VIP Relativistic Effects

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Evidence for Low-Temperature Melting of Mercury owing to Relativity**

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Dedicated to Professor Friedrich Hensel on the occasion of his 80th birthday

Mercury shows very unusual physical and chemical properties in the gas, liquid, and solid states, resulting in many known anomalies within the Group 12 series of elements. For example, the superconductivity transition temperature of mercury ($T_c = 4.153$ K) is unusually high compared to both zinc (0.875 K) and cadmium (0.56 K); mercury crystallizes in a rhombohedral structure in contrast to zinc and cadmium: the latter two elements adopt a hexagonal closed-packed structure; and the melting point of mercury ($T_m = 234.32$ K) is unusually low compared to those elements (692.68 K for Zn, 594.22 K for Cd).[1] Thus, mercury is the only elemental metallic liquid at room temperature, and it has the highest density amongst all liquids under normal conditions. It has long been speculated that these observed anomalies could be due to strong relativistic effects,[2,3] but this has never been confirmed.

The accurate melting simulation of materials is computationally a daunting task. This is especially the case for bulk mercury, where the complex many-body interactions between the mercury atoms have eluded chemists and physicists for years to perform such calculations. The bonding in mercury evolves from van-der-Waals-like in small clusters to metallic in the solid state.[3] The accurate simulation of the melting process from first-principles quantum theoretical methods became feasible only recently, and only for noble-gas systems.[4] Herein, for the first time, we demonstrate by using Monte Carlo (MC) simulations within a quantum diatomics-in-molecules (DIM) model for the interaction between mercury atoms, that the caloric curves of bulk mercury and mercury clusters are strongly affected by the effects of special relativity, leading to a strong lowering of the melting point of 105 K for the bulk.

Figure 1 shows the non-relativistic (NR) and relativistic (R) potential energy curves for the mercury dimer. The NR and R ground state curves are not too different in shape, with a relativistic bond contraction of 0.20 Å originating from the well-established energetic stabilization of the outermost 6s electrons that is due to relativistic effects. It might therefore (naively) be argued that, based on these curves with very similar potential depths (49 and 53 meV for the R and NR cases, respectively),[5] the hypothetical non-relativistic and the experimental (relativistic) melting points for solid mercury should also be similar. It was, however, pointed out previously

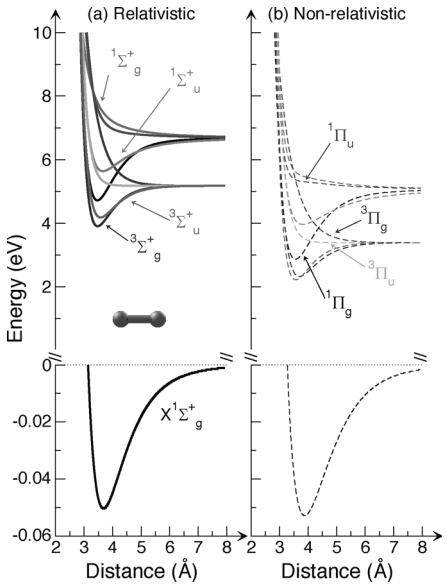

Figure 1. Calculated relativistic (left) and non-relativistic (right) potential energy curves for the ground and low-lying excited electronic states of mercury (spin–orbit splitting in the excited Π states is omitted for clarity).

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that bulk mercury cannot be described in terms of simple two-body interactions (for example, a Lennard-Jones potential) between mercury atoms.[6] This fundamental feature is connected to the change of chemical bonding in mercury clusters from van der Waals to covalent, and then to metallic, as their size increases from tens to hundreds of atoms.[7] The many-body interaction energy expansion as a sum of two-, three-, and higher-body contributions does not converge smoothly for mercury in its solid or fluid states, which is the reason why the simulation of phase transitions for mercury (and metals in general[8]) becomes so difficult. In the quantum diatomics-in-molecules (DIM) picture used herein, this translates into the importance of the off-diagonal matrix elements between the various electronic states depicted in Figure 1. The electronic excited state curves lie about 2 eV lower at non-relativistic level compared to the relativistic case, allowing for stronger mixing and an increase in the interaction energy. This significant increase of the energy gap upon including relativistic effects originates from the strong relativistic 6s contraction. This is already seen at the atomic level, where the electronic $^1S_0(6s^2)\rightarrow{}^3P_0(6s^16p^1{}_{1/2})$ transition occurs at 4.67 eV,[9] while non-relativistic coupled cluster calculations predict it at 3.40 eV.[10]

The non-convergence of the many-body expansion is clearly seen in our results obtained from cluster melting simulations, as shown in Figure 2 for the 13-, 19-, and 55-atom clusters that are primary or secondary magic numbers according to stability in van der Waals clusters.[11] Here no clear trend in relativistic effects is observed. While for Hg_{13} the non-relativistic peak in the heat capacity at constant volume comes at 265 K and above the relativistic peak at 245 K, for Hg_{19} the non-relativistic melting peak at 181 K occurs before the relativistic peak (227 K). For the largest cluster Hg_{55}, the heat capacity curve becomes very broad at the non-relativistic level, showing premelting behavior.[12] Complete melting occurs around 340 K and above the relativistic melting peak at 164 K. Melting even larger clusters

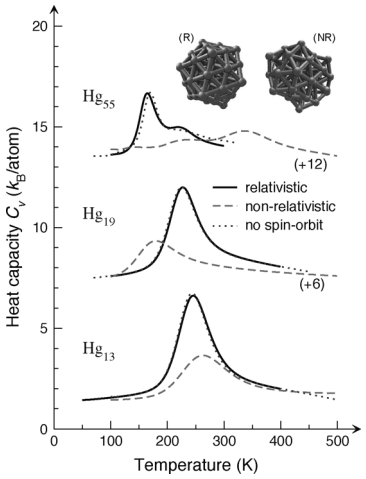

Figure 2. Heat capacity at constant volume of several Hg clusters across their melting temperature range. Curves with multiple peaks or shoulders are indicative of premelting. The most stable structures of Hg_{55} obtained with the relativistic (R) or non-relativistic (NR) DIM models are also shown.

becomes too demanding computationally. Nevertheless, the results do not show any monotonic behavior, with NR/R differences in melting temperatures of $\Delta_R T_m = +20$ K for Hg_{13}, $\Delta_R T_m = -46$ K for Hg_{19}, and $\Delta_R T_m = +176$ K for Hg_{55}. Those differences are partly ascribable to different global energy minima depending on whether relativistic effects are accounted for. In particular, while the relativistic Hg_{55} cluster is a two-layer Mackay icosahedron, the putative global minimum in the NR case has a less symmetric polytetrahedral structure with an anti-Mackay overlayer. Such a geometry is more prone to premelting, which explains the shoulder in the caloric curve seen near 220 K for this cluster. Although less drastic, relativistic effects also impact the most stable structures of the 13- and 19-atom clusters to the extent that they deform and lose their highly symmetric (poly)icosahedral character. It would be interesting to test such structural predictions about symmetry experimentally using photoelectron spectroscopy.[13]

The melting point of the bulk system evaluated under constant zero pressure and appropriate periodic boundary conditions decreases dramatically from 355 K (82 °C) to 250 K (−23 °C) upon inclusion of relativity (Figure 3). While the relativistic model correctly captures the experimental melting point at 234.32 K (−38.83 °C), neglecting relativity would make mercury a solid at room temperature, and Ga ($T_m = 302.92$ K) or Cs ($T_m = 301.59$ K) would be the elemental metals with the lowest melting points, in contrast to common experience. Interestingly, relativity also affects the density of the material. At room temperature the relativistic model predicts $\rho \approx 14.09\ g\,cm^{-3}$ for the liquid state, thereby slightly exceeding the experimental value of $13.6\ g\,cm^{-3}$. With the non-relativistic model, mercury is still a solid at room temperature and has a significantly higher density of about $16.1\ g\,cm^{-3}$.

To gain deeper insight into the causes of the observed shifts in the melting point, additional simulations were performed by considering the different contributions of relativity separately. First, the slightly deeper potential energy well in the ground electronic state of the non-relativistic dimer could be invoked to explain the difference in the calculated caloric curves. However, dedicated simulations of the bulk system considering only two-body interactions show very modest variations in the melting point at

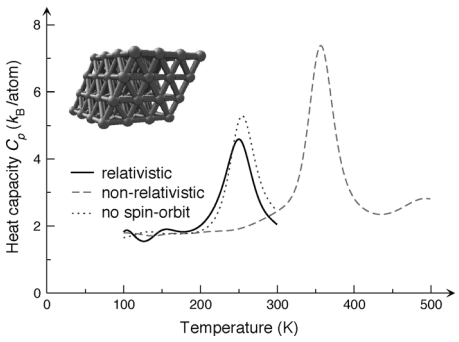

Figure 3. Heat capacity at constant zero pressure for the melting process of bulk mercury. The rhombohedral cell of the solid phase is shown as an inset.

constant zero pressure upon changing the pair potential from a relativistic ($T_m = 292$ K) to a non-relativistic ($T_m = 305$ K) one. Taking many-body effects into account through the DIM model, relativistic effects can be divided into scalar relativistic contributions incorporated in the diatomic potential energy curves and intrinsically relativistic spin–orbit (SO) coupling effects. In absence of SO coupling, but with the relativistic energy curves of the Hg dimer, the caloric curves are very close to the fully relativistic reference data, for clusters and for the bulk sample alike (see Figure 2 and 3). Spin–orbit coupling can thus be ruled out as a cause of the observed results, and the change in the melting point by −105 K is dominated by scalar relativistic effects through many-body contributions. The present study clearly shows that relativistic effects on chemical bonding, which are significantly enhanced within the Group 11 and 12 series of elements,[14] drastically change the thermodynamic state of mercury.

Methods

The melting simulations were carried out using a quantum many-body potential energy surface incorporated into the diatomics-in-molecules (DIM) method.[15] All components for the relativistic model, as originally proposed by Kitamura[16] but with an updated ground-state energy curve, were already available from a previous publication.[17] Spin–orbit coupling was included via the individual atomic contributions in the Hamiltonian matrix. For the non-relativistic model, the energy curves were obtained by electronic ground- and excited-state calculations along the interatomic distance coordinate.[18] The energy curves were fitted to analytic forms in order to be used in the DIM framework. Parallel tempering Monte Carlo simulations were performed at fixed temperature for the mercury clusters and the bulk. The simulations were enhanced using the nested Markov chain method, with the approximate energy surface resulting from first-order perturbation of the DIM model.[17] Simulations of the bulk system were performed in the isothermal–isobaric ensemble at zero pressure. For more details, see the Supporting Information.

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