



Exotic Inverse Kinetic Isotopic Effect in the Thermal Decomposition of Levitated Aluminum Iodate Hexahydrate Particles

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4 **ABSTRACT:** Aluminum iodate hexahydrate $([Al(H_2O)_6](IO_3)_3(HIO_3)_2; AIH)$ represents a 5 novel, oxidizing material for energetic applications. Recently, AIH was synthesized to replace 6 the aluminum oxide passivation layer of aluminum nanoenergetic materials (ALNEM). The 7 design of reactive coatings for ALNEM-doped hydrocarbon fuels in propulsion systems 8 requires fundamental insights of the elementary steps of the decomposition of AIH. Here, 9 through the levitation of single AIH particles in an ultrasonic field, we reveal a three-stage 10 decomposition mechanism initiated by loss of water (H₂O) accompanied by an unconven-11 tional inverse isotopic effect and ultimate breakdown of AIH into gaseous elements (iodine 12 and oxygen). Hence, AIH coating on aluminum nanoparticles replacing the oxide layer would 13 provide a critical supply of oxygen in direct contact with the metal surface thus enhancing 14 reactivity and reducing ignition delays, further eliminating decades-old obstacles of passivation 15 layers on nanoenergetic materials. These findings demonstrate the potential of AIH to aid in 16 the development of next-generation propulsion systems.



SI Supporting Information

ver since the discovery of Ruby Gold (colloidal suspensions 17 of gold nanoparticles) more than 150 years ago by Michael 18 19 Faraday,¹ metallic nanostructures have emerged as attractive 20 high-energy-density materials.² With a volumetric energy 21 density of 84 kJ cm⁻³,³ particular attention has been devoted 22 to the synthesis of aluminum nanoenergetic materials 23 (ALNEMs) as additives to hydrocarbon fuels such as 24 exotetrahydrodicyclopentadiene (C₁₀H₁₆, JP-10) in air-breath-25 ing propulsion systems.^{4,5} These nanoparticles exceed the 26 limited volumetric energy densities of traditional hydrocarbons $(35-40 \text{ kJ cm}^{-3})$. However, the exploitation of ALNEMs in 27 combustion systems revealed vital limitations in the form of an 28 29 inert layer of aluminum oxide (Al_2O_3) on the surface.⁶⁻⁸ This oxide layer significantly reduces the rate of reaction with the passivation layer not only acting as a heat sink but also limiting 31 the diffusion of oxygen and hence the combustion of the 32 aluminum core.^{6–8} Therefore, the replacement of the aluminum 33 34 oxide passivation layer with reactive coatings, which allow a 35 rapid supply of oxygen to the aluminum nanoparticle and hence 36 an increase in reactivity, would represent an attractive approach 37 to eliminate the long-standing obstacles of the passivation 38 layers.^{9–12}

Aluminum iodate hexahydrate ($[Al(H_2O)_6](IO_3)_3(HIO_3)_2$; 40 AIH) has attracted substantial attention for the replacement of 41 the aluminum oxide layer considering its low oxygen release 42 temperatures and potential in forming highly reactive oxidizer 43 gases including oxygen (O_2) and iodine (I_2) during its 44 decomposition.^{9–12} Preliminary studies exploiting AIH-doped 45 explosives such as trinitrotoluene (TNT) revealed a 30% 46 increase in detonation velocity;¹³ this allowed the particles to 47 react on time scales equivalent to the detonation event, hence ultimately enhancing the energy release rate in aluminum 48 nanoparticles.^{14,15} However, although AIH represents a 49 promising coating on aluminum nanoparticles, there is still a 50 critical lack of fundamental knowledge of the underlying 51 mechanisms of distinct stages in the thermal decomposition of 52 pure AIH. This understanding is vital to the development of 53 next-generation, metal nanoparticle-based propulsion systems 54 along with energy-generation technologies and requires the 55 systematic identification of key reaction intermediates along 56 with the underlying reaction mechanisms and decomposition 57 kinetics. 58

Here, exploiting ultrasonic levitation technology, three 59 distinct stages were exposed in the thermal decomposition of 60 single, levitated AIH and AID particles in an argon inert 61 atmosphere: a rapid loss of water (H₂O) along with a volume 62 increase of the levitated particle by 200% commencing at 375 ± 63 5 K, the slow conversion of iodic acid (HIO₃) into diiodine 64 pentoxide (I₂O₅) and water (H₂O) starting at 480 ± 5 K, and a 65 rapid decomposition of diiodine pentoxide accompanied by 66 vigorous gas release into its elements (iodine, oxygen) beginning 67 at 580 ± 5 K with onset decomposition temperatures 68 significantly *lower* for singly levitated particles than reported 69 for bulk AIH by up to 82 K.

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4000 3500 3000 2500 2000 1500 1000

1000

800

600

Wavenumber (cm⁻¹)

400

200



Figure 1. Raman Spectra of (a) AIH and (b) AID at 298 K. The far left panel is the full deconvoluted spectrum from 4000 to 200 cm⁻¹; the middle panel represents the high region peaks from 4000 to 2350 cm⁻¹; the far right panel is the deconvoluted peaks in the low region from 1200 to 200 cm⁻¹. The spectrum (black) is deconvoluted to make a peak fitted spectrum (red). Deconvoluted peaks are assigned to water (blue), iodic acid (pink), and iodate ion (green). See Table S1a,b for peak assignments.

Wavenumber (cm⁻¹)

3800 3600 3400 3200 3000 2800 2600 2400

4000

500

Wavenumber (cm-1)



Figure 2. (a) 3D image of the Raman spectra of AIH from 302 to 606 K. (b) High and low regions of the spectra taken in panel a. Arrows indicate the decrease and increase of the species H_2O (blue), HIO_3 (pink), and I_2O_5 (purple).

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	frequency (cm^{-1})	intensity	frequency (cm^{-1})	literature			1
peaks	(this work)	(this work)	(literature)	intensity	carrier	assignment	description
AIH							
4	813	m	817	vw	IO_3^-	combination	combination
5	808	S	808, 806, 789	S	IO ₃	ν_3	I–O antisymmetric stretching
		m	810	vs	I_2O_5	$ u_{\rm s}$	O-I=O stretch
a	726	m	724	8	I_2O_5		O-I=O stretch
b	613	m	607	m	I_2O_5		I–O stretch
c	533	w	535	vw	I_2O_5		combination
AID							
4	814	m	817	vw	IO_3^-	combination	combination
5	806	S	808, 806, 789	S	IO_3^-	ν_3	I–O antisymmetric stretching
		m	810	vs	I_2O_5	$ u_{\rm s}$	O-I=O stretch
a	728	m	724	s	I_2O_5		O-I=O stretch
b	627	m	607	m	I_2O_5		I–O stretch
с	501	w	535	vw	I_2O_5		combination

Table 1. Vibrational Mode Assignments for the Observed Peaks in the Raman Spectra of AIH and AID after Heating beyond 480 K

Against conventional wisdom, these studies also afford 71 72 persuasive testimony on an inverse isotope effect for the loss of 73 deuterated water versus water in levitated AID and AIH particles 74 with $k_1(D_2O)/k_1(H_2O) = 5.3 \pm 0.6$ at 375 \pm 5 K. A potential 75 rationale for this inverse isotopic effect is the red-shift of the 76 vibration modes to lower energies for deuterated water, 77 predominantly for the symmetric and antisymmetric stretching ⁷⁸ modes from 3531 to 2659 cm⁻¹ (AIH) and 2659 cm⁻¹ to 2000 $_{79}$ cm⁻¹ (AID) ranges, thus increasing the energy absorption of deuterated water compared to normal water and enhancing the 80 rate of D₂-water loss compared to normal water. Overall, the 81 82 fundamental knowledge obtained here reveals that AIH used as 83 an aluminum nanoparticle coating would not only replace the 84 aluminum oxide layers but also augment the thrust through the 85 development of gaseous decomposition products in propulsion 86 systems (H₂O, I₂, and O₂) with molecular oxygen released 87 throughout the decomposition of diiodine pentoxide, supplying 88 an extra source of an oxidizer directly in contact with the surface 89 of the aluminum nanoparticles, possibly reducing ignition 90 delays, and ultimately improving proficiency of propulsion 91 systems.

Raman spectroscopy represents an outstanding methodology to trace the decomposition of levitated AIH/AID particles in an inert atmosphere of argon and to identify new molecules formed in these processes. This requires first an assignment of the peaks in the nonprocessed AIH/AID samples at 293 K with the deconvoluted Raman spectra depicted in Figure 1; the resulting peaks were compared with literature data and are compiled in Table S1 for AIH and AID.^{16–22}

f1

In the high-wavenumber region covering 3600 to 2600 cm⁻¹, 101 the most intense features correspond to the antisymmetric and 102 symmetric OH stretching modes of the water (H₂O) ligands 103 coordinating the aluminum cation center, i.e., ν_3 (3137 cm⁻¹; 104 peak 1) and ν_1 (2946 cm⁻¹; peak 2). Note that contributions to 105 the latter feature can also originate from the symmetric 106 stretching of the OH moiety in iodic acid (HIO₃). In the low-107 wavenumber region from 900 to 500 cm⁻¹, four features linked 108 to iodic acid (HIO₃) are noticeable: $\nu_8 + \nu_L$ (834 cm⁻¹; peak 3), 109 ν_8 (777 cm⁻¹; peak 6), ν_3 (713 cm⁻¹; peak 8), and ν_4 (631 cm⁻¹; 110 peak 9). The $\nu_8 + \nu_L$ features are characterized as a combination 111 of the IO₂ antisymmetric stretch (ν_8) and a libration mode; ν_3 112 and ν_4 correspond to IO₂ and IO symmetric stretching modes. Along with these bands, three bands from the iodate anion 113 (IO_3^{-}) are visible: a combination band, the IO antisymmetric 114 stretch (ν_3), and the IO symmetric stretch (ν_1) positioned at 816 115 cm⁻¹ (peak 4), 790 cm⁻¹ (peak 5), and 752 cm⁻¹ (peak 7), 116 respectively. Finally, the peak at 618 cm⁻¹ (peak 10) could be 117 associated with the lattice and/or vibration mode (ν_L) of 118 $[Al(H_2O)_6]^{3+}$. If we compare the spectrum for AID, we find in 119 the high-wavenumber region the same ν_1 symmetric stretching 120 of HIO₃ (3084 cm⁻¹; peak 1) as seen in AIH. Along with this 121 feature, the OD bending mode is red-shifted compared to AIH 122 and identified for the D₂O ligand (2 x $\delta(OD_2)$) at 2427 cm⁻¹ 123 (peak 2). For the low-wavenumber region, all bands hold 124 essentially the same assignments as for AIH shifted by between 5 125 and 30 cm⁻¹.

Having benchmarked the Raman spectra of the neat AIH and 127 AID samples, the inherent changes of the Raman spectra upon 128 heating with a carbon dioxide (CO_2) laser from 302 K until the 129 particles detrap at about 606 K are explored (Figure 2 and Table 130 f2t1 1). 131 t1

As the temperature of the heated AIH particles approached 132 375 K, the features attributed to water (3137, 2946, and 618 133 cm⁻¹) began to decrease (Figure 2a). This finding can be 134 recognized as a loss of water from the hexacoordinated 135 aluminum ion to the gas phase (eq 1). Once the temperature 136 reached 450 K, a sudden rise in the intensity of the peaks 137 associated with iodic acid (777, 713, and 631 cm^{-1}) was noticed; 138 upon further increasing the temperature, at 480 K these features 139 started to decline. Simultaneously, a rise in intensity of diiodine 140 pentoxide (I_2O_5) features centered at 726, 613, and 533 cm⁻¹ 141 was clearly visible. These observations reveal the decomposition 142 of iodic acid (HIO₃) to diiodine pentoxide (I_2O_5) plus water 143 (H_2O) (eq 2). Above 580 K, the diiodine pentoxide peaks begin 144 to decline, suggesting thermal decomposition of diiodine 145 pentoxide (I_2O_5) into iodine (I_2) and oxygen (O_2) (eq 3). 146

$$[Al(H_2O)_6](IO_3)_3(HIO_3)_2 \rightarrow Al(IO_3)_3(HIO_3)_2 + 6H_2O$$
(1) 147

$$Al(IO_3)_3(HIO_3)_2 \rightarrow Al(IO_3)_3 + I_2O_5 + H_2O$$
 (2) ₁₄₈

$$I_2O_5 \to I_2 + \frac{5}{2}O_2$$
 (3) 149



Figure 3. (a and b) Optical images of two different levitated AIH particles, at varying temperatures. Particle a was heated to a max temperature of 650 K where it detrapped soon after reaching 650 K. The appearance of red smoke was observed around 580 K. Flames appeared past 600 K. Particle b showed flame starting at 604 K. The two frames after 604 K were observed to show intense flames with an ejection of a small particle soon after. (c and d) Corresponding infrared images of the two different levitated AIH particles from panel a. Infrared images were taken in units of Kelvin.

Simultaneously with the Raman study, high-speed optical videos and infrared images were collected to observe changes as the particles approached the temperatures of 375 ± 5 , 480 ± 5 ,

and 580 ± 5 K, where significant alterations were observable in 153 the Raman spectra (Supporting Information; Movies M1–M8). 154



Figure 4. Fitted time traces of selected bands in the Raman spectra for (a) AIH and (b) AID at each step in the heating process. The component/ species are also mentioned in the parentheses of the corresponding band positions. See Tables S2 and S3 for rate constants.

¹⁵⁵ Critical snapshots are displayed in Figure 3 for the AIH system ¹⁵⁶ for two particles (a) (M1-M6) and (b) (M7, M8).

f3

As the heating commences to $371 \pm 5K$ (Figure 3a), the AIH 158 particles slowly increase in volume by about 20%; upon reaching 371 ± 5 K, a "popcorning" effect was visible, supported by a ¹⁵⁹ rapid enhancement of the particle volume by nearly 200% of its ¹⁶⁰ original size. As the temperature increases further, at 387 ± 5 K, ¹⁶¹ a maximum volume increase of about 600% was observed. This ¹⁶²

163 phase of the volume expansion corresponds to the spectroscopi-164 cally detected loss of water molecules from the coordination 165 sphere of the aluminum ions into the gas phase. The persistent 166 temperature increase to 450 ± 5 K was accompanied by an 167 increase in reflectivity of the surface of the levitated particle. 168 Recall that at 450 \pm 5 K, the Raman features of iodic acid 169 (HIO₃) also rose in intensity. We may therefore conclude that 170 iodic acid diffused from the inner AIH particle to the surface. 171 Starting at about 480 \pm 5 K, the temperature when iodic acid 172 decomposed to diiodine pentoxide (I_2O_5) and water (H_2O) , the 173 particle started to decrease in volume by about 20%, and the 174 surface darkened. As the temperature increased further, the 175 surfaces of both particles became darker and released reddish-176 purple vapor; this phase was accompanied by a reduction in 177 volume by about 50% at 582 \pm 5 K. Considering eq 3, these 178 reddish-purple vapors are associated with iodine released from 179 the particles. Considering the balanced chemical equation, this 180 process also releases molecular oxygen. As a result, both particles 181 self-ignited, producing flames followed by rapid detrapment of 182 the particles at temperatures exceeding 600 ± 5 K. Recall that 183 the thermal decomposition was conducted in an argon inert 184 atmosphere. Therefore, the ignition of the AIH particle is the 185 result of the enhanced concentration of oxygen released from 186 the levitated particle, which allows the particle to ignite and 187 burn.

The aforementioned studies provide compelling evidence on 188 189 a three-step process of the decomposition of AIH and AID: the 190 loss of water at T1 = 375 ± 5 K (eq 1), the conversion of iodic 191 acid into diiodine pentoxide and water at T2 = $480 \pm 5 \text{ K} (\text{eq } 2)$, 192 and the decomposition of diiodine pentoxide into its elements 193 (iodine and oxygen) starting at T3 = 580 ± 5 K. Vital 194 quantitative information on the decomposition process can be 195 gained by extracting time profiles of key species in the 196 decomposition process (water, iodic acid, and diiodine 197 pentoxide), which in turn can be fit kinetically to report rate 198 constants. To provide this information, Raman spectra were 199 collected at three distinct temperatures (T1, T2, and T3) over 200 time for AIH and AID. These spectra were then deconvoluted, 201 and the peak areas were integrated and plotted over time 202 (Supporting Information, Figures S1–S7).

At a constant temperature of 375 ± 5 K, the collected Raman 204 spectra were deconvoluted for both the levitated AIH and AID 205 particles exploiting a Python code (see Supporting Information 206 S1 and S2). The temporal evolution of the water features in AIH 207 are displayed in Figure 4a (1 and 2) for 3137 and 618 cm⁻¹; the 208 decay of the D₂-water peaks in the AID sample are traced in 209 Figure 4b (1 and 2) at 2427 and 607 cm⁻¹. Both the water and 210 D₂-water losses could be formally fit with a unimolecular decay 211 (first-order reaction) following eq 4 with [A]_t representing the 212 concentration of reactant A at time *t* expressed via the peak area, 213 [A]₀ is the initial concentration expressed via the peak area, k_1 214 the rate constant at 375 K, and *t* the time.²³ Laser fluctuations 215 and particle movements account for the errors of the traces.

$$[A]_{t} = [A]_{0}e^{-\kappa_{1}t}$$
(4)

This strategy provides a first-order rate constant of 0.047 ± 218 0.001 min⁻¹ for AIH averaged over both traces (Tables S2 and 219 S3). However, for the AID system, a first-order rate constant of 220 0.24 ± 0.02 min⁻¹ was determined. This suggests that the loss of 221 D₂-water proceeds faster than the loss of water revealing an 222 *inverse* isotope effect with $k_1(D_2O)/k_1(H_2O) = 5.3 \pm 0.6$ for T1 223 = 375 ± 5 K.

For a constant temperature of 480 ± 5 K, the traces of the 224 decay of iodic acid (HIO₃; 777 cm⁻¹, 777 cm⁻¹) and the 225 emergence of diiodine pentoxide (I₂O₅; 726 cm⁻¹, 728 226 cm⁻¹)^{17,20-22,24} are displayed in Figure 4a (3 and 4) and Figure 227 4b (3 and 4) for AIH and AID, respectively. Fits were achieved 228 by formally treating iodic acid as a dimer ((HIO₃)₂). [A]_t follows 229 a pseudo-first order reaction (eq 5); fits for the diiodine 230 pentoxide product follow eq 6 with [B]_t being the concentration 231 of product B at time t.²³ For both the AIH and AID system, the 232 rate of reaction, k_2 , was found to be identical, i.e. $k_2 = 0.020 \pm 233$ 0.001 min⁻¹. Hence, no isotope effect is observable. Note that 234 the rate constant k_2 is about half of k_1 , revealing a faster 235 dehydration of water in the coordination sphere of the 236 aluminum ion (eq 1) than the condensation reaction of two 237 iodic acid molecules to diiodine pentoxide plus water (eq 2). 238

$$[A]_t = [A]_0 e^{-k_2 t}$$
(5) 239

$$[B]_t = [A]_0 (1 - e^{-k_2 t})$$
(6) 240

For a constant temperature of 580 ± 5 K, the decomposition 241 of diiodine pentoxide (eq 3) was monitored via the first-order 242 decay (k_3) in the AIH and AID systems through the features at 243 726, 613, and 533 cm⁻¹ (AIH) and 728, 627, and 501 cm⁻¹ 244 (AID). The rate constants, k_{3} , were determined to be 0.125 \pm 245 0.051 min⁻¹ and 0.099 \pm 0.004 min⁻¹ for AIH and AID, 246 respectively, i.e., identical rates within the error limits. The 247 absence of isotope effects in steps II and III is reflected in the fact 248 that no deuterated reactants were involved in the decomposition 249 processes. Note that phase II is accompanied by a facile 250 detrapment of the particle considering the release of the gases 251 and self-ignition. However, we were also able to extract kinetic 252 traces for the AIH system at 600 ± 5 K yielding a rate constant of 253 $1.01 \pm 0.07 \text{ min}^{-1}$ (Table S2 and Figure S8), i.e., a $810 \pm 380\%$ 254 enhancement of the reaction rate by increasing the temperature 255 by only about 3%, i.e., 20 ± 10 K. Following the Arrhenius law, ²³ 256 this translates into a classical activation energy of 303 ± 180 kJ $_{257}$ mol⁻¹ for the decomposition of diiodine pentoxide to its 258 elements via eq 3 being endothermic by 173 kJ mol⁻¹ at 298 K. 259

In conclusion, the decomposition of single, levitated AIH and 260 AID particles in an argon inert atmosphere involves three 261 discrete stages: the loss of water (H₂O) commencing at $375 \pm 5_{262}$ K (phase I), the conversion of iodic acid (HIO_3) into diiodine 263 pentoxide (I_2O_5) and water (H_2O) starting at 480 ± 5 K (phase 264 II), and the decomposition of diiodine pentoxide into the 265 elements (iodine and oxygen) beginning at 580 ± 5 K (phase 266 III). Most critically, for phase I and III, the decomposition onset 267 temperatures are significantly lower for singly levitated particles 268 than those reported for bulk AIH exploiting differential scanning 269 calorimetry by up to 82 K.¹⁰ This discovery stipulates 270 conducting decomposition studies with single particles, i.e., 271 the real conditions under which the additives are injected into 272 combustion systems, to obtain precise onsets of decomposition, 273 which might otherwise be masked by the bulk material. These 274 studies provide compelling evidence on an inverse isotope effect 275 for the loss of deuterated water versus water in levitated AID and 276 AIH particles with $k_1(D_2O)/k_1(H_2O) = 5.3 \pm 0.6$ at 375 ± 5 K. 277 Our findings of an *inverse isotopic effect* would gain support from 278 previous dehydration studies of mono- and hexa-hydrated main 279 group II (M = Ca^{2+},Sr^{2+}) iodates [M(D₂O)(IO₃)₂] versus 280 $[M(H_2O)(IO_3)_2]$ and $[M(D_2O)_6(IO_3)_2]$ versus [M- 281 $(H_2O)_6(IO_3)_2$] exploiting thermogravimetric (TG) and differ- 282 ential thermal analysis (TGA); these works report temperatures 283 of D₂-water losses lower by 10 to 20 K compared to normal 284

285 water with averaged dehydration enthalpies of 115 versus 93 286 kJ mol⁻¹.^{25–27} The *inverse isotopic effect* observed for AIH versus 287 AID operates against conventional wisdom that due to the 288 heavier mass of deuterium versus hydrogen, heavier isotopo-289 logues have lower vibrational frequencies compared to their 290 lighter counterparts. This in turn would require a greater energy 291 input for heavier isotopologues to overcome the transition state ²⁹² of a chemical reaction, thus reducing the rate constants;²³ this 293 was observed, e.g., in catalytic reactions,²⁸ and in the combustion of metallic and organic energetic materials of, e.g., 294 ²⁹⁵ nanoaluminum with water,²⁹ and octahydro-1,3,5,7-tetranitro-²⁹⁶ 1,3,5,7-tetrazocine (HMX);³⁰ these normal kinetic isotopic effects evidenced the critical role of a kinetically controlled 297 combustion process. The inverse isotopic effect of the dehydration 298 299 of AIH versus AID here is challenging to reconcile with formerly 300 postulated diffusion-limited dehydration steps of minerals with 301 water in the coordination sphere of metal ions,²⁷ which should 302 cause a normal kinetic isotope effect with the dehydration being 303 faster for water compared to deuterated water. A promising 304 rationalization for the inverse isotopic effect is the red-shift of the 305 vibration modes to lower energies for deuterated water, 306 predominantly the symmetric and antisymmetric stretching $_{307}$ modes covering the 3531-2659 cm⁻¹ (AIH) and 2659-2000 308 cm^{-1} (AID) ranges (Figure 5).



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Figure 5. Blackbody spectra for 370, 375, and 380 K. The blackbody spectra are overlaid with the vibrational modes of water (H₂O) and deuterated water (D₂O). Relative absorbances of the water bands $(3137, 2946, \text{and } 618 \text{ cm}^{-1})$ and deuterated water $(2427 \text{ and } 607 \text{ cm}^{-1})$ are shown.

Since these regions reveal a significantly enhanced overlap 309 310 with the blackbody emission spectrum of the particles at 375 ± 5 311 K, this could result in an enhanced energy absorption of deuterated water compared to normal water.³¹ This in turn 312 313 would lead to a boosted loss of deuterated water compared to water due to the increased energy absorption and higher rate to 314 overcome the transition state of the reaction. 315

The fundamental knowledge obtained from the decom-316 317 position studies of singly levitated AIH and AID particles along 318 with the observation of an inverse isotopic effect provide 319 quantitative insights into discrete stages, onsets of decom-320 positions, intermediates (I_2O_5) , and gases formed (H_2O, I_2, O_2) 321 covering temperatures up to about 600 K. Therefore, AIH as a 322 coating of aluminum nanoparticles would not only replace the 323 oxide layers^{9,10,12,32} but also amplify the thrust through the

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development of gaseous decomposition products in propulsion 324 systems. The molecular oxygen released via the decomposition 325 of diiodine pentoxide also provides an additional source of an 326 oxidizer which, in direct contact with the surface of the 327 aluminum nanoparticles, could potentially reduce ignition 328 delays, thus enhancing the efficiency of propulsion systems. 329 Further, the iodine gas produced neutralizes bacteria and 330 ultimately sterilizes potentially biologically contaminated 331 environments including engine systems.³ 332

Overall, these results represent a very first step to a systematic 333 understanding of the decomposition processes of energetic 334 coatings such as AIH on metal nanoparticles ultimately aiding in 335 the development of next-generation, metal nanoparticle-based 336 propulsion systems along with energy-generation technologies 337 exploiting AIH-coated aluminum nanoparticles. This work 338 further provides an experimental benchmark for prospective 339 high-level computational investigation of the decomposition of 340 AIH and AID in the condensed phase, in particular the inverse 341 isotope effect as observed here, which is currently beyond reach. 342 From the experimental aspect, ignition studies of single levitated 343 JP-10 fuel droplets doped with AIH-coated aluminum nano- 344 particles are highly desirable to explore the impact of the AIH 345 coating on the combustion stages of JP-10 and ignition delays 346 ultimately augmenting the proficiency of propulsion systems.³⁴ 347

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at 350 https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00273. 351

Details of the materials and methods used in exper- 352 imentation; Raman vibrational assignments for AIH and 353 AID at 293 K; AIH Raman spectra at 375, 480, 580, and 354 600 K; AID Raman spectra at 375, 480, and 580 K; time 355 traces of AIH at 600 K; AIH and AID rate constants; 356 Python script; levitator diagram; and pulse sequence 357 (PDF) 358

Movie M1, particle 1 size increase seen at 375 K; Movie 359 M2, corresponding IR video for particle 1 at 375 K; Movie 360 M3, particle 1 view at 480 K; Movie M4, corresponding IR 361 video for particle 1 at 480 K; Movie M5, particle 1 view at 362 580 K, particle gas release and ignition; Movie M6, 363 corresponding IR video for particle 1 at 580 K; Movie M7, 364 particle 2 view at 580 K, intense particle gas release and 365 ignition; Movie M8, corresponding IR video for particle 2 366 at 580 K (ZIP) 367

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390 Author Contributions

391 G.L.R. designed and performed experiments, analyzed data, and 392 prepared the manuscript. S.B. mentored G.L.R. and helped in 393 experiments. I.A. wrote the Python script for analysis of kinetic 394 data. K.K.M. and M.L.P. provided AIH and AID particles. All the 395 authors contributed to reviewing and editing. R.I.K. designed, 396 oversaw, and secured resources for the research project and 397 supervised the manuscript preparation.

398 Notes

399 The authors declare no competing financial interest.

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408 **REFERENCES**

409 (1) Faraday, M. Experimental Relations of Gold (and Other Metals) 410 to Light. *Philos. Trans. R. Soc. London* **1857**, *147*, 145–181.

411 (2) Edwards, P. P.; Thomas, J. M. Gold in a Metallic Divided State-412 From Faraday to Present-Day Nanoscience. *Angew. Chem., Int. Ed.* 413 **2007**, *46*, 5480–5486.

414 (3) Dreizin, E. L. Metal-Based Reactive Nanomaterials. *Prog. Energy* 415 *Combust. Sci.* **2009**, 35, 141–167.

416 (4) E, X. T. F.; Pan, L.; Wang, F.; Wang, L.; Zhang, X.; Zou, J. J. Al-417 Nanoparticle-Containing Nanofluid Fuel: Synthesis, Stability, Proper-418 ties, and Propulsion Performance. *Ind. Eng. Chem. Res.* **2016**, *55*, 2738– 419 2745.

420 (5) Lucas, M.; Brotton, S. J.; Min, A.; Pantoya, M. L.; Kaiser, R. I. 421 Oxidation of Levitated exo-Tetrahydrodicyclopentadiene Droplets 422 Doped with Aluminum Nanoparticles. *J. Phys. Chem. Lett.* **2019**, *10*, 423 5756–5763.

424 (6) Dikici, B.; Dean, S. W.; Pantoya, M. L.; Levitas, V. I.; Jouet, R. J. 425 Influence of Aluminum Passivation on the Reaction Mechanism: Flame 426 Propagation Studies. *Energy Fuels* **2009**, *23*, 4231–4235.

427 (7) Gesner, J.; Pantoya, M. L.; Levitas, V. I. Effect of Oxide Shell
428 Growth on Nano-Aluminum Thermite Propagation Rates. *Combust.*429 Flame 2012, 159, 3448–3453.

(8) Trunov, M. A.; Umbrajkar, S. M.; Schoenitz, M.; Mang, J. T.;
Heizin, E. L. Oxidation and Melting of Aluminum Nanopowders. J.
Phys. Chem. B 2006, 110, 13094–13099.

433 (9) Shancita, I.; Miller, K. K.; Silverstein, P. D.; Kalman, J.; Pantoya,
434 M. L. Synthesis of Metal Iodates From an Energetic Salt. *RSC Adv.*435 2020, *10*, 14403–14409.

436 (10) Kalman, J.; Smith, D. K.; Miller, K. K.; Bhattacharia, S. K.;

437 Bratton, K. R.; Pantoya, M. L. A Strategy for Increasing the Energy
438 Release Rate of Aluminum by Replacing the Alumina Passivation Shell
439 with Aluminum Iodate Hexahydrate (AIH). *Combust. Flame* 2019, 205,
440 327–335.

441 (11) Smith, D. K.; McCollum, J.; Pantoya, M. L. Effect of 442 Environment on Iodine Oxidation State and Reactivity with Aluminum. 443 *Phys. Chem. Chem. Phys.* **2016**, *18*, 11243–11250. (12) Smith, D. K.; Bello, M. N.; Unruh, D. K.; Pantoya, M. L. 444 Synthesis and Reactive Characterization of Aluminum Iodate 445 Hexahydrate Crystals $[Al(H_2O)_6](IO_3)_3(HIO_3)_2$. Combust. Flame 446 **2017**, 179, 154–156. 447

(13) Gottfried, J. L.; Smith, D. K.; Wu, C. C.; Pantoya, M. L. 448 Improving the Explosive Performance of Aluminum Nanoparticles with 449 Aluminum Iodate Hexahydrate (AIH). *Sci. Rep* **2018**, *8*, 8036. 450

(14) Smith, D. K.; Unruh, D. K.; Wu, C. C.; Pantoya, M. L. Replacing $_{451}$ the Al₂O₃ Shell on Al Particles with an Oxidizing Salt, Aluminum Iodate $_{452}$ Hexahydrate. Part I: Reactivity. *J. Phys. Chem. C* **2017**, *121*, 23184– 453 23191.

(15) Miller, K. K.; Gottfried, J. L.; Walck, S. D.; Pantoya, M. L.; Wu, C. 455 C. Plasma Surface Treatment of Aluminum Nanoparticles for Energetic 456 Material Applications. *Combust. Flame* **2019**, *206*, 211–213. 457

(16) Adams, D. M.; Hills, D. J. Single-Crystal Raman and Infrared 458
 Study of Aluminum Trichloride Hexahydrate. J. Chem. Soc. Dalt. Trans. 459
 1978, 782–788.

(17) Sherwood, P. M. A.; Turner, J. J. Vibrational Spectra of 461
Compounds in the Iodine Pentoxide -Water System and Sodium 462
Iodate. Spectrochim. Acta A Mol. Biomol. Spectrosc. 1970, 26, 1975-463
1992. 464

(18) Durig, J. R.; Bonner, O. D.; Breazeale, W. H. Raman Studies of 465 Iodic Acid and Sodium Iodate. J. Phys. Chem. **1965**, 69, 3886–3892. 466

(19) Degen, I. A.; Newman, G. A. Raman Spectra of Inorganic Ions. 467 Spectrochim. Acta A Mol. Biomol. Spectrosc. **1993**, 49, 859–887. 468

(20) Hibben, J. H. The Raman Effect and Its Chemical Applications; 469 Reinhold Publishing Corp.: New York, NY, 1939. 470

(21) Ngo, N.; Kalachnikova, K.; Assefa, Z.; Haire, R. G.; Sykora, R. E. 471 Synthesis and Structure of $In(IO_3)_3$ and Vibrational Spectroscopy of 472 $M(IO_3)_3$ (M = Al, Ga, In). J. Solid State Chem. **2006**, 179, 3824–3830. 473

(22) Bushiri, M. J.; Kochuthresia, T. C.; Vaidyan, V. K.; Gautier- 474 Luneau, I. Raman Scattering Structural Studies of Nonlinear Optical 475 $M(IO_3)_3$ (M = Fe, Ga, α -In) and Linear Optical β -In(IO₃)₃. J. Nonlinear 476 Opt. Phys. Mater. **2014**, 23, 1450039. 477

(23) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. Chemical Kinetics and 478 Dynamics; Prentice Hall, Inc.: Upper Saddle River, NJ, 1999. 479

(24) Ellestad, O. H.; Woldbæk, T.; Kjekshus, A.; Klæboe, P.; Selte, K. 480 Infrared and Raman Studies of Crystalline I_2O_5 , $(IO)_2SO_4$, $(IO)_2SO_4$ 481 and I_2O_4 . Acta Chem. Scand. A **1981**, 35a, 155–164. 482

(25) Maneva, M.; Koleva, V. Thermal and Calorimetric Investigations 483 of $M(IO_3)_2 \cdot H_2O$ and $M(IO_3)_2 \cdot D_2O$ ($M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$). 484 *Thermochim. Acta* **1992**, 207, 85–93. 485

(26) Maneva, M.; Koleva, V. Thermal and Calorimetric Studies of 486 $M(IO_3)_2 \cdot 6H_2O$ and $M(IO_3)_2 \cdot 6D_2O$ for $M^{2+} = Ca^{2+}$ and Sr^{2+} . *J. Therm.* 487 *Anal.* **1992**, 38, 2491–2499. 488

(27) Koleva, V.; Maneva, M. Kinetic Analysis of the Dehydration 489
 Processes in Some Iodate Hydrates. *Thermochim. Acta* 1994, 242, 233–490
 237. 491

(28) Rubtsov, N. M.; Tsvetkov, G. I.; Chernysh, V. I.; Troshin, K. Y. 492 Features of Hydrogen and Deuterium Ignition Over Noble Metals at 493 Low Pressures. *Combust. Flame* **2020**, *218*, 179–188. 494

(29) Tappan, B. C.; Dirmyer, M. R.; Risha, G. A. Evidence of a Kinetic 495 Isotope Effect in Nanoaluminum and Water Combustion. *Angew.* 496 *Chem., Int. Ed.* **2014**, 53, 9218–9221. 497

(30) Shackelford, S. A.; Goshgarian, B. B.; Chapman, R. D.; Askins, R. 498 R.; Flanigan, D. A.; Rogers, R. N. Deuterium Isotope Effects During 499 HMX Combustion: Chemical Kinetic Burn Rate Control Mechanism 500 Verified. *Propellants Explos. Pyrotech.* **1989**, *14*, 93–102. 501

(31) Scott Tonner, D.; Tholmann, D.; McMahon, T. B. Deuterium 502 Isotope Effect on the Radiatively Induced Unimolecular Dissociation of 503 Small Cluster Ions. *Chem. Phys. Lett.* **1995**, 233, 324–330. 504

(32) Smith, D. K.; Unruh, D. K.; Pantoya, M. L. Replacing the Al_2O_3 505 Shell on Al Particles with an Oxidizing Salt, Aluminum Iodate 506 Hexahydrate. Part II: Synthesis. *J. Phys. Chem. C* 2017, 121, 23192–507 23199. 508

(33) Miller, K. K.; Creegan, S. E.; Unruh, D. K.; Pantoya, J. D.; Hill, K. 509 J.; Tran, Q.; Pantoya, M. L. Acid Base Synthesis of Aluminum Iodate 510 Hexahydrate Powder as a Promising Propellant Oxidizer. *Chem. Eng. J.* 511 **2023**, 453, 139953. 512 513 (34) Antonov, I.; Chyba, A.; Perera, S. D.; Turner, A. M.; Pantoya, M. 514 L.; Finn, M. T.; Epshteyn, A.; Kaiser, R. I. Discovery of Discrete Stages 515 in the Oxidation of exo-Tetrahydrodicyclopentadiene ($C_{10}H_{16}$) 516 Droplets Doped with Titanium-Aluminum-Boron Reactive Mixed-517 Metal Nanopowder. J. Chem. Phys. Lett. **2022**, 13, 9777–9785.