Small lanthanide clusters have interesting magnetic properties, but their structures are unknown. We have identified the structures of small terbium cluster cations $\mathrm{Tb}_n^+ (n = 5 - 9)$ in the gas phase, by analysis of their vibrational spectra. The spectra have been measured via IR multiple photon dissociation of their complexes with Ar atoms in the $50 - 250 \text{ cm}^{-1}$ range with an infrared free electron laser. Density functional theory calculations using a $4f$-in-core effective core potential (ECP) accurately reproduce the experimental far-IR spectra. The ECP corresponds to a $4f^85d^16s^2$ trivalent configuration of terbium. The assigned structures are similar to those observed in several other transition metal systems. From this, we conclude that the bonding in Tb clusters is through the interactions between the $5d$ and $6s$ electrons, and that the $4f$ electrons have only an indirect effect on the cluster structures.
LIX) in Nieuwegein, the Netherlands, was used as the far-IR source for these experiments. The experimental setup and methods have been described in previous publications\textsuperscript{10,13} and we only give a brief summary of the relevant details here. Tb clusters are produced in a laser vaporization cluster source which is in part cooled to 77 K. The He carrier gas is seeded with 5 % Ar, which leads to the formation of a small population of weakly bound Ar complexes of the Tb$^+_n$ clusters. The cluster beam is irradiated by the tunable far-IR radiation from FELIX and mass analyzed with a reflectron time-of-flight mass spectrometer. The FELIX beam used in the experiment delivers an energy on the order of $\approx 10 \text{ mJ}$ within a pulse of about 7–9 $\mu$s duration. Mass spectra of alternating shots from the cluster source with FELIX toggled on and off are stored into separate channels of a digitizer and in total about 500 mass spectra are averaged per channel and frequency interval. The IR induced relative depletion of the mass signals for the Tb$^+_n$-Ar complexes is evaluated as a function of IR frequency to obtain the size specific far-IR spectra.

The experimental IR spectra for Tb$_n^+$ ($n = 5 - 9$) are shown in Figs. 1 - 3. There are well-resolved absorption bands for most cluster sizes. The spectra of the smaller sizes, $n = 5, 6,$ and $7$, are dominated by a single intense feature, which may suggest a highly symmetric structure, while the larger sizes, $n = 8$ and 9 have more richly featured spectra. For the studied cluster sizes we find absorption bands in the 50–160 cm$^{-1}$ range, which is approximately the range where the optical phonon branches of the bulk metal were observed by neutron scattering\textsuperscript{17}. With few exceptions, all observed metal cluster vibrations are below the reported value for the stretching frequency of the neutral Tb$_2$ of 137 cm$^{-1}$\textsuperscript{15}. To identify the clusters’ structures based on the experimental spectra we perform quantum chemical calculations using density functional theory (DFT). We use the Perdew-Burke-Ernzerhof (PBE) functional\textsuperscript{20} for exchange and correlation as implemented in Turbomole 6.2\textsuperscript{20}. The treatment of the 4$f$ electrons with DFT remains a challenge because they occupy an open shell and are highly localized to their parent atoms, where correlation effects are strong. Their strong localization also implies that they do not directly participate in chemical bonding. Standard DFT functionals are known to falsely delocalize the 4$f$ electrons, and explicit treatment of the 4$f$ states requires corrections such as LDA+U\textsuperscript{21}. Alternatively, it is possible to exploit the localization of the 4$f$ states and treat them as a part of the core with an effective core potential. We follow this approach, using the ECP$54$MWB effective core potential developed by Dolg et al.\textsuperscript{22} The valence orbitals are described with the (6s6p5d)/[4s4p4d] + 2s1p1d (ECP54MWB-II) basis set\textsuperscript{23}. The ECP includes 8 4$f$ electrons in the core. This corresponds to the commonly observed trivalent (4$f^85d^16s^2$) configuration of the terbium atom.

For metal clusters the interrogation of the configurational space becomes rapidly more complex with growing size and many locally stable arrangements of atoms, in addition to the true global minimum, may be identified for any given cluster size. We investigated a wide range of possible isomers starting our search with geometries that have been reported for transition metal clusters (after scaling the interatomic distances to values which match the bulk values for Tb) including those that have been identified in our previous studies\textsuperscript{24-28} followed by local optimization. In addition, for several sizes, we used Monte-Carlo basin-hopping sampling\textsuperscript{29} to locate other local minima. No symmetry constraints have been applied. For all local minima found the IR spectra have been calculated analytically based on the harmonic approximation; the frequencies are not further scaled. For $n = 5 - 7$, alternative isomers are typically much higher in energy. This suggests that the potential-energy surface is quite smooth.

An additional parameter of the calculations is the elec-
For the small clusters, Tb$_5^{+}$–7, the best matches to the predicted IR spectra for Tb$_5^{+}$ are obtained with the putative ground states which are calculated to have 4, 1, and 2 unpaired 5$d$/6$s$ electrons, respectively. For a given structure, different spin states are often close in energy, but their calculated IR spectra can differ remarkably, as seen for Tb$_5^{+}$. In this case, the doublet state 8$b$ is higher in energy than the quartet 8$a$, but the spectrum of 8$a$ fits the experiment better. The presence of (several) unpaired 5$d$/6$s$ electrons is consistent with Stern-Gerlach experiments on La and Y clusters, which found many sizes with net magnetic moments (0.2 $\mu_B$/atom). La and Y have very similar valence electronic structure to the lanthanides, but no 4$f$ electrons. Thus the observation of high spin in these clusters supports our finding, even without properly accounting for the possibility of a 5$d$/6$s$ spin polarization induced by the large localized 4$f$ moments.

We find no evidence of multiple isomers for any of these small Tb clusters, although for Tb$_7^{+}$ there are several isomers based on two structural motifs (9$a$/9$b$ and 9$c$/9$d$) which are close in energy (within 0.2 eV) and which have similar spectra. 9$a$/9$b$ is formed by capping three adjacent faces of an octahedron and 9$c$/9$d$ can be described as two interpenetrating decahedra. Both of these could be present, but structure 9$a$/9$b$ fits the experimental spectra better, and the energy difference of 0.1 eV is too small to be considered meaningful.

The lowest energy isomer identified by theory does not always give the best match to the theory, a case illustrated by Tb$_6^{+}$. Tb$_6^{+}$ has 17 (5$d$/6$s$) electrons, one fewer than the 18 needed to satisfy a spherical shell closing. This
would indicate a preference for a low-spin distorted geometry 6c over the octahedral 6a. However, the highly symmetric octahedral structure has high density of states at the HOMO, which increases the energy gained by exchange splitting in a high spin state. It is possible for this effect to stabilize a highly symmetric structure against a Jahn-Teller distortion. Indeed, the calculations predict that the $2S = 5$ octahedral structure 6a is 0.3 eV lower in energy than the distorted low-spin ($2S = 1$) structure 6c, but 6c appears to match the experimental spectrum better. It is important to note, however, that the geometric difference between 6a and 6c is small, (the bond lengths differ by 2-5%) and their vibrational spectra are very similar. The octahedral structure 6a actually has a triply degenerate vibrational mode located at 100 cm$^{-1}$, which is close to where an intense feature is observed in the experimental spectrum. However, the IR intensities calculated for these modes are very low. Further investigation is required to understand whether the presence of the Ar, or the inclusion of the 4f electrons would change the IR intensities of these modes. Thus our experiment cannot determine conclusively whether Tb$^+_6$ is a perfect octahedron.

To conclude, we have demonstrated that far-IR spectroscopy allows for structural assignment for small lanthanide clusters. Our theoretical approach, where the 4f electrons are treated as a part of the core, predicts the frequencies and IR intensities of the cluster vibrational modes with remarkable accuracy. This confirms that, like the bulk materials, the 4f electrons remain tightly localized in metal clusters and do not directly participate in bonding. The structures identified are similar to the geometries found for transition metal clusters. In this sense, heavy lanthanides behave like early transition metals with small d-occupation. It is also highly surprising that the structures can be determined while the magnetic order and 4f – (5d6s) exchange interaction are completely neglected. Knowledge of the cluster structures will enable the application of higher level theory for an explicit treatment of the 4f electrons, which in turn will provide a detailed understanding of lanthanide cluster magnetism.

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3Gd, Tb, Dy, Pr, Ho, and Tm have been studied.
23The ECP and basis set are available at: http://www.theochem.uni-stuttgart.de/pseudopotentials/.
25See Supplemental Material at [URL will be inserted by publisher] for atomic coordinates, energies, and calculated IR-spectra of all isomers.