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# Indium atoms snorkeling in superfluid helium: Switching the atomic solubility by electronic excitation<sup>†</sup>

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Combining a He-droplet experiment with computational studies, we show that the solubility of In atoms in superfluid helium can be modified via electronic excitation. In the electronic ground state of atomic indium, the strengths of the He-In and the He-He interactions are comparable to each other, which renders the In atom 'heliophilic' and therefore soluble in helium. However, the optical excitation of the atom from 5p to the 6s and its inherent spatial diffusion of the electronic density distribution forces the now 'heliophobic' In atom onto the surface of the helium droplet. The extra amount of energy needed for this process causes a significant blueshift of the adsorption line in the measured spectrum, which is explained and reproduced by a theoretical model based on ab initio calculations and helium density functional theory.

## 1 Introduction

Lieber Markus, bitte um reichlich Input hier von Deiner Seite! Johann, bitte auch um Links zu Theoriearbeiten, insbesondere die von Martin Ratschek The spectroscopy of atoms or molecules in He nanodroplets has a long tradition and allowed ... HENDI als Begriff definieren... However, most of these studies were dedicated to the investigation of either heliophilic or heliophobic dopants, i.e. species preferring to be either inside or on the surface of the helium nanodroplet. For this study we decided to pick a borderline-element...

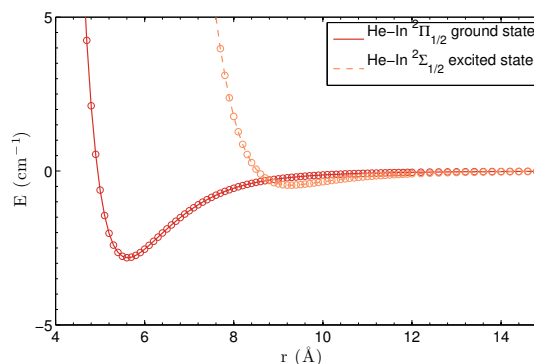
## 2 Computational Details

### 2.1 Ab initio calculation of diatomic potentials

Lieber Ralf, bitte hier alles checken und gegebenenfalls aktualisieren. The potential energy surface of the He-In diatomic molecule, a necessary ingredient for the He-DFT approach discussed below, is calculated for the  $^2\Pi_{1/2}$  ground state and the  $^2\Sigma_{1/2}$  electronically excited state. We use the Def2-QZVPD family of basis sets.<sup>1</sup> For indium, the basis set was combined with the ECP28MDF effective core potential of the Stuttgart/Köln group.<sup>2</sup> All ab initio calculations are performed with the MOLPRO software package.<sup>3</sup>

A combination of multiconfigurational self consistent field calculations (MCSCF<sup>4,5</sup>) and multireference configuration interaction (MRCI<sup>6,7</sup>) is applied to the diatomic system in order to capture the very weak van der Waals-type binding between He and

In. In the MRCI approach, 3 valence electrons are included in the active space. The core orbitals are optimized in the preceding MCSCF treatment, but are kept doubly occupied. The active space in the MCSCF and the subsequent computations comprises 3 electrons in 8 shells, with an occupation pattern of (9,4,4,1) 'occupied' and (5,2,2,1) 'closed' shells in the MOLPRO nomenclature and internal ordering ( $A_1, B_2, B_1, A_2$ ) for the  $C_{2v}$  point group. Both He-In curves have been corrected for basis superposition errors due to their significance for the extremely weak attractive interaction in both states.<sup>8</sup> The correction gives rise to geometry shifts in the range of about XX Å. It also reduces the dissociation energies by XX and XX cm<sup>-1</sup> in both states, respectively.



**Fig. 1** Ab initio PES for the diatomic HeIn molecule in its  $^2\Pi_{1/2}$  ground and  $^2\Sigma_{1/2}$  electronically excited state. Both asymptotes have been set to zero energy for a direct comparison of the curvature. The experimental 6s $\leftarrow$ 5p excitation energy for Indium is given by 24 372.957 cm<sup>-1</sup>.<sup>9</sup>

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The *ab initio* PES for the HeIn molecule in the  $^2\Pi_{1/2}$  ground state and the  $^2\Sigma_{1/2}$  electronically excited state, obtained with the combined CASSCF and MRCI approach described above, are plotted in Figure 1. Both states are very weakly bound with dissociation energies of 3 and  $0.5\text{ cm}^{-1}$  for the ground and the excited state, respectively. Note that in both cases the molecular bond is even weaker than the He-He interaction ( $7.7\text{ cm}^{-1}$ , according to the Aziz potential<sup>10</sup> used in the He-DFT ansatz), which already suggests heliophobic behavior on He nanodroplets in both electronic states. Equilibrium distances of 5.6 and  $7.2\text{ \AA}$  can be found for the ground and the excited state, respectively.

## 2.2 Helium density functional theory

The two *ab initio* PES are then used to calculate the helium density distribution and the free energy of a In-atom-doped He nanodroplet ( $\text{He}_N$ ) via helium density functional theory (He-DFT) based on the Orsay-Trento-density functional.<sup>11</sup> In contrast to DFT approaches of electronic structure theory, this functional is mapping the helium density onto the energy, not the electron density. One-dimensional PES scans of the  $\text{He}_N$ -In system can be obtained by a minimization of the free energy as a function of the distance of the In atom from the  $\text{He}_N$  center of mass. The free energy  $F[\rho]$  is written as a functional of the helium density  $\rho$ ,

$$F[\rho] = E[\rho] + U_{\text{ext}}[\rho] - \mu N[\rho] - \mathbf{F} \cdot \mathbf{R}[\rho], \quad (1)$$

with  $E[\rho]$  denoting the Orsay-Trento-density functional and  $U_{\text{ext}}[\rho]$  representing the external interaction potential describing the interaction between the droplet and the indium atom in either the  $^2P_{1/2}^0$  ground or the  $^2S_{1/2}$  electronically excited state. The remaining terms of Equation ?? reflect two constraints put on the minimization procedure: the conservation of  $N$ , the particle number, and  $\mathbf{R}$ , the He droplet mass center.



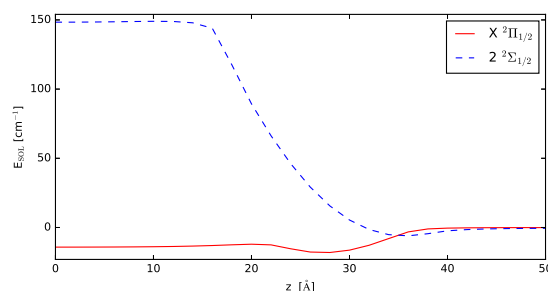
**Fig. 2** Experimental spectrum for the  $6s \leftarrow 5p$  transition of In in helium nanodroplets.

## 3 Experimental Setup

Liebes Team Femtosleep, bitte hier ordentlich zuschlagen

## 4 Results

We start with the discussion of our experimental observations. Figure 2 shows a spectrum of the  $6s \leftarrow 5p$  electronic excitation of In atoms attached to helium nanodroplets consisting of approximately XXX He atoms. **Lieber Bernhard, hier bitte weitermachen und modifizieren: Verschiebung diskutieren, Breite diskutieren, Vergleich zur freien Atomlinie [letztere eventuell auch gleich einzeichnen]** This significant blueshift and the symmetric broadening of the electronic excitation are characteristics which deviate from the typical spectral features observed for surface-bound dopants such as alkali or alkali earth atoms. **Recherche: Alkalien, AEarth, Al, etc.** This experimental finding suggests a much stronger interaction of the In atom with the helium environment upon electronic excitation, indicating already a full submersion of the atom in its ground state or at least the formation of more pronounced ‘dimple’ on the droplet surface after pickup. In order to answer this question we develop a theoretical model of the atomic excitation process in the provided He environment. This is done in three steps.



**Fig. 3** PES scans over the distance between  $\text{He}_{2000}$  and a single In atom, measured from the helium center of mass. The droplet radius is approximately 28  $\text{\AA}$ . The solid line corresponds to the  $5p$  ground state of the In atom, the dashed line to an  $6s$  excitation.

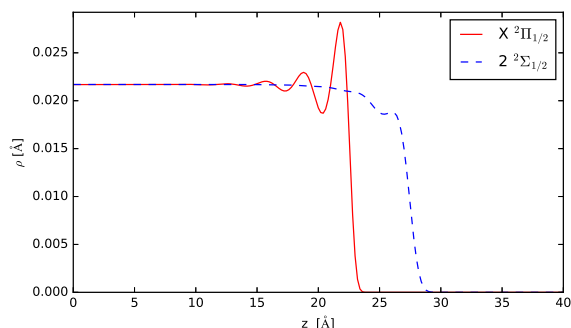
First, we fall back on the diatomic He-In potential curves for the two relevant states, and use them to calculate the corresponding external potentials  $U_{\text{ext}}$  of equation 1 via a summation over pair potentials. The latter are then used as input for the He-DFT code to obtain helium density distributions as well as total energies for a system consisting of 2000 helium atoms and a single In atom in either the  $^2P_{1/2}^0$  ground or the  $^2S_{1/2}$  electronically excited state. By varying the distance between the In atom and the center of mass of the He nanodroplet, we obtain the one-dimensional PES plotted in Figure 3. As expected from the relatively weak In-He interaction in the  $^2S_{1/2}$  electronic state, the In- $\text{He}_{2000}$  PES shows a clearly heliophobic behavior in the excited state. Defining the solvation energy  $S(\text{In})$  of a single In atom in  $\text{He}_N$  as

$$S(\text{In}) = E(\text{In}@\text{He}_N) - E(\text{He}_N), \quad (2)$$

we obtain a positive value of  $XX\text{ cm}^{-1}$  in this case. For indium in its electronic ground state, on the other hand, a negative value of  $-XX\text{ cm}^{-1}$  is found, which confirms the heliophilic character in this electronic state. Interestingly, due to qualitatively similar binding energies of He-He and He-In in their electronic ground

states, a global minimum near the droplet surface can be observed for indium in its  $^2P_{1/2}^o$  ground state. This minimum represents a compromise between two counteracting tendencies which underline the uniqueness of the chosen element: On one hand, the system is aiming at maximizing the interaction between the In atom at the He environment. On the other hand, it also tries to keep the perturbations in the He density distribution as small as possible by locking the dopant in an outer region of reduced helium density, effectively avoiding the propagation of density oscillations throughout the whole droplet. Note that the barrier for a full immersion of the In atom is very small ( $\text{XX cm}^{-1}$ ). In fact, assuming an initial motion of the In atom at a Landau speed of 56 m/s, i.e. the maximum velocity for frictionless motion in superfluid helium, we obtain a maximum kinetic energy of approximately  $\text{XX cm}^{-1}$ , suggesting that those In atoms which remain bound to the droplet after pickup are either located in pronounced dimples near the surface or keep effectively traveling throughout the whole droplet volume. However, even in the latter case, their probability density is also highest near the surface, where the motion of the indium atom has its turning point and the velocity approaches zero.<sup>12</sup>

The situation changes completely upon excitation of In from the 5p into the 6s state. Now the In atom perceives a strong radial force towards the droplet surface due to the strongly repulsive character of the excited state PES in Figure 3, which has its origin in extended electron density of the 6s state and proposes the analogy to a lifejacket which makes the In atoms ‘emerge’ from their helium bath. They either leave the droplet or float on its surface for near zero kinetic energies due to a very shallow surface minimum of less than  $1.5 \text{ cm}^{-1}$ .



**Fig. 4** Helium density distribution along the  $z$ -axis for a pure (dashed) and In-doped (solid) helium nanodroplet consisting of 2000 He atoms, the latter calculated at the minimum free energy internuclear distance for the  $^2P_{1/2}^o$  ground or the  $^2S_{1/2}$  excited state of the indium atom. The helium distribution near the surface is strongly dependent on the electronic state of the In atom. A shorter intermolecular distance and increased He compression are a consequence of the stronger interaction in the electronic ground state.

Figure 4 provides convenient cuts through the helium density of a pure and an In-doped He nanodroplet, showing the density distributions along the intermolecular axis of the In-He<sub>2000</sub> system (or any radial direction in the case of a pure, radially symmetric He nanodroplet). The densities for the doped droplet are

calculated for the minimum free energy geometries in both studied states of the In-He<sub>2000</sub> system. Note the compression of the helium due to the interaction with the dopant, which is more pronounced in the electronic ground state of In and appears at shorter intermolecular distance due to the stronger van der Waals interaction between the In atom and its neighboring He atoms. Figure 5 shows contour plots of the helium density for both electronic states of the In atom. The formation of a pronounced ‘dimple’ is clearly visible for the  $^2P_{1/2}^o$  electronic ground state, while the density is barely affected by the In atom in its  $^2S_{1/2}$  excited state.

The second step of our modeling approach is dedicated to the electronic excitation of the near-surface immersed In atom. Assuming a vertical excitation, justified by the different timescales for the electronic excitation and the relaxation of the He density, we can estimate the extra energy needed for a  $6s \leftarrow 5p$  transition of a partly immersed In atom by an inversion of the pair-potential technique used to obtain  $U_{\text{ext}}$ , which is also known as the ‘frozen-droplet approximation’: Assuming no He relaxation at all upon electronic excitation of the In atom, we can calculate this extra energy by a summation of pairwise interactions between He and In in the  $^2S_{1/2}$  excited state for the initial helium density distribution  $\rho_G$  obtain for the electronic ground state of the In atom. Repeating this for various distances between the In atom and the droplet center of mass we obtain this extra energy  $\Delta E(z)$  needed for electronic excitation as a function of distance as shown in Figure 6.

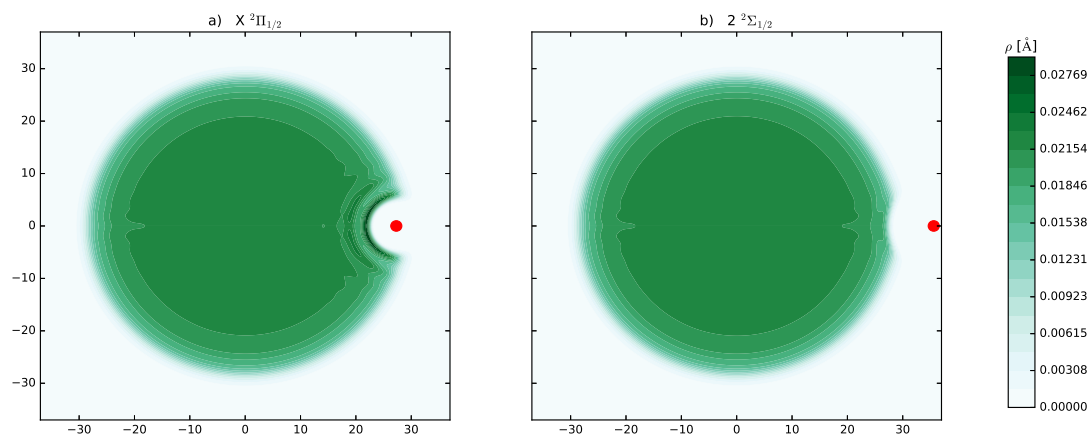
In the third and final step we use this curve of extra energy to estimate the position and the width of the perturbed electronic excitation for a direct comparison to the experiment. In order to do this, we solve the nuclear Schrödinger equation for the motion of the In atom in its electronic ground state potential to obtain the first few vibrational levels. The corresponding differential equation is solved numerically via finite differences and a discretization of the radial distance  $z$  in the diatomic picture. Assuming a Boltzmann distribution at 0.37 K, the temperature of the He droplet, for the occupation of the vibrational levels, we then calculate an averaged probability  $\rho_{\text{av}}(z)$  from the corresponding nuclear wavefunctions and use this result to obtain an estimate for the perturbed  $6s \leftarrow 5p$  transition via an integration over vertical transitions at different  $z$  positions weighted with  $\rho_{\text{av}}(z)$ ,

$$\bar{I}(\nu) = I(\nu) + \int_0^\infty dz \rho_{\text{av}}(z) \Delta E(z), \quad (3)$$

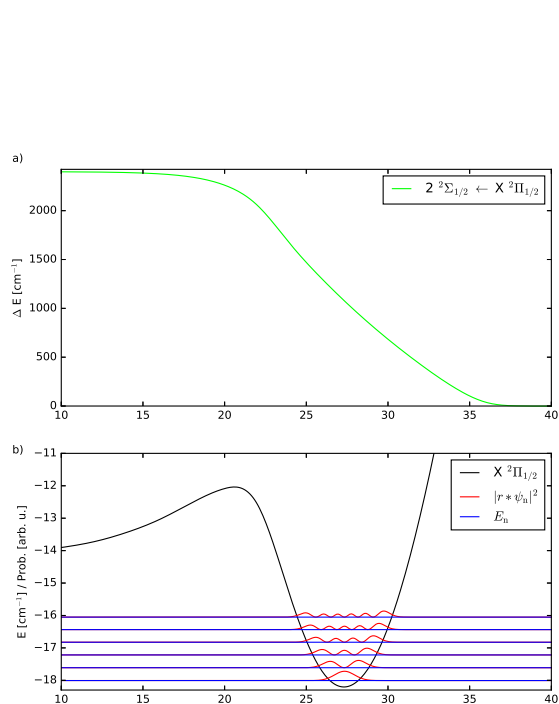
with  $I(\nu)$  denoting the intensity of the unperturbed electronic excitation as a function of the frequency  $\nu$  and  $\bar{I}(\nu)$  as the final, perturbed spectrum. The result of this approximation is shown in Figure 7.

## 5 Conclusion

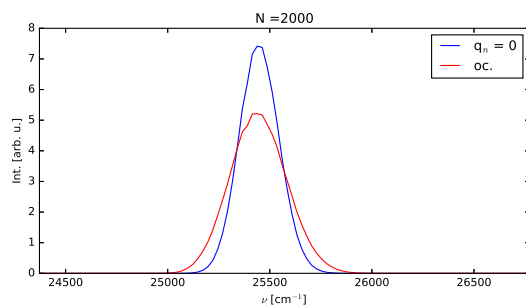
In this article we studied the blueshift of the  $6s \leftarrow 5p$  transition of atomic indium in helium nanodroplets. The experimental finding could be explained by a combination of quantum chemistry calculations and helium density functional theory. It is a consequence of the extra cost for the electronic excitation of the In atom, which is almost completely immersed in the helium in its elec-



**Fig. 5** Contour plots of a He<sub>3000</sub> nanodroplet with a single In atom in its  $^2P_{1/2}^o$  ground state (a) and its  $^2S_{1/2}$  excited state (b). Note the almost complete immersion of the atom in the electronically excited state.



**Fig. 6** The upper plot (a) depicts the correction energy  $\Delta E$  obtained in the frozen-droplet approximation for the  $6s \leftarrow 5p$  transition of In. It can be interpreted as the extra energy needed to form the electronically excited state in the He environment of the relaxed ground state of the atom. The lower plot (b) shows the near-surface minimum of the potential energy surface for ground state In in He<sub>2000</sub>, together with the first few vibrational states and their corresponding probability densities. The latter are used as weights in the calculation of the blueshifted transition line.



**Fig. 7** Comparison of the experimentally observed and the simulated  $6s \leftarrow 5p$  transition of In in He<sub>2000</sub>. The blueshift is nicely reproduced by the frozen-droplet assumption, deviating from the experimental line position by less than XXX cm<sup>-1</sup>. **Lieber Johann, hier bitte aktualisieren, sobald die Experimentatoren uns die Daten fuer den Peak schicken.**

tronic ground state, forming a pronounced dimple on the droplet surface. Upon excitation, the interaction with the surrounding helium becomes fully repulsive and the In atom is removed from the droplet. Within the frozen droplet approximation, and assuming that the total interaction is well approximated by the summation over pair interactions, the extra energy needed for the excitation can be estimated from the He-In potential curve for the  $^2\Sigma_{1/2}$  state (corresponding to the  $^2S_{1/2}$  excited state of the In atom) via an integration over the unrelaxed or ‘frozen’ helium density of the system obtained for the electronic ground state of indium. Taking into consideration also the motion of the In atom in the electronic groundstate, we can reproduce the shift and the broadening of the atomic  $6s \leftarrow 5p$  transition due to the helium environment.

## References

- 1 D. Rappoport and F. Furche, *The Journal of Chemical Physics*, 2010, **133**, 134105.
- 2 B. Metz, H. Stoll and M. Dolg, *The Journal of Chemical Physics*, 2000, **113**, 2563–2569.

- 3 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardtson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinson and M. Wang, *MOLPRO, version 2012.1, a package of ab initio programs*, 2012, see <http://www.molpro.net>.
- 4 P. J. Knowles and H.-J. Werner, *Chem. Phys. Letters*, 1985, **115**, 259–267.
- 5 H.-J. Werner and P. J. Knowles, *J. Chem. Phys.*, 1985, **82**, 5053.
- 6 H.-J. Werner and P. J. Knowles, *J. Chem. Phys.*, 1988, **89**, 5803–5814.
- 7 P. J. Knowles and H.-J. Werner, *Theor. Chem. Acc.*, 1992, **84**, 95–103.
- 8 S. F. Boys and F. Bernardi, *Molecular Physics*, 1970, **19**, 553–566.
- 9 Y. Ralchenko, A. Kramida, J. Reader and NIST ASD Team, *National Institute of Standards and Technology, Gaithersburg, MD*, 2017.
- 10 A. R. Janzen and R. A. Aziz, *The Journal of Chemical Physics*, 1997, **107**, 914–919.
- 11 F. Dalfovo, A. Latri, L. Pricapenko, S. Stringari and J. Treiner, *Physical Review B*, 1995, **52**, 1193–1209.
- 12 A. W. Hauser, A. Volk, P. Thaler and W. E. Ernst, *Physical Chemistry Chemical Physics*, 2015, **17**, 10805–10812.