Temperature effects on the isomer's stability of van der Waals clusters

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Synopsis Small van der Waals(vdW) complexes have serve as prototypes for investigating energy transfer mechanisms and microsolvation processes. High-resolution spectroscopy techniques have provide valuable information, new aspects of these systems emerged from the interplay between theory and experiment, thus such systems are ideal for developing and testing theoretical methods and computational approaches.

High-level *ab initio* electronic structure calculations have shown that triatomic vdW clusters, formed by a dihalogen molecule and a noble gas atom, present double minima at both linear (L) and T-shaped (T) geometries in their ground electronic states [1]. In the case of the He-dihalogen (homonuclear) systems, such like $HeBr_2$ and HeI_2, the energy differences between them counts only to few cm^{-1}, while when nuclear quantum zero-point-energy effects are taking into account the relative stability of the corresponding isomers is less than 1 cm^{-1}. The existence and preferential stability of such isomers have been also supported by recent experimental studies from LIF and action spectra techniques [2]. However, discrepancies between theoretical predictions and even with experimental data of different sets of experiments have been reported, and this arises the question of whether there is a simple explanation of the theoretical point of view on the stability order of such isomers. Although, a number of experimental studies have detected different isomers of such vdW complexes in the supersonic expansions, the mechanisms for their formation, and their relative populations within the expansion under conditions of low temperature (below 3 K) are still uncertain and probably depend on the system. Thus, investigations on how thermodynamic factors (temperature) influence the isomers' formation, and thus their population in the supersonic beam expansion, could serve to improve deficiencies and shed light on our understanding of such processes.

As such a thermodynamic model was introduced [3] to compute the isomers' population as a function of temperature T, $Z^{L,T}(T) = Z_{vib}^{L,T}(T)Z_{rot}^{L,T}(T)$, where Z_{vib} and Z_{rot} the vibrational and rotational partition functions, respectively. Rovibrational quantum calculations for angular momentum values J up to 15 were carried out, all bound states were assigned and then vibrational and rotational partition functions were computed. On the basis of the present results, [3] the relative populations of the linear and T-shaped conformers show a strong dependence on the temperature for both $HeBr_2$ and HeI_2 vdW complexes (see Figure 1). We found that the linear $HeBr_2$ isomer is energetically more stable than the T-shaped ones by 1.14 cm^{-1} at T=0 K, whereas conversion from linear to T-shaped complexes was observed at temperatures above 2.87 K. In turn, for the HeI_2 system the population inversion occurs at 1.04 K, with the energy difference between them being just 0.21 cm^{-1}. Interestingly, for the $HeBr_2$ a nice accord between experiment and theory has been achieved, while the HeI_2 case is still under consideration, pushing for further improvements in the both theoretical and experimental directions.
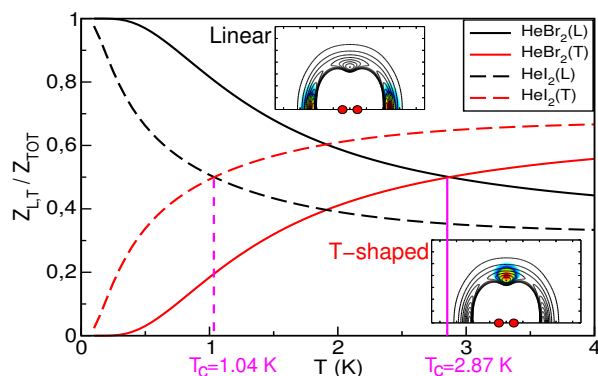

Figure 1. Population ratio of linear and T-shaped isomers as a function of temperature. The two populations become equal at T_C=1.04 and 2.87 K for the $HeBr_2$ (solid lines) and HeI_2 (dashed lines), respectively. In the inset panels the density distribution of each, linear and T-shaped, vibrational state are displayed in the ZX-plane together with the underlying potential energy surface.

References

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