On the Assignment of Band II in the Electronic Spectrum of $[Ni(H_2O)_6]^{2+}$

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Synopsis. $[Ni(H_2O)_6]^{2+}$ shows two absorption maxima in the red part of the visible spectrum. The one with the lower frequency has been assigned to the $^3A_{2g}\to{}^3T_{1g}(F)$ transition, and the other to the spin-forbidden $^3A_{2g}\to{}^1E_g$ transition. A closer comparison with related spectral data, however, makes the reverse assignment more reasonable.

As is well known, high-spin octahedral Ni(II) complexes show three d-d bands in their electronic spectra if there is no other absorption (CT and/or ligand band(s)) covering some of them. These bands are denoted by I, II, and III (in the order of increasing frequency) and are assigned to transitions $^3A_{2g}\to{}^3T_{2g}(F)$, $^3A_{2g}\to{}^3T_{1g}(F)$, and $^3A_{2g}\to{}^3T_{1g}(P)$, respectively, within the $3d^8$ electronic system. The spectra of $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ are typical examples of this spectral pattern. The spectrum of $[Ni(H_2O)_6]^{2+}$ is also very similar to these. However, its band II, which appears in the red part of the visible spectrum, is apparently composed of two maxima, *i.e.*, band IIa at 416 THz[1](721 nm) and band IIb at 457 THz(656 nm). The latter is somewhat weaker than the former.[2]

In 1950, Sone collected a number of spectral data regarding octahedral Ni(II) complexes and found that there is a reasonably good linear relationship between the frequencies of bands II and III. He also pointed out that this relation holds well in the case of $[Ni(H_2O)_6]^{2+}$, if its band IIb (and not band IIa which is apparently stronger) is identified with the band II of other complexes.[3]

In 1956, Ito measured the electronic spectra of many octahedral Ni(II) complexes with special care, and discovered that, in most cases, there is a very weak absorption band at the lower-frequency side of their band II. This band appears as a weak shoulder (or merely as a slight inflection) which often is scarcely discernible. Its position and intensity could be determined only by analyzing the whole spectrum into Gaussian-type components, which Ito carefully carried out. This band can now be assigned to the spin-forbidden $^3A_{2g}\to{}^1E_g$ transition which, according to the Tanabe-Sugano diagram, is expected to appear in the vicinity of band II. It should naturally be very weak. Figure 1 shows an example of such an analysis.[4,5]

Ito also studied the numerical relations among the ν_{max} values of the three bands, which he refined by the above-mentioned analyses. He found that a linear relationship which is similar to that found by Sone approximately holds between any two of the three ν_{max} values. These are denoted by ν_I, ν_{II}, and ν_{III}, respectively.[6] He also found another relation, $(\nu_{II})^2=\nu_I\nu_{III}$, which holds as well. He confirmed that band IIb of $[Ni(H_2O)_6]^{2+}$ satisfies these rules much better than band IIa. This shows again that the former should be taken as band II of this complex.[4]

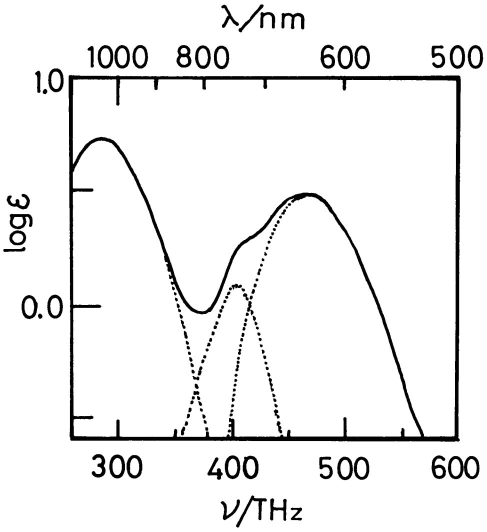

Fig. 1. Analysis of band II of $[Ni(gly)(H_2O)_4]^+$(gly= glycinate ion) in aqueous solution into two Gaussian-type components. After Ref. 4).

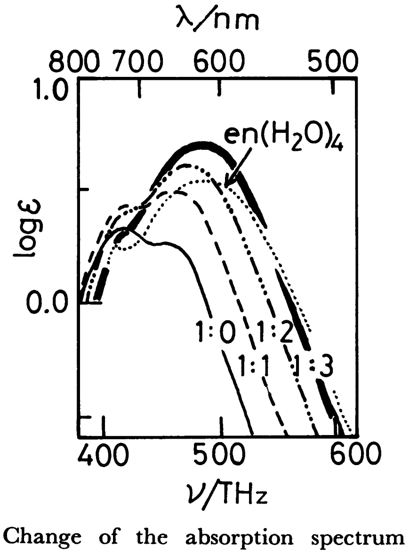

Fig. 2. Change of the absorption spectrum of $[Ni(H_2O)_6]^{2+}$ caused by the addition of NH_3. $C_{Ni^{2+}}$: 0.2 mol dm^{-3}, $C_{NH_4^+}$ (added as NH_4NO_3): 6 mol dm^{-3} The ratio Ni^{2+}: NH_3 is given on each curve. The spectrum of $[Ni(en)(H_2O)_4]^{2+}$ is also shown.

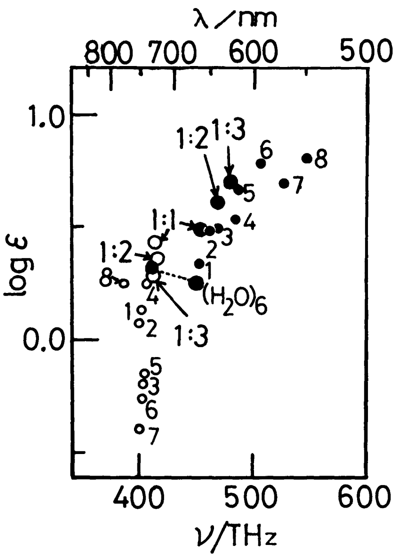

Fig. 3. The positions and intensities of band II (●) and spin-forbidden band (○) of various octahedral Ni(II) complexes in aqueous solution. Nonaqueous ligands in the coordination spheres of these complexes are: 1, asp(−I); 2, gly; 3, asp(−II); 4, en: 5, 2gly; 6, 5NH$_3$; 7, 6NH$_3$; 8, 3en. (asp(−I) and asp(−II) mean aspartate ions of charge −1 and −2, respectively). Apparent values taken from the curves 1 : 1 to 1 : 3 of Fig. 2 are also plotted. The points for bands IIa and IIb of $[Ni(H_2O)_6]^{2+}$ are shown by (●----●). For further details, *cf.* Refs. 4) and 10).

In spite of these early findings, later investigators generally identified band IIa of this complex with band II itself, and band IIb with the spin-forbidden band superposed on it, as may seem upon first glance.[7] There was also another explanation which denies the intervention of a spin-forbidden transition and ascribes the appearance of the two maxima to spin-orbit coupling.[8]

Recently, Ito examined the spectral data of aqueous solutions containing $[Ni(H_2O)_6]^{2+}$, NH$_3$, and various anions (ClO_4^-, NO_3^-, and Cl^-). Some of his curves are shown in Fig. 2. Here, one can see that, in going from a solution of $[Ni(H_2O)_6]^{2+}$ to those of Ni(II) ammine complexes, band IIa remains nearly at the same position. However, band IIb moves steadily in conformity with the spectrochemical series. This seems to be an indication that the former is the spin-forbidden band since, according to the Tanabe-Sugano diagram, its frequency should be quite insensitive to the variation in the ligand field strength. Band IIb should, thus, be identified with band II of other complexes, as was formerly pointed out by himself and Sone. A comparison with the curve of $[Ni(en)(H_2O)_4]^{2+}$, which is also shown in the same Figure, makes this view still more convincing.

On the basis of these findings, the earlier data of Ito[4] were reexamined, and the values of ν_{II} and ν_{sf} (*i.e.*, the frequency of the spin-forbidden band) of various Ni(II) complexes obtained by his curve analyses were plotted against their intensities (log ε), as shown in Fig. 3. It is now evident that the points for ν_{II} and those for ν_{sf} collect around two distinct curves. The former depend notably on the nature of the ligands and obey the spectrochemical series. However, the latter are nearly independent of the ligands, as expected from the Tanabe-Sugano diagram. Moreover, it can be observed, in general, that with the decrease of the frequency difference between band II and the spin-forbidden band, the intensity difference between them also tends to diminish (*i.e.*, band II tends to become weaker, and the spin-forbidden band stronger). This can be ascribed to an increased mixing of the nature of these transitions which occurs in the same direction.

The positions and intensities of bands IIa and IIb of $[Ni(H_2O)_6]^{2+}$, which were also refined by curve analyses, are plotted in Fig. 3. Now, it is easy to see that band IIa is better correlated with the spin-forbidden band of other complexes, and band IIb with their band II. Here, however, the two bands are so close that an exceptionally strong mixing takes place, making the former band quite spin-allowed and the latter somewhat spin-forbidden. Thus, they show a characteristic reversal of their intensities. In such a case, it may be reasonable to take the weighted mean (or center of gravity) of the two bands and assume it to be the ν_{II} of the system which should be used when the Tanabe-Sugano diagram and related formulas are applied to these data. Nephelauxetic parameters (B and β) of reasonable magnitude can be estimated in this way.[9]

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References

1) In this paper, the positions of the bands are shown in frequencies (THz=10^{12} s^{-1}) and not in wave numbers, to be consistent with the former publications of Sone[3] and Ito[4] where 10^{13} s^{-1} was used as their units.

2) For an elementary explanation of these spectra, *cf.*, *e.g.*, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 4th ed., Wiley, New York (1980), p. 786.

3) K. Sone, *Nippon Kagaku Zasshi*, **71**, 270 (1950).

4) H. Ito, *Nippon Kagaku Zasshi*, **77**, 1383 (1956).

5) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753, 766 (1954).

6) ν_{II}=1.467 ν_I+5.49; ν_{III}=0.940 ν_{II}+34.84; ν_{III}=1.418 ν_I+38.85.

7) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957); C. K. Jφrgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

8) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959); *Mol. Phys.*, **2**, 123 (1959).

9) *Cf.* A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam (1968), p. 216.

10) For more spectral data which support the view expressed in the present paper, and experimental technique employed to get them, *cf.* H. Ito, *J. Sci. Univ. Tokushima*, **18**, 15 (1985).