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Reply

Reply to the Comment on “The ν_3 infrared spectrum of the He–NH₄⁺ complex”

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Abstract

In a recent study, the angular anisotropy of the intermolecular potential of the He–NH₄⁺ ionic complex has been estimated using ab initio methods. In response, Read and Buckingham have calculated the anisotropic contributions arising from long-range induction and dispersion interactions and have found near quantitative agreement with the ab initio computations for the energy difference between the vertex-bound and face-bound minima. Thus encouraged, they have predicted minimum structures for Rg–NH₄⁺ complexes involving heavier rare gas (Rg) atoms and have concluded that the face-bound structure becomes more favorable as the size of the rare gas atom increases. However as discussed here, ab initio results for Ar–NH₄⁺ differ from their predictions.

In a recent Letter [1], we reported the ν_3 infrared photodissociation spectrum of the He–NH₄⁺ ionic complex. The similarity of the He–NH₄⁺ and NH₄⁺ spectra suggested that the anisotropy in the He···NH₄⁺ intermolecular potential is small. This result was supported by ab initio calculations performed at the MP2 level that showed that the barrier for internal rotation of the NH₄⁺ subunit is less than 30 cm⁻¹, with the vertex-bound global minimum ($R_e = 3.17$ Å, $D_e = 147$ cm⁻¹) being slightly more stable than the face-bound structure ($R_e = 2.96$ Å, $D_e = 130$ cm⁻¹).

Read and Buckingham [2] subsequently explored the angular anisotropy of the intermolecular

He···NH₄⁺ potential by considering the long-range induction and dispersion interactions up to terms in the inverse eighth power of the intermolecular separation. Their model predicts the vertex-bound configuration to be 19 cm⁻¹ lower in energy than the face-bound structure. This quantitative agreement with the ab initio value of 17 cm⁻¹ encouraged them to apply this approach to other Rg–NH₄⁺ clusters (Rg = rare gas). For Ar–NH₄⁺ the model predicts the vertex-bound geometry to be 10 cm⁻¹ lower in energy than the face-bound structure. Here we report ab initio investigations of the Ar–NH₄⁺ complex [3] which suggest a much larger difference in energies between the face-bound and vertex-bound sites (~200 cm⁻¹) than the Read–Buckingham model [2].

The computational procedure was similar to the one employed for He–NH₄⁺ [1]. The calculations were conducted at the MP2 level using the Gaussian 94 package [4] with a basis set composed of an

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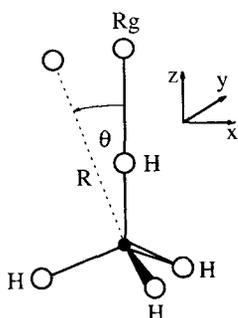


Fig. 1. Coordinate system for $Rg-NH_4^+$ complexes (Rg = rare gas).

Ahlrichs VTZ basis augmented with polarization and diffuse functions up to f for argon and nitrogen and d for hydrogen taken from an aug-cc-pVTZ basis set [5]. The full basis was contracted using the following scheme: (11s,7p,2d,1f) \rightarrow [7s,4p,2d,1f] on N, (6s,2p,1d) \rightarrow [4s,2p,1d] on H, and (13s,10p,3d,2f) \rightarrow [8s,6p,3d,2f] on Ar. All calculations for the complex were counter-poise corrected to account for the basis set superposition error.

To investigate the three-dimensional intermolecular potential energy surface, one-dimensional radial potentials were constructed for different angles θ by calculating several points along the intermolecular radial coordinate R (see Fig. 1). Variation of θ in the xz plane samples the most important structural configurations of the complex. D_e and R_e values extracted from the radial potentials as a function of θ are plotted in Fig. 2. As for $He-NH_4^+$ [1], the proton-bound structure was found to be the global minimum for the Ar containing complex ($\theta = 0^\circ$, $R_e = 3.39$ Å, $D_e = 930$ cm^{-1}). By increasing θ , the side-bound structure ($\theta = 55^\circ$, $R_e = 3.37$ Å, $D_e = 720$ cm^{-1}) is reached, representing the transition state into another vertex-bound geometry ($\theta = 109^\circ$).

Further increase in θ leads to the face-bound structure ($\theta = 180^\circ$, $R_e = 3.28$ Å, $D_e = 725$ cm^{-1}), which is a local minimum at this level of theory. The energy difference between the vertex-bound and face-bound minima is around 200 cm^{-1} , much larger than the value of 10.0 cm^{-1} predicted by the Read-Buckingham model [2]. There is experimental evidence that the vertex-bound structure for $Ar-NH_4^+$ is indeed more stable than the face-bound configuration and that the barrier for internal rotation along the path shown in Fig. 2 is indeed on the order of 200 cm^{-1} [6,7].

The discrepancy between the Read-Buckingham predictions and the ab initio and experimental results is possibly due to the choice of the input parameters R_+ and R_- , the radial intermolecular separations of the vertex-bound and face-bound structures, in the Read-Buckingham model. For $Ar-NH_4^+$ the values were estimated from hard-sphere values ($R_+ = 3.60$ Å, $R_- = 3.39$ Å [2]) and are somewhat larger than the ab initio distances ($R_+ = 3.39$ Å, $R_- = 3.28$ Å) obtained in the present work. In case of $He-NH_4^+$, the model calculations showed that the shorter intermolecular bond of the face-bound structure ($R_- < R_+$) results in a significant stabilization effect, mainly due to the increased charge-induced dipole interaction [2]. For $Ar-NH_4^+$, the value for $\Delta R = R_+ - R_- = 0.21$ Å used in the model [2] is significantly larger than the ab initio value of $\Delta R = 0.11$ Å probably leading to an overestimation of the binding energy for the face-bound geometry.

In conclusion, it seems that while the Read-Buckingham model presented in Ref. [2] may successfully account for difference in the energies of face-bound and vertex-bound geometries in $He-NH_4^+$ by taking into account long-range potential anisotropy terms, predictions for systems containing heavier

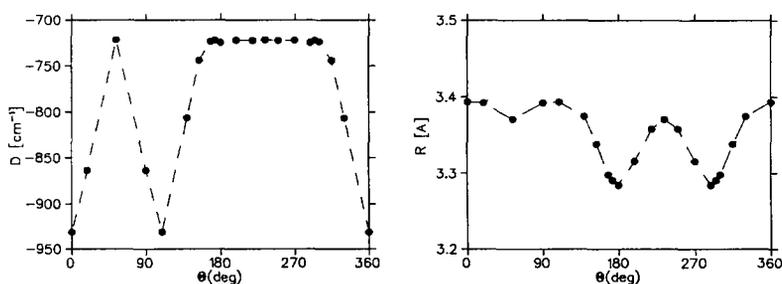


Fig. 2. Ab initio D_e (a) and R_e (b) values of one-dimensional intermolecular radial potentials of $Ar-NH_4^+$ as a function of the angle θ .

rare gases may be less reliable. While according to the model, the face-bound geometry gains in relative stability for larger rare gas atoms, the opposite effect is predicted by ab initio calculations for He–NH₄⁺ and Ar–NH₄⁺. Nevertheless, the approach is computationally cheap and provides insight into the physical nature of the long-range intermolecular interactions. The principal difficulty in applying the model to estimate ionic complex geometries and rotational barriers, appears to involve making an appropriate choice of intermolecular separation at different angular configurations.

Acknowledgements

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