Transition-Metal Halides

DOI: 10.1002/ange.200704667

TiF_2: Linear or Bent?**

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The shapes and geometries of the molecular transition-metal halides have interested and intrigued experimental and computational chemists for a long time. The majority of such halides are high-temperature vapor-phase species, which makes them challenging to study by structural and spectroscopic techniques. They are also a challenge to theoretical/computational chemists. The vapor composition is often complex, and spectral interpretation and assignment are not always straightforward.[1,2] The naturally occurring chlorine isotopes greatly enhance the reliability of spectral assignments, but monoisotopic fluorine can make rigorous assignments more difficult, especially in the absence of metal isotopic data. There is a consensus from the experimental data that all of the first-row transition-metal dichlorides, as well as $CaCl_2$ and $ZnCl_2$, are linear, that CrF_2 to ZnF_2 are linear, and that CaF_2 is bent (ca. 150–155°), but owing to the lack of isotopes for ScF_2 and VF_2, no inference can be made from their matrix IR spectra.[1,2] Therefore, because of the Ti isotopes, TiF_2 is the key molecule in understanding the geometric and electronic structures of the first-row transition-metal dihalides.

An early (1969) matrix isolation IR study of the vaporization of TiF_3/Ti mixtures indicated a bond angle of about 130° for TiF_2.[3] However, in 1989 Beattie et al. showed that this value was unreliable[4] by using a plot of the simple valence force field (SVFF) force constants (f_r–f_{rr}) from the ν_3 values of MF_2 versus those of MCl_2, as indicated in Figure 1 (this is essentially identical to Figure 1 in reference [4] except that the data is limited to linear species, and to those which are considered reliable[1,2,5]). The straight line is a fit to the solid circles of the Cr, Mn, Fe, Co, Ni, and Zn data. The Ti data point marked + is for the original ν_3 value of TiF_2, assuming linearity; it moves further away from the line if the molecule is bent. Given the good fit to the other elements, this was a good indication that the IR data supposedly for TiF_2 was erroneous, probably owing to the complexity of the titanium fluoride vapor-phase system and high volatility of TiF_4. The IR bands originally assigned to TiF_3 at about 790 cm^{-1} were reassigned to TiF_4 on the basis of gas-phase[6] and matrix data[4] obtained from the evaporation of TiF_4. Therefore, the bands at about 740 cm^{-1} originally assigned to TiF_2 were considered to be almost certainly due to TiF_3.[4] Hence, the reported 130° bond angle of TiF_2 is actually that of 120° in TiF_3, and analysis of the Ti isotope pattern confirmed this.[4] Although not explicitly stated in the previous paper,[4] Figure 1 gives an estimate of about 670 cm^{-1} for the ν_3 mode of linear TiF_2. The only other experimental report on molecular TiF_2 is a matrix ESR report published in 1977 in which the data were reported to be consistent with a bent triplet structure; however, the signals were weak and broad with no observable Ti or F hyperfine couplings.[7]

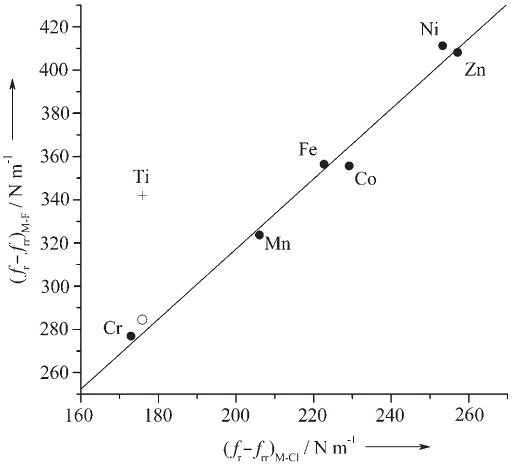

Figure 1. Plot of SVFF force constants (f_r–f_{rr}) for MF_2 versus MCl_2. See text for descriptions regarding the Ti data points.

A detailed DFT study found the difluorides and dichlorides of Mn to Zn were linear, but with soft, low-energy, large-amplitude, bending vibrations.[5] The dihalides of Ca to Cr (and especially the fluorides) were quasi-linear with large-amplitude vibrations over a linear-geometry saddle point, leading to imaginary harmonic frequencies for the bending mode of the linear molecules.[5] The ω_3 mode of TiF_2 was 744 cm^{-1} for the linear (saddle-point) geometry and 722 cm^{-1} for the bent (132.9°) ground-state structure. More recent multireference configuration interaction methods (icMRCI) found TiF_2 to be linear, but the near degeneracy of the ground and first excited states ($^3\Sigma_g^-$, $^3\Delta_g$) meant the ground state could not be determined.[8] The ω_3 value was 705 cm^{-1} for the $^3\Sigma_g^-$ state and 695 cm^{-1} for the $^3\Delta_g$ state. The better agreement between calculated and experimental vibrational data for $TiCl_2$ than TiF_2 was commented on,[8] but the unreliability[4] of the published TiF_2 experimental data[3] was not noted.

Therefore, as highlighted by Beattie,[1] TiF_2 is the key molecule in understanding the geometric and electronic structures of the first-row transition-metal dihalides, and the aim of this investigation was to obtain the first reliable experimental values of the ν_3 vibrational mode of molecular

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[**] This work was supported by an EPSRC research grant (GR/T09651) and a DTA studentship to A.V.W. Prof. Ian Beattie is thanked for many helpful discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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TiF_2 from matrix IR experiments and to use the Ti isotope pattern to determine the bond angle.

When Ti atoms were trapped in 0.6% F_2/Ar matrices (Figure 2a), four sets of IR bands were observed in the $\nu_{\text{Ti-F}}$ region at 792.0 (**A**); 743.4 and 739.7 (**B**); 678.0 and 674.0 (**C**); and 635.7 cm^{-1} (**D**). After broad-band Hg–Xe photolysis (Figure 2b) bands **C** and **D** reduced in intensity while **A** and **B** increased. In these spectra the titanium isotope pattern (central intense peak with a pair of weaker bands of similar intensity on each side) on bands **A**, **B**, and **C** is masked by site effects, and the presence of these is not surprising as they have been observed previously for TiF_4,[3,4] TiF_3,[7] $TiCl_2$,[9] and VF_3[10] in both Ar and Ne matrices. In 0.2% F_2/Ar matrices, (Figure 2c) the same four bands were observed, but with bands **C** (677.73 and 673.81 cm^{-1}) and **D** (635.55 cm^{-1}) having greater relative intensity than **A** (791.88 cm^{-1}) and **B** (743.68 and 739.70 cm^{-1}). After broad-band Hg–Xe photolysis and annealing to 25 K (Figure 2d), the most marked difference is the large increase in intensity of peak **A**. Despite the continued presence of site effects, the Ti isotope pattern is now present on bands **A**, **C**, and **D**, but the presence of multiple sites for band **B** is still problematic. In 10% F_2/Ar matrices, only two broad bands corresponding to **A** and **B** were observed at 792 and 738 cm^{-1}. The behavior at different F_2 concentrations (0.16%, 0.2%, 0.3%, 0.6%, 1%, 2%, 10%), as well as on annealing and photolysis, confirmed that the four sets of bands belonged to different species.

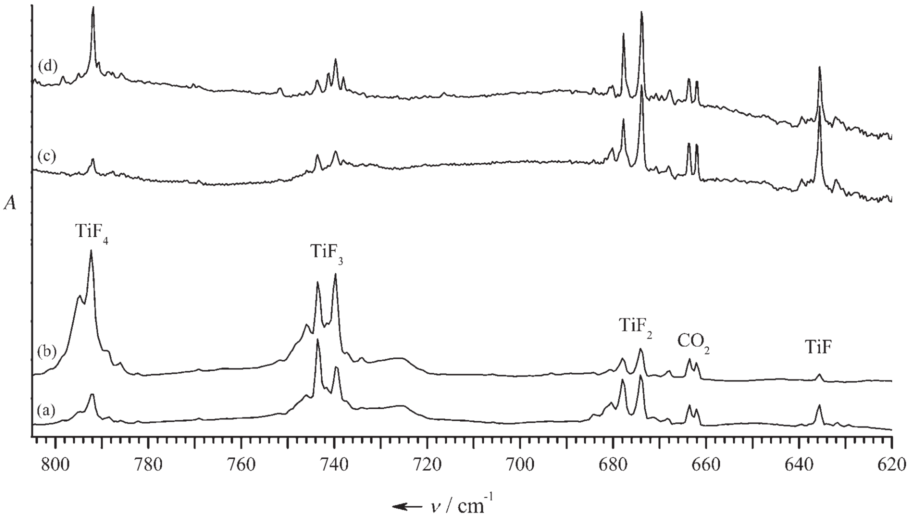

Figure 2. Matrix isolation IR spectra of Ti atoms isolated in F_2/Ar matrices. a,b) 0.6% F_2/Ar on deposition at about 10 K (a) and after broad-band Hg–Xe photolysis (b). c,d) 0.2% F_2/Ar on deposition at about 10 K (c) and after broad-band photolysis and annealing to 25 K (d).

Based on the previous gas-phase[6] and matrix work[4,11] it is straightforward to assign band **A** at 791.88 cm^{-1} in the 0.2% F_2/Ar matrix spectra to the ν_3 (T_2) mode of $^{48}TiF_4$. It should be remembered that in the original work this band was assigned to TiF_3.[3] The $\nu_{\text{Ti-F}}$ mode of gas-phase TiF has been observed at about 650 cm^{-1},[12] with calculated harmonic values of around 640 cm^{-1} for the $^4\Phi$ ground state.[13] Therefore, after allowing for a reasonable matrix shift, band **D** at 635.55 cm^{-1} can be assigned to argon matrix isolated ^{48}TiF, and the titanium isotope pattern is also consistent with this assignment (see the Supporting Information). With TiF_4 assigned to band **A** and TiF to band **D**, the only obvious assignment of the remaining peaks, **B** and **C**, is to TiF_3 and TiF_2, respectively. Therefore, the peaks at 743.68 and 739.70 cm^{-1} in 0.2% F_2/Ar matrices are assigned to $^{48}TiF_3$ in two different sites. The peaks at 677.73 and 673.81 cm^{-1} are assigned to $^{48}TiF_2$ in two different sites. These values are in excellent agreement with the value predicted from Figure 1, and an average of 675 cm^{-1} for linear TiF_2 is marked with an open circle (○; if the molecule is bent, this point will move up vertically). Furthermore, these values are also in excellent agreement with the most recent icMRCI-calculated harmonic values of ω_3 of 705 cm^{-1} for the $^3\Sigma_g^-$ state and 695 cm^{-1} for the $^3\Delta_g$ state,[8] especially as anharmonicity values of −6.5 cm^{-1} have been determined for CrF_2.[14]

While the site effects (as well as the gas-phase CO_2 bands) potentially complicate the determination of the bond angle, Figure 3 shows that the spectral motif arising from the overlap of the Ti isotope patterns from each of the sites is actually very diagnostic as the peak separation decreases with a reduction in bond angle. In particular, the double hump at about 680 cm^{-1} and the lack of any resolved peaks between the two main peaks at 677.73 and 673.81 cm^{-1} indicate that the bond angle is close to linearity. The vertical lines marking the positions of the $^{46}TiF_2$ peaks at 684.15 and 680.14 cm^{-1} and the $^{48}TiF_2$ peaks at 677.73 and 673.81 cm^{-1} imply that the bond angle is slightly less than linear. The best peaks for an accurate bond angle determination are the $^{46}TiF_2$ peak at 684.15 cm^{-1} and the corresponding $^{48}TiF_2$ peak at 677.73 cm^{-1} of the α site, and an SVFF calculation yields a bond angle of 166°. Analysis of the second-site (β) peaks of $^{46}TiF_2$ and $^{48}TiF_2$ at 680.14 and 673.81 cm^{-1} yields a bond angle

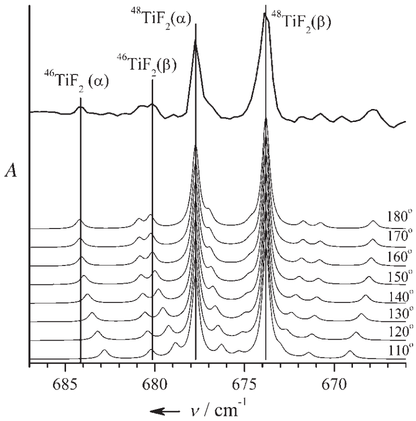

Figure 3. Expansion of Figure 2d in the $\nu_{\text{Ti-F}}$ region of TiF_2 (top) and SVFF-calculated spectra at different angles for the two sites of TiF_2.

of 160°; however, owing to overlapping peaks, this result is expected to be less accurate. Therefore, a bond angle of 165° was used to calculate the overlapping isotope pattern for both sites, and the result is shown in Figure 4. The fit is very good, especially for the peaks above 672 cm^{-1}, and while the fit below this value is still good, the presence of the vapor-phase CO_2 components causes some interference.

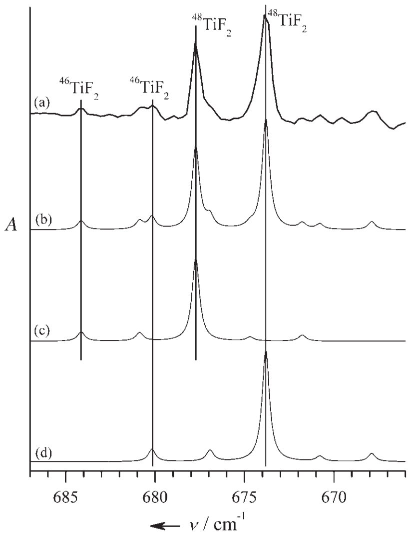

Figure 4. a) Expansion of Figure 2d in the $\nu_{Ti\text{-}F}$ region of TiF_2; b–d) SVFF-calculated spectra for TiF_2 with a 165° bond angle: combined sites (b), site α only (c), site β only (d).

Isotopic substitution at the central element, as in this case, is usually considered to give the lowest estimate of the bond angle.[1,2,15] Therefore, it can be concluded from these IR data that the titanium isotope pattern is inconsistent with a bent species having a bond angle of less than 160°. The sine function is notoriously insensitive for linear and near-linear geometries. Although, because of the lightness of Ti and separation of two mass units, this is a favorable case, the calculated difference between the 180° and 165° ν_3 modes of $^{46}TiF_2$ with $^{48}TiF_2$ at 677.73 cm^{-1} is only 0.06 cm^{-1}, which is well below the accuracy with which band positions can be measured in these types of experiments. Even a difference of 0.11 cm^{-1} for 180° and 160° bond angles is at the margin of detection. Therefore, as for all of these experiments which yield bond angles of 160° and above, it is not possible to distinguish the angles from linearity. Hence, these data indicate that TiF_2 is indistinguishable from linearity in argon matrices. There is an interesting philosophical point that even if the equilibrium geometry is linear, then the molecule actually spends most of its time bent.

In conclusion, this work has provided the first unambiguous IR characterization of TiF_2 with the ν_3 mode of $^{48}TiF_2$ at 675.73 and 673.81 cm^{-1} for two sites in argon. These values compare very well to the approximate value of 670 cm^{-1} predicted for linear TiF_2 in Figure 1. They are also in good agreement with the recent icMRCI-calculated ω_3 values of 705 and 695 cm^{-1} for the $^3\Sigma_g^-$ and $^3\Delta_g$ states, respectively.[8] The Ti isotope pattern for the ν_3 mode is incompatible with a substantially bent geometry (< 160°), and is indistinguishable from a linear geometry for TiF_2, which is also in agreement with the recent icMRCI calculations.[8] Therefore, there is now no reliable experimental evidence for the nonlinearity of any first-row transition-metal difluoride or dichloride.

Experimental Section

The general features of our matrix isolation experimental methodology have been described previously.[16] The titanium atoms were evaporated at about 40 A from Ti wire (0.25 mm, Goodfellows) wound on Ta wire (0.50 mm, Goodfellows). The F_2/Ar mixtures were prepared by using standard manometric procedures in a well-passivated metal vacuum line using 10% F_2/Ar supplied by Air Liquide. The Ti evaporation conditions were checked using matrix electronic absorption spectroscopy, and there was no evidence for Ti_2.[17] The SVFF calculations used SOTONVIB.[18]

Received: October 9, 2007
Published online: January 18, 2008

Keywords: halides · IR spectroscopy · matrix isolation · titanium

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