Matrix Isolation Studies on Ytterbium Dichloride: A Non-linear Molecule. Observation of Isotopic Structure on ν_1 and ν_3

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Studies of the infrared spectrum of ytterbium dichloride isolated in an argon matrix demonstrate that the molecule is non-linear. On the basis of chlorine isotope shifts and the relative intensities of ν_1 and ν_3 the bond angle is estimated to be 126 ± 5°.

During a recent matrix isolation study on the characterisation of molecular lanthanide trichlorides,[1] it became necessary to distinguish between the vibrational frequencies of monomeric MCl_3 species, the corresponding dimers M_2Cl_6, and possible lower halides such as molecular MCl_2. All three species are possible vaporisation products from the anhydrous solids. In particular, matrix i.r. spectra obtained by vaporising solid samples of $SmCl_3$, $EuCl_3$, and $YbCl_3$ contained features characteristic of MCl_2 vibrations. An independent series of experiments was therefore carried out on prepared samples of the anhydrous dichlorides.

Results and Discussion

The argon matrix i.r. spectra obtained from the lanthanide dichlorides were similar to those previously assigned to MCl_2 species by other authors,[2] but for the ytterbium system in particular, our bands were very much better resolved, and we were in a position to study the vibrational fundamentals of $YbCl_2$ in greater detail. Figure (*a*) shows the spectrum obtained from a sample of solid $YbCl_2$ (with chlorine isotopes in natural abundance), and the frequencies are summarised in the Table. When solid samples prepared using 90 atom % ^{35}Cl enrichment were similarly studied, only the two bands at 296.5 and 287.2 cm^{-1} were prominent.

High-temperature mass spectrometric studies on this system[3] have shown that the most likely molecular vapour species produced under our conditions is $YbCl_2$, and an obvious interpretation of spectrum (*a*) is that the six-line pattern is due to the two i.r. stretching modes of a bent (C_{2v}) $YbCl_2$ molecule. For chlorine isotopes in natural abundance (^{35}Cl, 75%; ^{37}Cl, 25%) two 9 : 6 : 1 triplets should be observed. This interpretation is supported by the observation that with 90 atom % ^{35}Cl samples, only the highest-frequency component of each triplet is prominent.

However, it is well known that argon matrices frequently exhibit multiple trapping sites, and it could be maintained that the six bands in (*a*) are due to the single i.r.-active stretching mode (ν_3) in a *linear* $YbCl_2$ molecule trapped on two different sites. Evidence that this is not the case, and that the spectrum corresponds to two different i.r.-active modes of the same molecule, comes from a consideration of the frequency spacings within the triplets. It is evident from spectrum (*a*) that the central component of the upper triplet (at 294.4 cm^{-1}) is higher in frequency than the mean position of the outer components. This is a common phenomenon, and indicates that for the partially substituted molecule, $Yb^{35}Cl^{37}Cl$, this mode is perturbed by a lower frequency mode of the same symmetry. In contrast, the central component of the lower frequency triplet (at 282.6 cm^{-1}) is perturbed to *lower* frequency. If a site effect were responsible for the appearance of two triplets, one would anticipate that this perturbation would be in the same direction. The observed pattern, however, is exactly what would be predicted if the two triplets arise from different modes of the same molecule. For $Yb^{35}Cl_2$ and $Yb^{37}Cl_2$, with C_{2v} symmetries, both the A_1 and B_2 stretching modes are i.r. active, but do not interact. In $Yb^{35}Cl^{37}Cl$, however, the symmetry is now C_s with the result that the two stretching modes (now both A') interact and repel each other.

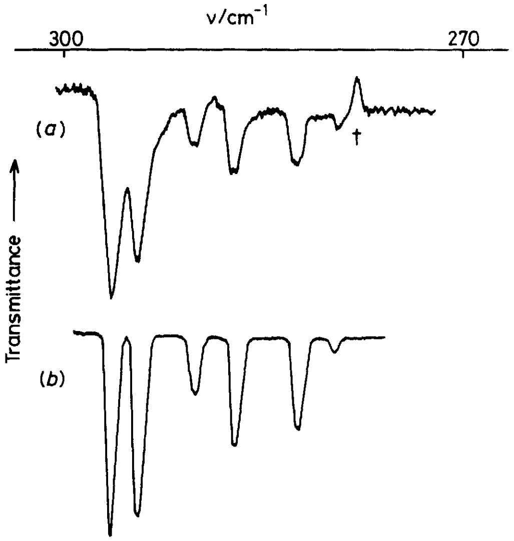

Figure. The infrared spectrum of ytterbium dichloride isolated in an argon matrix (*a*) observed (stretching region only), (*b*) calculated. († denotes inverse H_2O peak)

Table. Observed and calculated frequencies[a] (cm^{-1}) for $YbCl_2$ in argon matrices

Observed	Calculated[b]	Assignment
296.5[c]	296.5	ν_3 $Yb^{35}Cl_2$ (B_2)
294.4	294.4	ν_3 $Yb^{35}Cl^{37}Cl$ (A')
290.3	290.3	ν_3 $Yb^{37}Cl_2$ (B_2)
287.2[c]	287.2	ν_1 $Yb^{35}Cl_2$ (A_1)
282.7	282.6	ν_1 $Yb^{35}Cl^{37}Cl$ (A')
279.8	280.0	ν_1 $Yb^{37}Cl_2$ (A_1)

[a] Frequencies accurate to ±0.5 cm^{-1}. [b] Using F_R = 1.469 mdyn Å^{-1} and F_{RR} = 0.095 mdyn Å^{-1} (dyn = 10^{-5} N); bond angle = 125°. [c] Use of isotopically enriched (90% ^{35}Cl) material resulted in observation of only these two peaks.

This assignment is further confirmed by a quantitative comparison between the observed spectrum and the isotope pattern predicted for the C_{2v} model. Figure (*b*) shows the spectrum calculated for a bent $YbCl_2$ species (with natural abundance chlorine isotopes) assuming a bond angle Cl–Yb–Cl of 125°, and appropriate values for the principal (F_R) and interaction (F_{RR}) stretching constants. In this calculation, interaction with the bending mode is neglected. The calculated frequencies are summarised in the Table and the agreement with the observed frequencies is within experimental error.

The value of 125° chosen here for the bond angle is based on the $Yb^{35}Cl_2 \longrightarrow Yb^{37}Cl_2$ isotope shift for the upper triplet, and by comparison with similar calculations on matrix isolated MCl_2 species[4] will represent a lower limit in view of the neglect of anharmonicity. It is difficult to assess the likely error involved here, but we believe it to be $\lesssim 5°$. A second, independent estimate of the bond angle comes from the relative intensities of the two stretching modes for $Yb^{35}Cl_2$ *via* equation (1),[5] where 2θ is the bond angle. In this way, a value of 127° is obtained. This expression similarly assumes no interaction with the bending mode, and also that the bond dipole approximation is valid. Combining these values indicates a Cl–Yb–Cl bond angle of 126 ± 5°. Our principal conclusion, however, is that molecular $YbCl_2$ has C_{2v} symmetry, and as far as we are aware this is the first unambiguous result showing non-linearity for a transition element dichloride molecule.

$$\frac{I_{B_2}}{I_{A_1}} = \tan^2\theta \frac{(M_{Yb} + 2M_{Cl}\sin^2\theta)}{(M_{Yb} + 2M_{Cl}\cos^2\theta)} \qquad (1)$$

Experimental

The (visually colourless) lanthanide dichlorides were prepared by the reduction of the corresponding anhydrous trichlorides in a stream of hydrogen and dry hydrogen chloride.[6] Isotopically enriched samples of $YbCl_2$ (90 atom % ^{35}Cl) were prepared by reacting the metal with enriched hydrogen chloride: samples of natural abundance $YbCl_2$ prepared in this way gave identical spectra to those from trichloride reduction.

Prior to deposition, solid samples were purified by sublimation to remove traces of the more volatile trichloride and matrices were subsequently laid down over a period of *ca.* 1 h, with deposition temperatures slightly in excess of 1 000 °C. The general features of our matrix isolation apparatus have been described elsewhere.[7] I.r. spectra were recorded over the range 1 000—200 cm^{-1} using a Perkin-Elmer 225 spectrophotometer, and spectral peak simulations assumed a Gaussian function.

Acknowledgements

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