Metal Isotope Effect on the Raman Spectrum of Solid $[Zn(NH_3)_4]I_2$

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Summary The A_1 and F_2 Zn–N stretching vibrations of the Raman spectrum of solid $[Zn(NH_3)_4]I_2$ have been assigned by using the metal isotope technique: the A_1 mode shows almost no dependence on the isotopic substitution of the central metal atom, whereas the F_2 mode is metal isotope-sensitive.

WE have demonstrated[1] that the use of heavy-metal isotopes provides a unique method to assign the metal–ligand vibrations in the i.r. spectra of a variety of co-ordination compounds. We have now applied the metal isotope technique to the Raman spectrum of solid $[Zn(NH_3)_4]I_2$.

Theoretically, two metal–nitrogen stretching vibrations (A_1 and F_2) should be Raman-active for tetrahedral (T_d) ammine complexes. The totally symmetric A_1 mode involves no motion of the central metal atom and should thus be independent of the ^{64}Zn–^{68}Zn isotopic substitution. On the other hand, the F_2 mode involves the motion of the central metal atom and should be sensitive to the isotopic substitution.

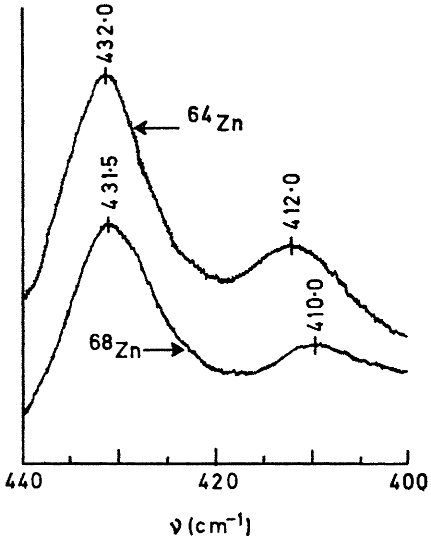
We have prepared $[^{64}Zn(NH_3)_4]I_2$ and $[^{68}Zn(NH_3)_4]I_2$ (isotopic purities, ^{64}Zn, 99·66% and ^{68}Zn, 98·50%) on a milligram scale, and measured their Raman spectra on a Spex Model 1401 Raman spectrophotometer equipped with an Argon ion laser. The instrumental resolution and reproducibility are 0·5 cm^{-1}. The Figure shows an actual tracing of the spectra obtained and the Table lists the observed frequencies in the Zn–N stretching region.[2] These frequencies were determined by multiple scans over the desired bands.

Raman-active Zn–N *stretching frequencies and isotopic shifts for* $[Zn(NH_3)_4]I_2$ (*cm*$^{-1}$)

^{64}Zn	^{68}Zn	Shift
432·0	431·5	0·5
412·0	410·0	2·0

As can be seen from the Table, the 432·0 cm^{-1} band gives a shift of 0·5 cm^{-1} which is within the experimental error, whereas the 412·0 cm^{-1} band gives a large shift of 2·0 cm^{-1}. Thus, it is possible to assign the former to the A_1 and the latter to the F_2 species based on the observed isotopic shifts alone. This assignment has also been confirmed by the observation that the 427 cm^{-1} band of approximately 4M-ammonia solution of $[Zn(NH_3)_4]I_2$ is strongly polarized.

Other vibrations such as NH_3 stretching, NH_3 degenerate and symmetric deformation, and NH_3 rocking modes[3] do not involve the motion of the metal atom and show only small (maximum 0·8 cm^{-1}) isotopic shifts on ^{64}Zn–^{68}Zn substitution. A more detailed discussion on the i.r. and Raman spectra of $[^{64}Zn(NH_3)_4]I_2$ and its ^{68}Zn and ND_3 analogues will be presented in separate papers. The present results are sufficient, however, to show the feasibility of this new technique in assigning the metal–ligand vibrations in the Raman spectra of co-ordination compounds.



FIGURE

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