NO_2)_6]$, *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$, and *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3$

Kan Kanamori,* Akio Shimizu, Hiroyuki Sekino, Shinji Hayakawa, Yuriko Seki, and Kiyoyasu Kawai
Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930, Japan

The resonance-Raman spectra of $K_3[Co(NO_2)_6]$, $Na_3[Co(NO_2)_6]$, *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$, and *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3$ have been measured at *ca.* 80 K with a view towards understanding the nature of the visible absorption band of nitro cobalt(III) complexes. Both intra-ligand vibrations (NO_2 symmetric stretching and NO_2 bending modes) and skeletal vibrations (Co–NO_2 and Co–NH_3 stretching modes) were found to be resonance-enhanced within the visible absorption band. The resonance enhancement occurred for the non-totally symmetric modes, as well as for the totally symmetric modes. This observation indicates B-term scattering which is concerned with two electronic excited states. The behaviour of the excitation profiles is discussed on the basis of the visible absorption bands partly having charge-transfer character.

Nitro transition-metal complexes have attracted a great deal of interest especially in view of their electronic absorption spectra, the co-ordination mode of nitrite including linkage isomerism, and photochemical behaviour.[1–4] Almost the full series of $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$ ($x = 0$—6) has been synthesized, with the exception of *cis*-$[Co(NO_2)_4(NH_3)_2]^-$, allowing us to study the nitrocobalt(III) complexes systematically. The anomalous behaviour of the visible absorption band of the nitrocobalt(III) complexes has long been the subject of innumerable investigations,[1,2] since although the nitrite ion has been recognized as having a stronger ligand field than ammonia, the visible absorption band, which is supposed to be *d–d* in origin, shows a red shift on going to $[Co(NO_2)_5(NH_3)]^{2-}$ and $[Co(NO_2)_6]^{3-}$ from $[Co(NO_2)_4(NH_3)_2]^-$. Caulton and Fenske[3b] proposed that the visible absorption band of $[Co(NO_2)_6]^{3-}$ was due to a ligand-to-metal charge-transfer (l.m.c.t.) transition and the lowest ligand-field or *d–d* band was masked under the intense u.v. band on the basis of a molecular orbital treatment. There has also been a disagreement on the nature of the lowest energy u.v. band. Caulton and Fenske[3b] assigned it to a metal-to-ligand charge-transfer (m.l.c.t.) transition. Barnes *et al.*[3d] however, pointed out that if this assignment was correct then $[Co(NO_2)_6]^{3-}$ should be more readily oxidized than reduced.

Resonance-Raman spectroscopy has been recognized as an important means of understanding the nature of the electronic absorption band of transition-metal complexes.[5] One of its advantages is the information it provides about resonant transitions through the resonance-enhanced modes, namely, there is a close connection between the nature of resonant transitions and those vibrations which are resonance enhanced. The purpose of this paper is to shed new light on the electronic absorption spectra of nitrocobalt(III) complexes using resonance-Raman spectroscopy.

Experimental

Preparation of Complexes.—$K_3[Co(NO_2)_6]$, $Na_3[Co(NO_2)_6]$, *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$, and *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3{\cdot}H_2O$ were prepared by standard methods and identified by their electronic absorption spectra and elemental analysis.[6]

Raman Measurements.—Samples were provided as discs containing an appropriate amount of K_2SO_4 or Na_2SO_4 as an intensity standard. Potassium bromide was also added to the sample in order to reduce self-absorption by the sample. Mol ratios in the stock mixture of the sample were: $Na_3[Co(NO_2)_6]:Na_2SO_4 = 1.12$, $K_3[Co(NO_2)_6]:K_2SO_4:KBr = 1:4:1$, *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]:K_2SO_4:KBr = 1:6:1$, and *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3{\cdot}H_2O:K_2SO_4:KBr = 1:6:1$. The sample disc was cooled by attaching to a brass finger which was cooled by liquid nitrogen. A laser beam was defocused on the disc to avoid local heating. With this technique, photo and thermal decomposition were considered to be negligible, as ascertained by monitoring the intensity of the Raman bands throughout the measurements.

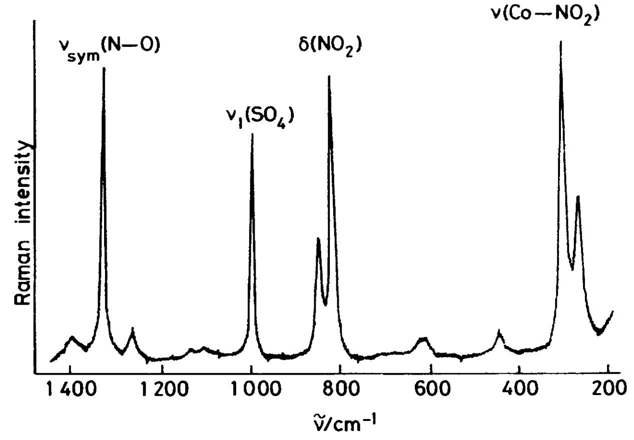

Figure 1. Raman spectrum of $K_3[Co(NO_2)_6]$ (including K_2SO_4) with 632.8-nm excitation at *ca.* 80 K; spectral band width = 5 cm^{-1}

Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer using a Spectra Physics 164 Ar^+ laser and a Coherent Radiation model CR599 dye laser employing Rhodamine 6G dye. The laser power was below 50 mW. Intensity measurements were made relative to the ν_1 band of the sulphate incorporated in the sample. Corrections of the observed intensity were applied to the fourth power of the wavenumber of scattered radiation and the instrumental response.

Electronic absorption spectra were measured with a Hitachi 220 spectrophotometer and reflectance spectra obtained with a Hitachi 330 spectrophotometer.

Results and Discussion

Assignments of the Raman Spectra.—Figures 1—4 show the Raman spectra of $K_3[Co(NO_2)_6]$, $Na_3[Co(NO_2)_6]$, *trans*-

Table 1. Molecular symmetries and Raman-active modes of $[Co(NO_2)_6]^{3-}$, *trans*-$[Co(NO_2)_4(NH_3)_2]^-$, and *trans*-$[Co(NO_2)_2(NH_3)_4]^+$

Complex	Molecular symmetry	Raman-active modes			
		ν_{sym}(N–O)	$\delta(NO_2)$	$\nu(Co–NO_2)$	$\nu(Co–NH_3)$
$[Co(NO_2)_6]^{3-}$	T_h, S_6	A_g, E_g	A_g, E_g	A_g, E_g	
trans-$[Co(NO_2)_4(NH_3)_2]^-$	D_{4h}	A_{1g}, B_{1g}	A_{1g}, B_{1g}	A_{1g}, B_{1g}	A_{1g}
trans-$[Co(NO_2)_2(NH_3)_4]^+$	D_{2h}	A_g	A_g	A_g	A_g, B_g

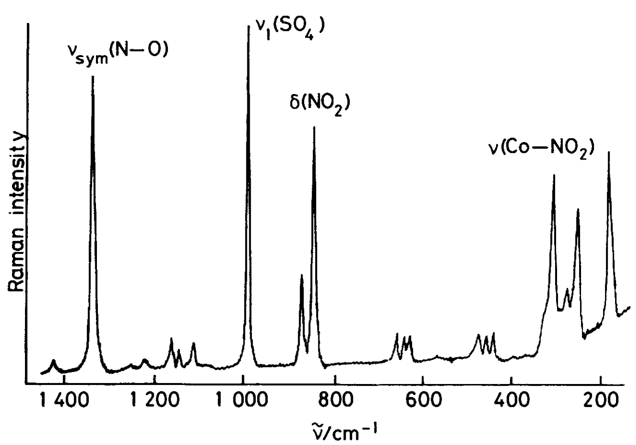

Figure 2. Raman spectrum of $Na_3[Co(NO_2)_6]$ (including Na_2SO_4) with 632.8-nm excitation at *ca.* 80 K; spectral band width = 5 cm^{-1}

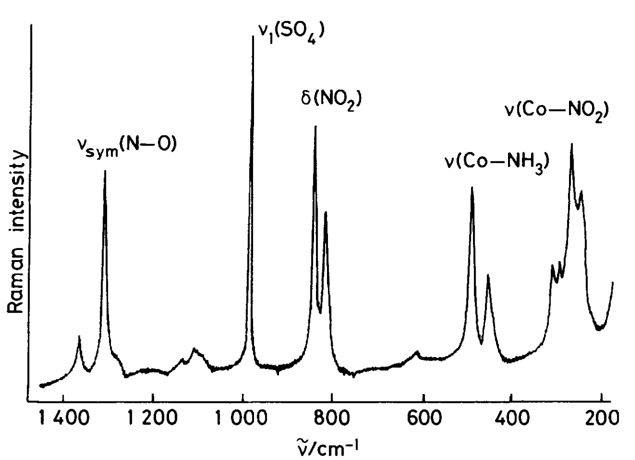

Figure 3. Raman spectrum of *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$ (including K_2SO_4) with 632.8-nm excitation at *ca.* 80 K; spectral band width = 5 cm^{-1}

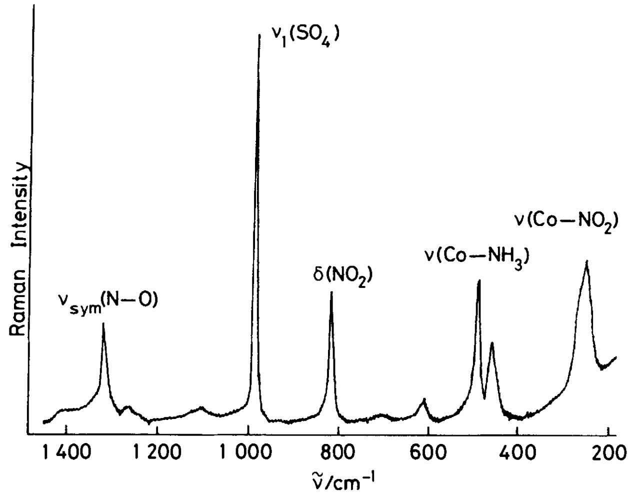

Figure 4. Raman spectrum of *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3{\cdot}H_2O$ (including K_2SO_4) with 632.8-nm excitation at *ca.* 80 K; spectral band width = 5 cm^{-1}

$[NH_4][Co(NO_2)_4(NH_3)_2]$, and *trans*-$[Co(NO_2)_2(NH_3)_4]$-$NO_3{\cdot}H_2O$ including K_2SO_4 or Na_2SO_4 as an internal standard of intensity. Table 1 summarizes the Raman active modes of each complex assuming that each complex takes its idealized symmetry. We have already reported the Raman spectral study of $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$ (x = 1—6), both in aqueous solution and in the solid state at room temperature.[6] The results have shown that a close correlation exists between the solid state and aqueous solution spectra. No drastic changes were observed after cooling the sample to *ca.* 80 K from room temperature indicating that the molecular symmetry of the complex does not change down to 80 K. The present Raman spectra were, therefore, assigned on the basis of our earlier work.

The complex anion of $K_3[Co(NO_2)_6]$ has been recognized to take T_h symmetry.[7,8] In this symmetry, A_g and E_g modes become Raman active for Co–NO_2 stretching, NO_2 bending, and NO_2 symmetric stretching vibrations (see Table 1). In accordance with the depolarization study of the aqueous solution of the complex, the bands at 263 and 291 cm^{-1} can be assigned to the E_g and A_g Co–NO_2 stretching modes, respectively. On the same basis, the bands at 805 and 820 cm^{-1} are assignable to the E_g and A_g NO_2 bending modes, respectively, and that at 1 313 cm^{-1} to the A_g NO_2 symmetric stretching mode. The Raman band due to the E_g mode of the NO_2 symmetric stretching may be assigned to the weak band at *ca.* 1 400 cm^{-1}.

Nakagawa and Shimanouchi[7] have shown that the complex anion of $Na_3[Co(NO_2)_6]$ takes S_6 symmetry on the basis of the i.r. spectrum. Caulton and Fenske,[3b] on the other hand, have proposed the lowering of the symmetry to D_2. Since the Raman spectrum of $Na_3[Co(NO_2)_6]$ does not show a further splitting due to the lowering of the symmetry to D_2 in the NO_2 symmetric stretching and NO_2 bending regions, the results obtained here are not inconsistent with the complex ion adopting the higher symmetry (S_6) conformation under the conditions used to collect the spectra. In the Co–NO_2 stretching region, although some weak additional bands were observed, the bands at 252 and 306 cm^{-1} were tentatively assigned to the E_g and A_g (S_6 symmetry) modes. The Raman bands at 839 and 863 cm^{-1} can be assigned to the E_g and A_g modes of the NO_2 bending and that at 1 328 cm^{-1} to the A_g mode of the NO_2 symmetric stretching under the assumption of S_6 symmetry.

The *X*-ray study of *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$[9] has shown that the four nitro groups are tilted to the square plane with different angles and consequently the complex anion lacks a centre of symmetry. In spite of this lowering of the molecular symmetry, Raman spectral features in the NO_2 bending and

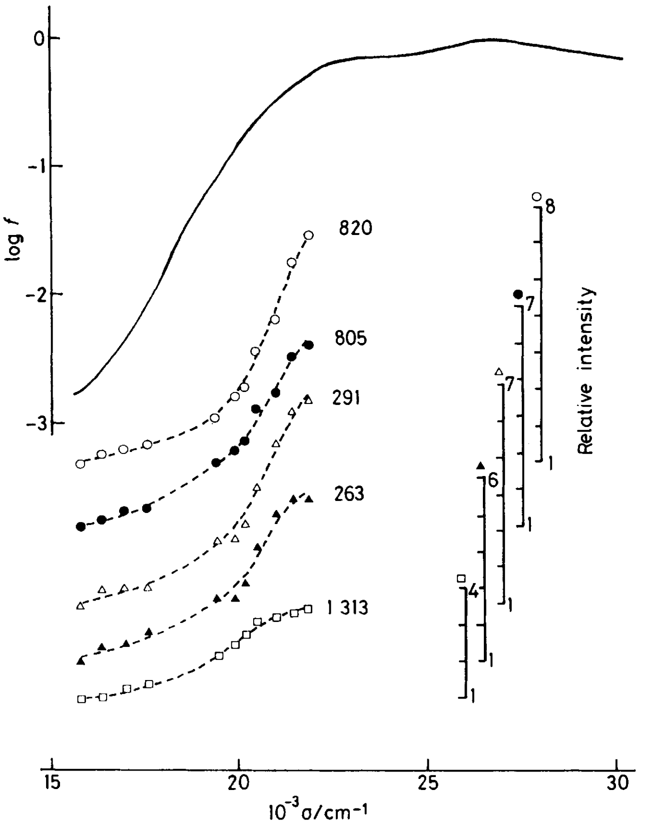

Figure 5. Excitation profiles and diffuse-reflectance spectrum of $K_3[Co(NO_2)_6]$ (uncertainty of intensity was less than ±0.2 and within the size of the symbols)

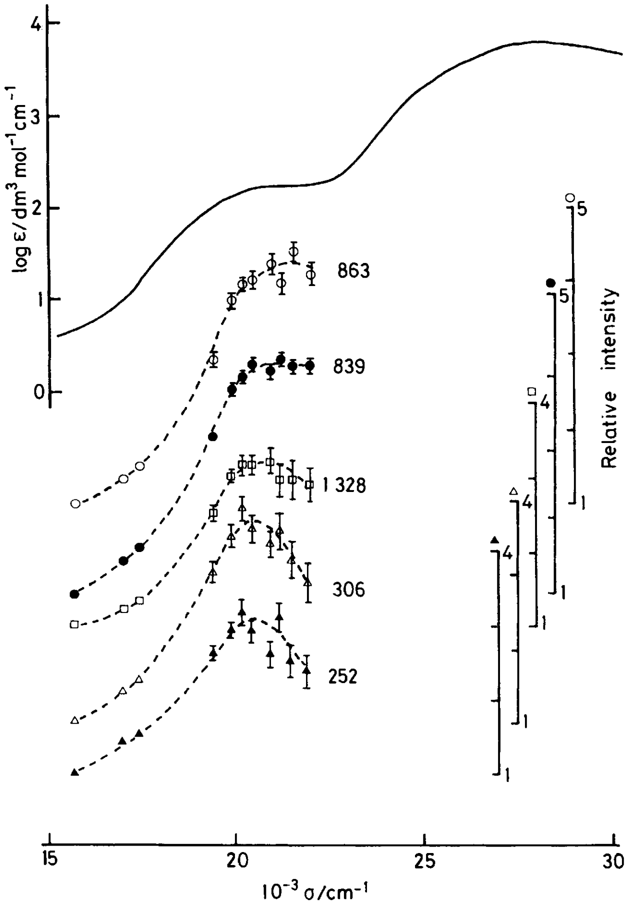

Figure 6. Excitation profiles and electronic absorption spectrum of $Na_3[Co(NO_2)_6]$ (error bars which are shorter than the size of the symbols were omitted)

NO_2 symmetric stretching regions correspond well to those obtained in an aqueous solution, where the complex anion is supposed to take an idealized D_{4h} symmetry. The effective symmetry of the complex anion is, therefore, reasonably regarded to be D_{4h}, and the bands at 824, 835, and 1 316 cm^{-1} are assignable to the B_{1g} and A_{1g} NO_2 bendings, and A_{1g} NO_2 symmetric stretching modes, respectively. The observed small splitting in the Co–NO_2 stretching modes may reflect the slight lowering of the symmetry from D_{4h}. The band at 496 cm^{-1} can be assigned to the A_{1g} mode of Co–NH_3 stretching. The band at 450 cm^{-1} is due to ν_2 of the sulphate.

The *X*-ray study of *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$[10] shows that the complex cation has approximately D_{2h} symmetry. We therefore assigned the bands at 281, 822, and 1 337 cm^{-1} to the A_g modes of the Co–NO_2 stretching, NO_2 bending, and NO_2 symmetric stretching, respectively. The band at 497 cm^{-1} is assignable to the A_g mode of the Co–NH_3 stretching, and that at 450 cm^{-1} to overlapping of the B_g mode of the Co–NH_3 stretching and ν_2 of sulphate.

The NO_2 antisymmetric stretching modes were observed near 1 400 cm^{-1} as weak bands in the above complexes and the excitation profiles of these modes were not obtained because of their low intensity.

Excitation Profiles.—Figure 5 shows the excitation profiles for the potassium salt of $[Co(NO_2)_6]^{3-}$ along with its reflectance spectrum. Since this salt is almost insoluble in conventional solvents, the reflectance spectrum is shown here. Figure 6 shows the excitation profile for the sodium salt along with the electronic absorption spectrum. The reflectance spectrum of the sodium salt was found to correspond well with the absorption spectrum. As is obvious from these figures, it is apparent that the visible band of the potassium salt shows a blue shift compared with that of the sodium salt, *i.e.* the position is 21 500 cm^{-1} for the sodium salt, while *ca.* 23 000 cm^{-1} for the potassium. This difference is reflected in their apparent colours: the sodium salt is dark brown, while the potassium is light yellow. The large blue shift led to the postulation that the visible absorption band is not of a pure ligand-field transition in origin. Even though the molecular symmetry of the complex anion is different in each salt, such a large difference in the peak position should not be expected for a pure ligand-field band.

According to Albrecht's theory,[11] Raman bands can be resonance-enhanced through two mechanisms, namely A- and B-term scattering. A-term scattering involves a single electronic excited state and can contribute only to the resonance enhancement of totally symmetric vibrations. On the other hand, B-term scattering involves two electronic excited states and the vibrations of any symmetry which cause vibronic coupling between the two states may become active in resonance enhancement. In other words, non-totally symmetric vibrations can be resonance-enhanced only through B-term scattering.

Appreciable enhancement was observed for the totally symmetric modes as well as for the non-totally symmetric modes. The totally symmetric modes can be enhanced through A- or B-term scattering. On the other hand, the non-totally symmetric modes require an enhancement due to B-term scattering. Since the resonance behaviour of the totally symmetric modes is very similar to that of the non-totally symmetric modes, a B-term mechanism is more likely to occur

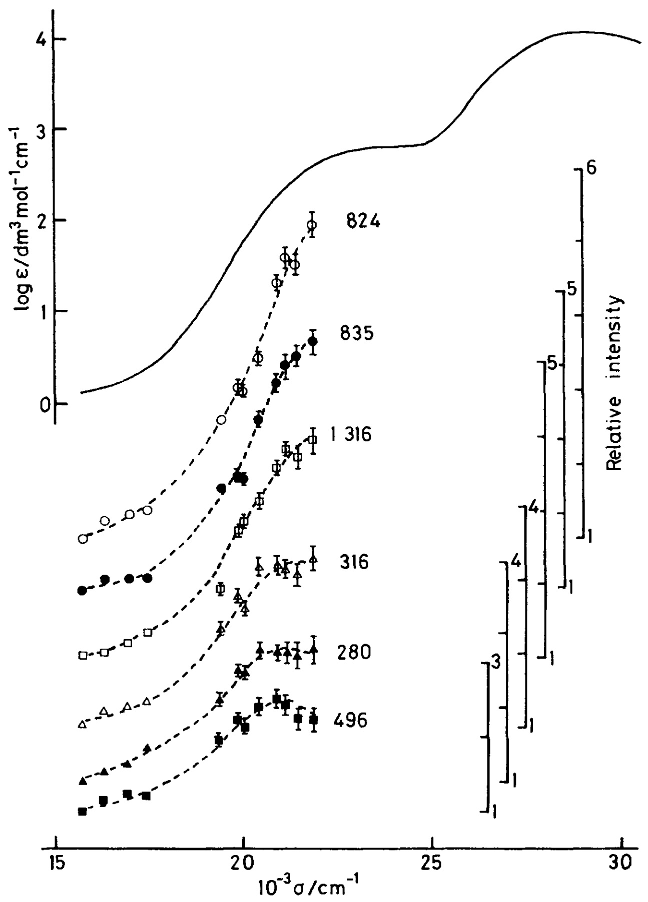

Figure 7. Excitation profiles and electronic absorption spectrum of *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$ (error bars which are shorter than the size of the symbols were omitted)

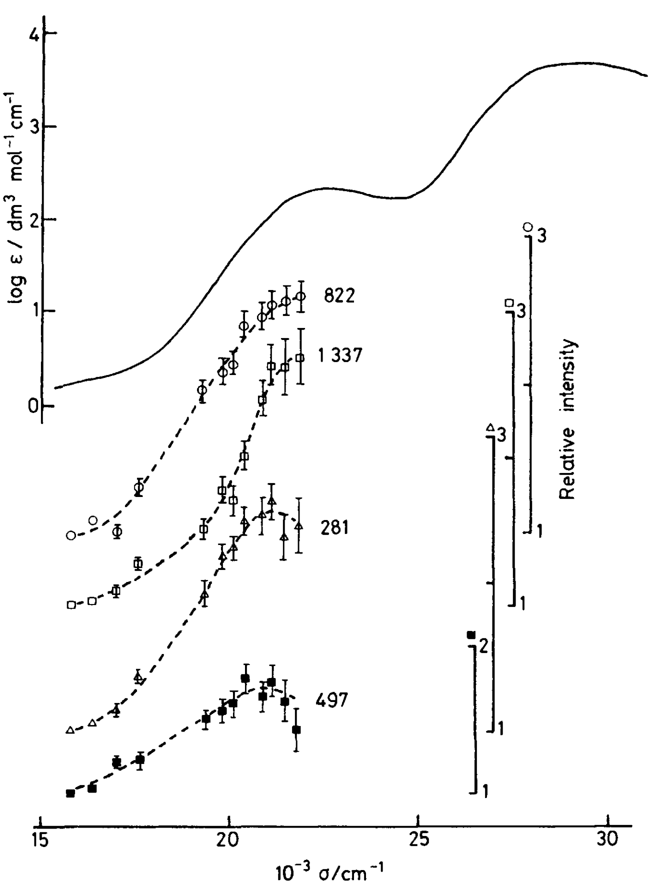

Figure 8. Excitation profiles and electronic absorption spectrum of *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3{\cdot}H_2O$ (error bars which are shorter than the size of the symbols were omitted)

also for the resonance enhancement of the totally symmetric modes.

It seems reasonable to infer from Figure 5 that the excitation profiles of the sodium salt are recognized to follow the envelope of the visible absorption band. Though the excitation profiles of the potassium salt do not reach a maximum because of a limitation of available laser lines, it might be thought that the profiles have a maximum just beyond the higher energy end of the profile, namely at the maximum of the visible band.

The intra-ligand vibrations (NO_2 symmetric stretching and NO_2 bending), as well as the skeletal vibration of the octahedron (Co–NO_2 stretching), were found to be resonance-enhanced in a similar manner. This observation indicates that the resonant states should have a charge-transfer character.[12,13]

From a comparison of the extent of the resonance enhancement of both salts, it seems to relate to the molar absorptivity of the visible absorption bands. Though the molar absorptivity of the potassium salt was not measurable because of its insolubility, it can reasonably be expected, from the relative intensity of the visible band to that of the u.v.-1 band in the reflectance spectra of both salts, that the molar absorptivity of the visible absorption band for the potassium salt should be much higher than that of the sodium salt. The similar dependence of the extent of a resonance enhancement on the molar absorptivity of the visible absorption band was observed for the tetranitro and dinitro complexes, which will be shown later.

In Figure 6, the excitation profiles of the bands at 1 328, 306, and 252 cm^{-1} show distinct maxima, while those at 863 and 839 cm^{-1} only give shoulders. This may result from different contributions to the Raman intensity due to pre-resonance enhancement involving one of the higher-energy electronic transitions. Similar variations of the excitation profiles were observed for *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$ and *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3{\cdot}H_2O$ (see Figures 7 and 8).

The excitation profiles of *trans*-$[NH_4][Co(NO_2)_4(NH_3)_2]$ are shown in Figure 7. The behaviour of the resonance enhancement of the nitro-related vibrations was found to be very similar to that observed for the hexanitro complex. Almost the same excitation profiles were obtained for the bands at 302 and 266 cm^{-1} as those for the bands at 316 and 280 cm^{-1}, and so the former are omitted in Figure 7 for clarity. In addition to the above nitro-related modes, the Co–NH_3 stretching mode at 496 cm^{-1} also shows a resonance enhancement. Because the Co–NH_3 stretching mode in this complex hardly couples with the Co–NO_2 stretching mode, as confirmed by the observation that the Co–NO_2 stretching frequency was not affected by a deuteriation of the co-ordinated ammonia, the Co–NH_3 stretching mode cannot gain intensity through a mechanical coupling with the Co–NO_2 stretching mode. Therefore, the observed enhancement of the Co–NH_3 stretching mode is also suggestive of the resonant states having a charge-transfer character.

Figure 8 shows the excitation profiles of *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3{\cdot}H_2O$. The excitation profiles seem to follow the envelope of the visible band, indicating that the visible band relates to the resonance enhancement in this complex also. As mentioned earlier, a small resonance enhancement was observed in this complex as compared with

Table 2. Absorption bands of $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$ (x = 1—6) complexes: $10^{-3}\sigma/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)

Complex	Visible band	u.v.-1	u.v.-2	u.v.-3
$[Co(NO_2)(NH_3)_5]^{2+}$	21.8	30.8	41.8	
	(100)	(1 660)	(13 800)	
cis-$[Co(NO_2)_2(NH_3)_4]^+$	22.5	30.9	42.7	
	(158)	(4 170)	(19 100)	
trans-$[Co(NO_2)_2(NH_3)_4]^+$	22.7	28.8	39.5	
	(234)	(4 790)	(18 200)	
fac-$[Co(NO_2)_3(NH_3)_3]$	22.7	30.3	39.7	44.1
	(229)	(6 610)	(19 100)	(17 800)
mer-$[Co(NO_2)_3(NH_3)_3]$	23.1	29.1	39.8	
	(309)	(6 610)	(21 900)	
trans-$[Co(NO_2)_4(NH_3)_2]^-$	23.4	28.9	39.5	51.5
	(525)	(11 200)	(24 000)	(22 900)
$[Co(NO_2)_5(NH_3)]^{2-}$	22 (sh)	28.4	38.9	
	(250)	(8 130)	(18 600)	
$[Co(NO_2)_6]^{3-}$	21.5 (sh)	28.2	37.6	48.1
	(235)	(5 130)	(10 500)	(32 400)

the tetranitro complex, and may relate to the small molar absorptivity of the visible band of this complex (see Table 2).

Interpretation of the Electronic Spectra of Nitrocobalt(III) *Complexes*.—On the basis of the excitation profiles of the four nitrocobalt(III) complexes obtained here, the following speculation on the resonant transitions could be made. Since the resonance enhancements observed for the present complexes are considered to be caused by B-term scattering predominantly and this type of scattering requires two resonant states, it is most probable that the visible absorption band and the lowest-energy u.v. absorption band (u.v.-1) are resonant states. In this case, the visible absorption band should have the allowed character at least partly. In support of this assumption, the visible absorption bands of amminenitrocobalt(III) complexes have a larger molar absorptivity compared with those of the pure ammine and amminehalogeno complexes.[2]

It has been known for a long time that the visible absorption bands of $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$ complexes do not obey the average environment rule (see Table 2). Caulton and Fenske[3b] studied the electronic spectrum of hexanitrocobaltate(III) in some detail. They have proposed that the visible band in $[Co(NO_2)_6]^{3-}$ is in fact due to a charge-transfer band which is orbitally forbidden and the '*d–d*' band is masked under the intense u.v. band. According to their assignment, the visible absorption band of the dinitro and tetranitro complexes should be mainly '*d–d*' in origin, while that of the hexanitro complex is charge-transfer in origin. This explanation clearly contradicts the behaviour of the excitation profiles of the nitrocobalt(III) complexes obtained here. No change in the selectivity on the resonance-enhanced modes was observed as a function of the number of nitro groups. Namely, both intra-ligand and skeletal modes gain intensity in a similar manner for the four nitrocobalt(III) complexes and all of the profiles follow the envelopes of the visible bands. This fact strongly indicates that the visible absorption bands of the nitrocobalt(III) complexes must have a common factor in origin. In other words, the $[Co(NO_2)_6]^{3-}$ is not the only anomalous complex in the series of $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$, but the visible absorption bands in all of the nitrocobalt(III) complexes have a more or less charge-transfer character.

Anomalous behaviour of nitrocobalt(III) complexes was also found in the photochemistry of $[Co(NO_2)(NH_3)_5]^{2+}$.[4] The characteristic feature of the photochemistry of this complex is the observation that the same photochemical processes, namely redox decomposition and nitro–nitrito linkage isomerization, are caused by an excitation within the visible and u.v.-1 bands.[4c] In order to explain this phenomenon, 'intersystem crossing' has been proposed, where the dissociative charge-transfer states cross the ligand-field state, allowing the ligand-field state to have an efficient population of the charge-transfer state.[4] A similar inter-system crossing could be expected for the complexes having more than one nitro ligands. Gaining charge-transfer character through an inter-system crossing would be one of the probable mechanisms for the resonance enhancement under the visible absorption band observed here.

It is clear that a full understanding of the visible absorption bands of nitrocobalt(III) complexes needs a more systematic study on the series $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$.

The u.v.-1 band can be considered to be the most probable resonant transition required for B-term scattering. However, there has also been some disagreement concerning the assignment of this band.[1,2] Caulton and Fenske[3b] assigned u.v.-1 of $[Co(NO_2)_6]^{3-}$ to a m.l.c.t. transition on the basis of a molecular orbital treatment. On the other hand, Linhard and Weigel[14] assigned u.v.-1 of $[Co(NO_2)(NH_3)_5]^{2+}$ to a l.m.c.t. transition. In the photochemistry of $[Co(NO_2)(NH_3)_5]^{2+}$,[4] homolytic cleavage of the Co–NO_2 bond, namely reduction of cobalt and oxidation of nitrite, was found to be the result of irradiation within the u.v.-1 band. This observation gives support to the assignment of the u.v.-1 band as l.m.c.t. As demonstrated in this study, the u.v.-1 band must have the same origin among all the present nitrocobalt(III) complexes. Therefore, considering the u.v.-1 band of $[Co(NO_2)_6]^{3-}$ as l.m.c.t. seems to be more reasonable.

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References

1 M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.*, 1982, **55**, 42.

2 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1984.

3 (*a*) H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, 1966, **5**, 669; (*b*) K. G. Caulton and R. F. Fenske, *ibid.*, 1967, **6**, 562; (*c*) J. C. Barnes and R. D. Peacock, *J. Chem. Soc. A*, 1971, 558; (*d*) J. C. Barnes, C. S. Duncan, and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 1972, 1875; (*e*) D. Reinen, C. Friebel, and K. P. Reetz, *J. Solid State Chem.*, 1972, **4**, 103.

4 (*a*) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 1968, **7**, 1398; (*b*) F. Scandola, C. Bartocci, and M. A. Scandola, *J. Am. Chem. Soc.*, 1973, **95**, 7898; (*c*) F. Scandola, C. Bartocci, and M. A. Scandola, *J. Phys. Chem.*, 1974, **78**, 572; (*d*) J. F. Endicott, *Inorg. Chem.*, 1975, **14**, 448; (*e*) J. F. Endicott and G. J. Ferraudi, *ibid.*, p. 3133; (*f*) J. F. Endicott, *ibid.*, 1977, **16**, 494; (*g*) M. A. Scandola, C. Bartocci, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta*, 1978, **28**, 151.

5 R. J. H. Clark, 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heydon, London, 1975, vol. 1, p. 143; R. J. H. Clark and B. Stewart, *Struct. Bonding* (*Berlin*), 1979, **36**, 1.

6 K. Kanamori, T. Morikawa, and K. Kawai, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2787.

7 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, Part A*, 1967, **23**, 2099.

8 I. Nakagawa, T. Shimanouchi, and K. Yamasaki, *Inorg. Chem.*, 1968, **7**, 1332.

9 Y. Komiyama, *Bull. Chem. Soc. Jpn.*, 1957, **30**, 13.

10 I. Oonishi, F. Muto, and Y. Komiyama, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2791.

11 A. C. Albrecht, *J. Chem. Phys.*, 1961, **34**, 1476; A. C. Albrecht and M. C. Hutley, *ibid.*, 1971, **55**, 4438.

12 R. J. H. Clark, P. C. Turtle, D. P. Strommen, B. Streusand, J. Kincaid, and K. Nakamoto, *Inorg. Chem.*, 1977, **16**, 84.

13 R. S. Czernuszewicz, K. Nakamoto, and D. P. Strommen, *J. Am. Chem. Soc.*, 1982, **104**, 1515.

14 M. Linhard and M. Weigel, *Z. Anorg. Chem.*, 1952, **271**, 101.

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