



Estimation of nuclear volume dependent fractionation of mercury isotopes in equilibrium liquid–vapor evaporation experiments

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ABSTRACT

To confirm theoretical predictions of the isotopic signature of the nuclear volume effect (NVE) for Hg, liquid–vapor Hg isotope fractionation was investigated under equilibrium conditions in the dark at room temperature. Since the other mass independent fractionation (MIF) mechanism proposed for Hg is a kinetic phenomenon only, equilibrium experiments are the best approach to isolate the NVE. Because of the small magnitude of NVE MIF, previous equilibrium experimental results have had relatively large error. The equilibrium evaporation experiment resulted both in mass dependent fractionation (represented by $\delta^{202}\text{Hg}$) and MIF ($\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$). The average liquid–vapor $\delta^{202}\text{Hg}$ difference was $1.34 \pm 0.18\%$ (2SE) and $1.08 \pm 0.07\%$ (2SE) for two sets of experiments with the vapor phase isotopically lighter than the liquid. A positive MIF of the odd isotopes in the vapor phase was observed with an average $\Delta^{199}\text{Hg}$ of $0.14 \pm 0.01\%$ (2SE) and an average $\Delta^{201}\text{Hg}$ of $0.09 \pm 0.01\%$ (2SE). For the 6 experiments, the average ratio of NVE MIF of the two odd isotopes ($\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$) in the vapor phase was 1.59 ± 0.05 (2SE) confirming a recent estimation of the NVE $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of ~ 1.65 . A conceptual model applying first principles was used to explain the fractionation observed between Hg liquid and Hg vapor under equilibrium conditions.

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1. Introduction

The fundamental theory of the chemical isotope effect (Bigeleisen and Mayer, 1947; Urey, 1947), which predicted mass-dependent fractionation (MDF), needed to be expanded to explain the mass-independent fractionation (MIF) that was observed for U isotopes in laboratory experiments (Fujii et al., 1989; Nomura et al., 1996). Isotope enrichment factors for even mass uranium isotopes ^{234}U , ^{236}U and ^{238}U showed no resolvable deviation from theoretical MDF relationship, while that of ^{235}U deviated from the predicted MDF. This deviation from MDF was termed as the “odd/even isotope effect” and an additional isotope fractionation mechanism called the nuclear volume effect (NVE) or nuclear field shift effect was used to explain the even–odd effect (Bigeleisen, 1996a,b; see review Fujii et al., 2009a,b). The NVE results from the difference in nuclear sizes and shapes of isotopes and is proportional to the isotopic difference in mean squared nuclear charge radii, $\delta\langle r^2 \rangle$ (King, 1984; Aufmuth et al., 1987). In atomic spectra, mean square charge radii of odd neutron

isotopes are shifted towards the adjacent even isotope of lower atomic mass number (Kurn, 1969; King, 1984) thus causing the odd–even staggering. The expression of NVE in equilibrium reactions is strongly dependent on chemical properties like types of bonding orbitals. NVE will tend to enrich heavier isotopes in the phase with fewer s electrons, or where s-electrons are more diffuse because of chemical bonding, e.g. for Hg the correlation will always be with s-electron density since the valence electrons of Hg are s-electrons, where Hg(II) is $[\text{Xe}]4f^{14}5d^{10}6s^0$ and Hg(0) is $[\text{Xe}]4f^{14}5d^{10}6s^2$. For some elements, NVE will also enrich heavier isotopes in the phase with more p, d or f electrons, e.g. U(IV) $\sim [\text{Rn}]5f^2$ vs. U(VI) $\sim [\text{Rn}]5f^0$. In redox reactions the correlation with s-electron density is expected to reinforce typical MDF and may lead to large overall fractionation effects, while p, d, f correlations may work in the opposite direction of MDF (Bigeleisen, 1996a,b). Because valence electrons of Hg are in the 6s orbital, it is expected that MDF and NVE will reinforce each other.

Recent studies of Hg isotopes have reported significant mass-independent fractionation (MIF) displayed by the odd Hg isotopes ^{199}Hg and ^{201}Hg (Bergquist and Blum, 2007; Biswas et al., 2008; Epov et al., 2008; Ghosh et al., 2008; Estrade et al., 2009; Gantner et al., 2009; Zheng and Hintelmann, 2009; Wiederhold et al., 2010; Zheng and Hintelmann, 2010). Another possible cause of mass

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independent fractionation (MIF) of Hg isotopes is the magnetic isotope effect (MIE), due to the non-zero nuclear spin and the nuclear magnetic moments of odd-mass isotopes (Buchachenko et al., 2004; Bergquist and Blum, 2007; Buchachenko et al., 2007). Schauble (2007) has made NV estimations of equilibrium $^{202}\text{Hg}/^{198}\text{Hg}$ separation factors for a number of mercury species relative to Hg(0) vapor and estimated that the NVE should be more significant than zero-point energy differences (vibrational frequency) in effecting isotopic separation for heavy elements like thallium and mercury. Since MIE is a strictly kinetic phenomenon (Buchachenko, 2001), MIF observed in equilibrium reactions should be attributable to the NVE only. This is one potential way to isolate NVE-driven MIF from MIE-driven MIF.

So far, detailed theoretical modeling of the NVE has been completed for the three elements; uranium (Bigeleisen, 1996a,b; Abe et al., 2008), thallium and mercury (Schauble, 2007; Wiederhold et al., 2010). Knyazev and Myasoedov (2001), Schauble (2007) and Abe et al. (2008) have also estimated the NVE fractionation for a variety of other elements, although in much lesser detail. These estimations were based on electronic structure and spectroscopic models of NV fractionation. Additionally, there have been some recent theoretical models of NV fractionation of zinc isotopes (Fujii et al., 2009a,b, 2010) and nickel isotopes (Fujii et al., 2011), where NVE is predicted to be much smaller than MDF. In contrast to uranium, with one odd and one even isotope and thallium with two odd isotopes, mercury has two odd isotopes and five even isotopes (four with significant natural abundance), thus making it potentially more straightforward to distinguish NVE from MDF and (potentially) MIE.

Bergquist and Blum (2007) postulated that the MIF slopes may be characteristic of different mechanisms in nature and it might be possible to use MIF slope signatures in natural samples to identify fractionation mechanisms. If that is indeed the case, then determining precise and accurate $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ for MIE versus NVE is an absolute necessity. The NVE slope ($\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$) theoretically predicted by Schauble (2007) based on tabulated nuclear charge radii by Angeli (2004) and recalculated based on radii by Hahn et al., 1979 (Ghosh et al., 2008 and Estrade et al., 2009) varied between 2.2 to 2.7. Estrade et al. (2009) conducted equilibrium mercury liquid–vapor evaporation experiments that displayed MIF for the odd isotopes of Hg and resulted in a slope of 2.0 ± 0.6 (2SE). Recently, another study (Wiederhold et al., 2010) predicted a very different NVE slope of 1.65 based on radii compiled in Fricke and Heilig (2004) and their equilibrium experimental data exhibited a slope of 1.54 ± 0.44 (2SE). Zheng and Hintelmann (2010) reported a slope of 1.61 ± 0.06 (2SE) for a dark kinetic reaction, which is significantly different than $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ (~ 1.0 – 1.3) observed in kinetic photochemical reactions (Bergquist and Blum, 2007) that are likely due to the magnetic isotope effect (MIE). This slope of ~ 1.6 was interpreted to represent the NVE signature of MIF, however, both experiments that expressed NVE in equilibrium reactions (Estrade et al., 2009 and Wiederhold et al., 2010) did not have sufficient precision to confirm this interpretation. Since it has not been confirmed yet whether MIE will be expressed only in photochemical reactions, it is difficult to attribute MIF observed in dark reactions to the NVE without more precise equilibrium experimental evidence. Since MIE can only be expressed in kinetic reactions, the best way to confirm the NVE slope is in equilibrium reactions. As mentioned above this has been done, but with large errors due to the small magnitude of MIF expressed in the experiments. Thus, the objective of this study was to reproduce mercury liquid–vapor evaporation experiments under equilibrium conditions in the dark at room temperature (similar to Estrade et al., 2009) with lower uncertainties to obtain a better estimate of the NVE MIF slope. In addition a conceptual theoretical model, calibrated to first principles calculations, is used to explain the fractionation observed between Hg liquid and Hg vapor under equilibrium conditions.

2. Experimental

2.1. Reagents

All acids used in experiments were trace metal grade quality and all water used was Millipore deionized water (MQ; 18 M Ω cm). Glassware was cleaned with both 10% HCl and 2% trace metal grade BrCl followed by rinsing 5 times with MQ water.

2.2. Evaporation experiments

Equilibrium liquid–vapor experiments conducted were similar to those of Estrade et al. (2009) except they were done in the dark to exclude any possibility of photochemistry (and thus MIE, Bergquist and Blum, 2007). Also the experiments in this study were all conducted at room temperature since the isotopic results from six equilibrium evaporation experiments conducted by Estrade et al. (2009) showed no correlation with temperature (2–22 °C). Approximately 10 g of liquid mercury was introduced into 40 ml glass vials with Teflon lined caps, and aluminum foil was wrapped around the vials to keep the experiments in the dark. The experiments were done under atmospheric pressure and room temperature. After 48 h the mercury vapor above the liquid was collected with a 5 ml Hamilton Gastight syringe and immediately injected into a second 40 ml vial containing concentrated HNO₃ acid (for the first set of experiments with sample names Hg-7 V, Hg-8 V and Hg-9 V) and 10% BrCl (for the second set of experiments with sample names Hg-22 V, Hg-24 V and Hg 32-V). It was found that concentrated HNO₃ acid caused problems in the gas–liquid-separator during isotopic analysis, so 10% BrCl was used to dissolve injected Hg vapor in the second set of experiments. The two sets of experiments were separated by several months, and probably under slightly different laboratory conditions (such as temperature). The first set was performed in the months of January–February whereas the second set was performed in May–June (temperature slightly higher than January–February). In experiments with concentrated HNO₃, multiple sample aliquots were extracted from the vapor with the syringe, potentially reducing the head-space pressure significantly, so prior to each aliquot an equal volume of high-grade helium gas (Hg free) was injected into the vial to maintain atmospheric pressure. In the 10% BrCl experiments vapor, sampling was accomplished in a single-syringe aliquot making helium injections unnecessary. Vials with trapped mercury vapor were then shaken for a period of 24 h to ensure complete dissolution. Estimates of the mass of sampled vapor were made from the sample volumes, assuming saturation vapor pressure laws (Alcock et al., 1984) and subsequent measurements indicated yields of $90 \pm 10\%$ of this saturation volume/mass conversion estimate. This close agreement provides evidence of near-equilibrium evaporation conditions in the experiments. After sampling the Hg vapor, an aliquot of the residual liquid Hg was dissolved in concentrated HNO₃. Final concentrations were adjusted by dilution to match both solution matrix (concentrated HNO₃ or 10% BrCl) and Hg concentrations in vapor and liquid aliquots to within 5%. Concentrations of Hg were measured using a Tekran 2600 cold vapor atomic fluorescence spectrometer following reduction with SnCl₂, and pre-concentration of released Hg(0) gas onto two gold traps in series (using method EPA 1631).

2.3. Hg isotope analysis

The Hg isotopic compositions of preserved vapor and residual liquid Hg samples from the evaporation experiments were analyzed by continuous flow cold vapor generation (Lauretta et al., 2001; Blum and Bergquist, 2007) using a Neptune multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the University of Toronto (UT). Some of the samples were also analyzed at University of Michigan (UM) using a Nu Instruments MC-ICP-MS. Prior to cold

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