

## Spin Forbidden Bands in Cr III Hexamine

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A large deuterium isotope effect has been found in the spin forbidden bands of the chromium III hexamine complex. The significance of this is discussed.

Chromium III hexamine has a visible absorption system (1) near 15 000  $\text{cm}^{-1}$  with well-developed structure which has not hitherto been assigned. According to theory (2), transitions in this region should be  ${}^2E_g \leftarrow {}^4A_{2g}$  and/or  ${}^2T_{1g} \leftarrow {}^4A_{2g}$  as have been experimentally verified in the spectrum of ruby (3) and other  $d^3$  complexes.

We have examined the spectrum using both the hexamine and the fully deuterated hexamine and find that there is a marked isotope shift in at least two bands (see Fig. 1). Other bands are also shifted but by a much smaller amount (see Table I). The spectral observations are very similar to those of Piper and Koertge (4), who examined  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  and its deuterated analog, but the chromium system is far better resolved and free from the diffuse absorption found by Koertge and Piper in the nickel complex. It is possible, therefore, to locate the origin of the absorption (vibronic or electronic) fairly accurately and we conclude that the band which is strongly isotope shifted is not a simple N—H or N—D totally symmetric stretching frequency superposed upon the origin. The bands which are strongly isotope affected lie about 910–975 and 700–790  $\text{cm}^{-1}$  from the first band in the proto and deutero cases, respectively, and in view of their large isotope effect ( $\sim 165$ – $175 \text{ cm}^{-1}$ ) they can be correlated only with one of the essentially  $\text{NH}_3$  vibrations  $\nu_2(a_1)$ ,  $\nu_5(e)$ , or  $\nu_6(e)$  which are frequently given the descriptive labels  $\delta_s(\text{NH}_3)$ ,  $\delta_d(\text{NH}_3)$ , and  $\rho_r(\text{NH}_3)$ , respectively. The related frequencies in the chromium and cobalt hexamine complexes (5, 6) are known for both the protonated and deuterated compounds and have the values 1310, 1025 ( $\nu_2$ ); 1620, 1160 ( $\nu_5$ ); and 750, 580? ( $\nu_6$ ) for the — $\text{NH}_3$  and — $\text{ND}_3$  compounds, respectively.

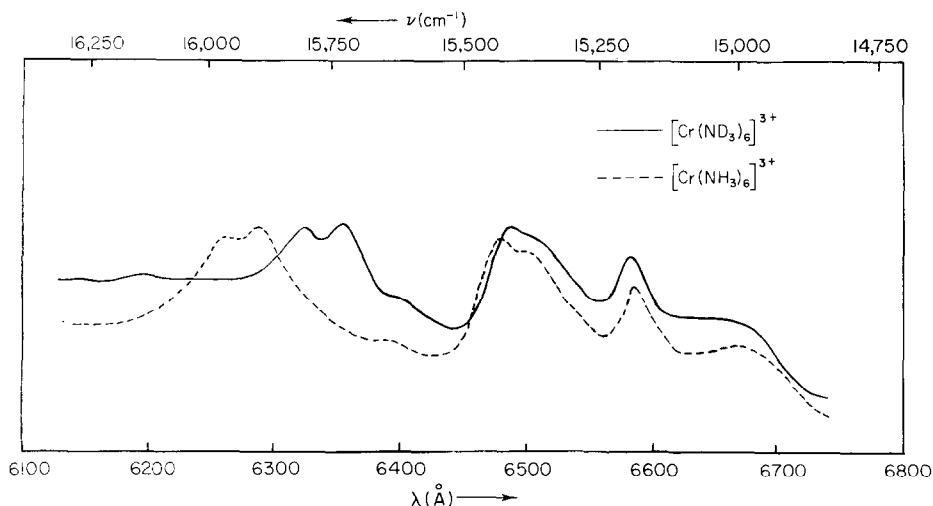


FIG. 1. The low frequency spin forbidden system of Cr III hexamine and its deuterio analog.

It is not possible to say, *a priori*, whether the electronic origins of the system(s) will be shifted to high or low frequencies upon deuteration although, from the type of transition involved ( $t_{2g} \rightarrow t_{2g}$  configurationally), supported by the sharpness of the vibrational structure, it would be surprising if the shift were to be a large one. Both the lowest and next to lowest frequency bands are at slightly higher frequencies for the deuterio compound although the lowest frequency bands are so broad as to make it difficult to assess them accurately.

In the absence of Raman data it is not possible to make an exact assignment but two things appear to be clear. The first is that the isotope affected pair of bands must be essentially  $-\text{NH}_3$  ( $-\text{ND}_3$ ) in type rather than skeletal ( $\delta$ ) and the second is that the most likely correlation to be made is with the  $\nu_6(e)$  rocking mode. This choice is made for a number of reasons. In the first place it does not seem likely that the N—H or N—D frequencies will suffer a catastrophic change *either* in the process of combining their phases to conform to the over-all symmetry of the molecule or in the excited state of such a transition as this and, in the second place, even though the frequency of  $\nu_6$  in the hexamine is not known, it can be assessed from the data for  $\text{NH}_3$  and  $\text{ND}_3$  and the value of  $580 \text{ cm}^{-1}$  was obtained from this source. It is an almost invariant rule that the difference of the proto and deuterio frequencies is very close to the same for the ground and excited electronic states so that the ground-state vibrations should differ by about the same order of magnitude as the isotope shift in the visible absorption spectrum—i.e.,  $\sim 160\text{--}175 \text{ cm}^{-1}$ . The  $\nu_6(e)$  vibration is the only one which fulfills this requirement and this is a further reason for the assignment suggested here.

TABLE I  
BAND FREQUENCIES ( $\text{cm}^{-1}$ )

Band No.	Proto	Deutero	$\Delta\nu(\text{D} - \text{H})$
1 (broad)	14 990	15 030	+40
2	15 175	15 185	+10
3	15 380	15 370	-10
4	15 430	15 410	-20
5 (shoulder)	15 650	15 640	-10
6	15 905	15 730	-175
7	15 975	15 810	-165
8	16 525	16 445	-80

The choice of  $\nu_6(e)$  as the type of vibration, requires that the next to lowest frequency bands ( $15\ 175\ \text{cm}^{-1}$  and  $15\ 184\ \text{cm}^{-1}$  for proto and deutero compounds, respectively) be chosen as either vibronic or electronic origins, probably the former (7) in view of the presence of the lower frequency very broad band. The upper-state frequencies thus become  $730$  and  $800\ \text{cm}^{-1}$  for the proto and  $545$  and  $625\ \text{cm}^{-1}$  for the deutero compound. One further important point needs to be noted, namely, that it is not possible to construct a vibration totally symmetric in  $O_h$  from a combination of  $\nu_{6(e)}$  species, whereas it is possible to construct one which is totally symmetric in the point group  $D_{3d}$ , to which the most symmetric conformation of the  $[M(\text{NH}_3)_6]^{n+}$  ion belongs. The small differences between the infrared active frequency and the frequencies observed in the visible spectrum are, of course, to be expected because of the nonzero interactions between the individual  $-\text{NH}_3$  distortion modes, and the difference observed ( $\sim 60\text{--}80\ \text{cm}^{-1}$ ) is a not unreasonable one.

The above assignment stresses the fact that the intensities of such "octahedral" type molecule transitions do depend upon the exact local microsymmetry, i.e., the central ion is aware of the deviations from an  $O_h$  point group symmetry brought about by the presence of the hydrogens (deuteriums) attached to the nitrogens. In fact, from the spectrum it can be seen that a considerable portion of the intensity is to be found in the deuterium affected bands so that even if the specific assignment of the vibration species is in error, the conclusions still hold—e.g., in the event that the isotope affected bands are additional vibronic origins and that the molecular vibration is an infrared active one, it is still true that the central metal orbitals are considerably perturbed by the motions of the hydrogen atoms on the nitrogens.

A series of runs was also made on the intermediately deuterated chromium compounds by simply quenching the exchange of the hydrogens and deuteriums at different times and taking the spectrum of the products. These spectra showed a series of bands intermediate between the ones given in the figure and completely

confirmed what seemed evident—that the bands being discussed in this paper are analogous ones in the proto and deutero compounds, respectively.

The evidence and the conclusions thus suggest that even in those cases where the transitions are not sharp enough to be assigned (e.g., in the octahedral hydrates), the intensity will be found to depend both upon the motion of the nearest neighbor atoms (e.g., oxygens) and the motion of the next-to-nearest neighbor atoms (hydrogens). The spectrum reported here does not enable any choice between an electronic assignment of  ${}^2E_g$  or  ${}^2T_{1g}$  to be made.

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