

Spectroscopy of weakly-bound complexes in highly excited electronic states: the He-I₂(E³Π_g) ion-pair state

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 J. Phys.: Conf. Ser. 488 102007

(<http://iopscience.iop.org/1742-6596/488/10/102007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 161.111.22.69

This content was downloaded on 08/04/2015 at 08:57

Please note that [terms and conditions apply](#).

Spectroscopy of weakly-bound complexes in highly excited electronic states: the He–I₂(E³Π_g) ion-pair state

Rita Prosmi^{*1}, Apostolos Kalem[†], Álvaro Valdés^{*}

^{*} Institute of Fundamental Physics, IFF-CSIC, Serrano 123, 28006 Madrid, Spain

[†] National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Physical Chemistry, Panepistimiopolis, Athens 15771, Hellas

Synopsis The study of electronically excited van der Waals (vdW) systems presents a challenge for the theory of intermolecular interactions, and here we show how far *ab initio* computations can go. We found that the interaction energies for such electronically excited systems can indeed be determined, providing a reliable and accurate description for the E state potential of the HeI₂, that in combination with the ground X and electronic excited B state of the complex, is useful to model experimental data related with potential minima and also predict higher vibrational vdW states.

A theoretical study on the potential energy surface and vibrational bound states of the E electronic excited state of the HeI₂ vdW system is presented [1]. The interaction energies are computed using accurate *ab initio* methods and large basis sets. Relativistic small-core effective core potentials in conjunction with an augmented quintuple-zeta quality basis set are employed for the heavy iodine atoms in multireference configuration interaction calculations of the ³A' and ³A'' states. Spin-orbit effects have been taken into account indirectly by the average of the ³A' and ³A'' states.

For the representation of the potential energy surface we used a general interpolation technique for constructing potential surfaces from *ab initio* data based on the reproducing kernel Hilbert space method [2]. The surface presents global and local minima for T-shaped configurations with well-depths of 33.2 and 4.6 cm⁻¹, respectively (see Figure 1). In general it shows a rather complicated topology with wide plateau for bending configurations, and thus large anisotropy around the T-shaped well.

Vibrational energies and states are computed through variational quantum mechanical calculations (see Figure 1, bottom panel). We found that the binding energy of the HeI₂(E) T-shaped isomer is 16.85 cm⁻¹, in excellent agreement with recent experimental measurements [3]. In lieu of more experimental data we also report our predictions on higher vibrational levels, and we analyze the influence of the underlying surface on them. This is the first attempt to represent the potential surface of such a highly excited electronic state of a vdW complex, and it demonstrates the capability of the *ab initio* technology to provide accurate results for carrying out reli-

able studies to model experimental data.

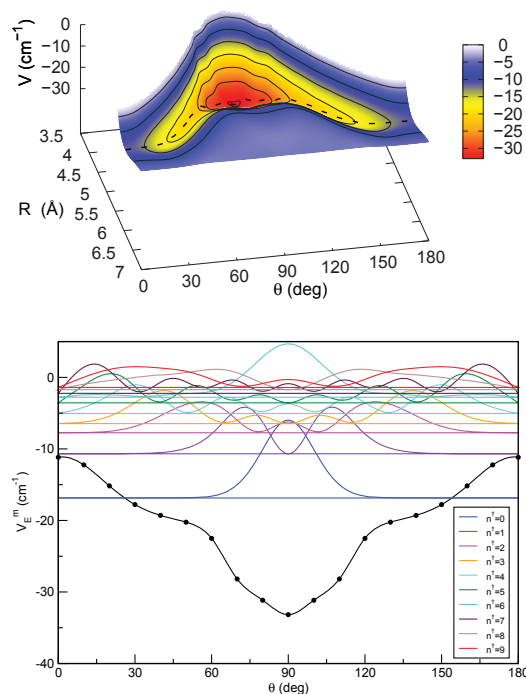


Figure 1. 3-dimensional plot of the potential energy surface for the E state of HeI₂ (top panel). Minimum energy path of the PES as a function of θ , together with the energies and angular probability distributions of the lowest ten bound intermolecular vdW levels (bottom panel).

References

- [1] A. Kalem[†], A. Valdés, and R. Prosmi 2012 *J. Chem. Phys.* **137** 034303
- [2] T-S. Ho, and H. Rabitz 1996 *J. Chem. Phys.* **104** 2584
- [3] S.E. Ray *et al* 2006 *J. Chem. Phys.* **125** 164314

¹E-mail: rita@iff.csic.es