COMMENT

Comment on "Electronic Structures, Vibrational and Thermochemical Properties of Neutral and Charged Niobium Clusters Nb$_n$, $n = 7-12$"

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In a recent article Nhat et al. report a comprehensive theoretical study on the structures of small niobium clusters Nb$_n$ in different charge states.[1] Structural assignments are presented for the smaller clusters up to $n = 9$ that largely rely on far-IR vibrational spectra published by us before.[2] For most sizes the structures assigned by Nhat et al. agree with those we identified earlier via comparison of the far-IR spectra with the results of DFT calculations. Most interesting, however, the authors also make predictions for the structures of larger clusters up to $n = 12$ and include calculated IR spectra that may allow one to verify the predictions. Although measured simultaneously with the data set reported previously, we had not published the experimental spectra for clusters containing more than nine Nb atoms so far due to the absence of high-quality theoretical spectra to which these could be compared.

Therefore we present here the experimental far-IR spectra of Nb$_{10-12}$ and Nb$_{10-12}^+$ (Figure 1). These size-specific vibrational spectra of gas-phase metal clusters have been measured via far-IR photodissociation of weakly bound complexes of the clusters with single Ar atoms formed at 80 K. For intensity reasons, for Nb$_{10}^+$ and Nb$_{12}$ the spectra of the complexes with two Ar atoms are reported. The experimental spectra are amended by calculated IR spectra for the structures reported in ref 1 using the meta-GGA functional by Tao, Perdew, Staroverov, and Scuseria.[3] We have shown before that this approach is capable of predicting the IR spectra for this kind of system particularly well.[4] Our recalculated structures and spectra deviate only slightly from the findings of Nhat et al. (Figure 1). The clusters' geometries are cage-like, i.e., distorted versions of a bicapped anticube (Nb$_{10}$), a C_{2v} symmetric deltahedron (Nb$_{11}$), and an icosahedron (Nb$_{12}$).

Comparing experimental and these calculated spectra, we find good agreement for Nb$_{10}$, Nb$_{11}$, Nb$_{11}^+$, and Nb$_{12}^+$. Unfortunately, the quality of the experimental spectra for the cationic clusters in this size range is not exceptionally high; the D_4 isomer of Nb$_{10}^+$ may be present, although the predicted band at 172 cm^{-1} is hardly visible in the experimental spectrum. Only for the neutral Nb$_{12}$ cluster do the predictions not match the experimental findings at all and also none of the higher energy isomers reported by Nhat et al. show IR spectra that agree reasonably with the experimental one. Interestingly, we found bands at relatively high frequencies for Nb$_{12}$, at 293 and 330 cm^{-1}, whereas all smaller sizes show bands only clearly below 300 cm^{-1}. The appearance of such high frequency bands can be related to encapsulated atoms, i.e., the formation of structures that do not have all atoms on the surface.[5] In fact, when further exploring the configurations, we find an isomer **B** with an encapsulated Nb atom that gives convincing agreement with the experimental band pattern, though the relative band intensities do not match perfectly. This isomer is 0.26 eV higher in energy than the distorted isocahedron **A**. Structure **B** had been predicted as lowest energy isomer before.[6] Therefore the question arises if our
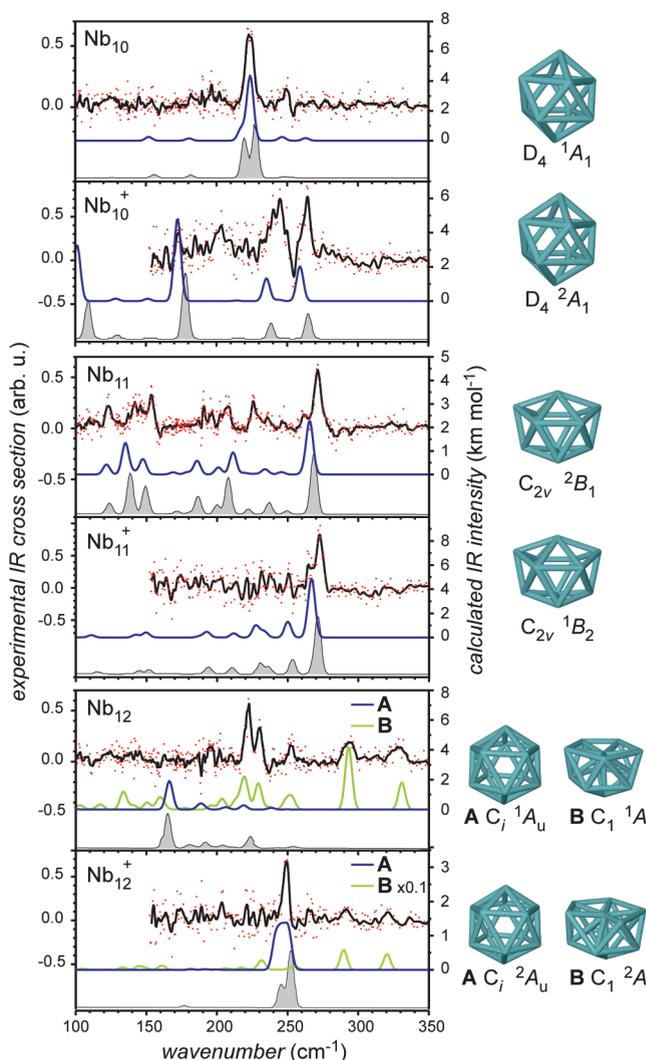

Figure 1. Comparison of experimental IR spectra of Nb$_n$ and Nb$_n^+$ ($n = 10-12$) and calculated IR spectra using density functional theory. For all sizes the predicted spectra for the ground state taken from ref 1 (gray) are shown as well as the recalculated spectra for their structures using the TPSS functional (blue lines); for Nb$_{12}$ a different isomer is experimentally observed (green line). For the cation Nb$_{12}^+$ this structure **B** appears to be a minority species (IR intensities scaled by 0.1). The experimental raw data (red dots) are overlaid with their binomial weighted 7 point running average to guide the eye. The calculated frequencies are scaled by a factor of 0.96, and the spectrum is folded with a Gaussian line shape function with 5 cm^{-1} full width at half-maximum.

flavor of DFT favors the "wrong" isomer or if the identification of **B** is an experimental artifact. Indeed, rare gas complex formation may be enhanced by isomer **B** as it has a significant dipole moment of 2.04 D, while the icosahedron **A** has none. The calculated vertical ionization energies (IE) of **A** and **B** are 4.24 and 4.8 eV, respectively, and should not be a discriminating factor as in the experiment ionization is performed with 6.4 eV photons. While the IE of **B** would fit the experimental value for one of the known isomers relatively well (4.96 vs 5.15 eV),[7] the calculated IE of **A** is much lower.

Interestingly, also for the cation Nb_{12}^+ a similar isomer **B** might be present in the experiment and could explain the additional weak bands at higher frequency. However, this isomer is calculated to be 0.86 eV higher in energy than **A**. On the basis of the relative intensities of the bands, it can be estimated that the ratio of **A** to **B** is on the order of 1:10.

For all clusters discussed here, with the exception of Nb_{10}^+, the presence of isomers is well documented experimentally.[7,8] For the neutral clusters the relative abundance of the isomers has been estimated from reactivity studies.[7] While the distribution is found to be dominated in all cases by a single isomer, complex formation with the rare gases might be highly selective and might favor the minority, i.e., less stable, isomer. Further studies are needed to investigate if the experimental method discriminates among isomers or indeed at low temperature for Nb_{12} if only a single isomer is present. In this sense, theory can provide relevant insights into the isomerism by detailed investigation of the clusters' configurational space.

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