

Same Atomic Number, Same Charge, Same Electrons: Change Only the Mass and the Rate Moves Sevenfold

— The C--H to C--D frequency ratio is **0.734230**, which is not $1/\sqrt{2} = 0.707107$ — A zero-point difference of **4.7690** kJ/mol makes $k_H/k_D = \mathbf{6.8468}$ at room temperature — [Paper 341]

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September 2026

— *From thinking to syncing.* —

Abstract

Replace hydrogen with deuterium and a reaction rate changes. This paper asks why changing only the mass moves the rate—the answer is that the energy of standing still is set by the mass. No new mathematical theorem and no new law is claimed. First, the C--D stretch is **2202.69** cm⁻¹, a factor **0.734230** of C--H (Section 2). Second, that ratio is not $1/\sqrt{2} = 0.707107$. Because the reduced mass carries the 12 of carbon (Section 2). Third, this is the core of the paper. What makes the difference is not the passage of the reaction but the state of rest before it (Section 3). Fourth, a zero-point difference of **4.7690** kJ/mol makes $k_H/k_D = \mathbf{6.8468}$ at room temperature (Section 3). Fifth, it moves strongly with temperature. **8.1650** at 0 °C and **4.6512** at 100 °C (Section 4). Sixth, the separator is whether the light atom sits on the bond that breaks (Section 5).

Scope of this paper (scope note): No new mathematical theorem and no new law is claimed—the zero-point energy of a harmonic oscillator, the reduced mass, and the primary kinetic isotope effect are all standard. We do not settle any mechanism—rate-determining steps and transition-state structures of particular reactions are not entered. Only a semiclassical upper bound is looked at. We do not treat tunnelling—the anomalously large k_H/k_D observed at low temperature comes from tunnelling; this paper stays where zero-point energy suffices. It is mentioned and no more. We do not treat secondary isotope effects—substitution away from the breaking bond is not entered. We do not treat equilibrium isotope effects—shifts in equilibrium constants rather than rates are not the subject. We do not treat anharmonicity—real vibrations are not harmonic and 3000 cm^{-1} is a representative value. Relation to earlier papers: Paper 314 showed there is only one kind of constant one can ask “has it changed?” about—there only dimensionless constants could be asked. This paper runs the other way: within one element, only the mass is moved. Not moving a constant but exchanging a specimen. Paper 283 showed the same “double the Q ” differing by 10^{17} across three mechanisms—that was in the nucleus and this is in a chemical bond. Both are “a small difference in mass or energy reaches the rate through an exponential”. Paper 300 showed whether two things share a root is decidable—here the isotope effect and the temperature effect live inside the same exponential. Paper 272 showed the same “twice as strong” opening by 6.70 on the stimulus side—there too a small input difference became a large output difference. What is added is computing the frequency ratio from reduced masses and showing in numbers why it is not $1/\sqrt{2}$, giving k_H/k_D at three temperatures from the zero-point difference, repeating the calculation for O–H and for carbon 12/13 to confirm the size is set by the mass ratio, and putting the separator on whether the light atom sits on the breaking bond.

1. Notation and the Question

Setting: Replace hydrogen (^1H , mass 1.007825) with deuterium (^2H , mass 2.014102). Atomic number, charge and electron configuration are unchanged—the chemistry ought to be the same.

Observation 1.1

And yet the rate changes. A typical primary kinetic isotope effect is a factor of six to eight—with identical electrons, the rate moves by nearly a decade.

Observation 1.2

Only the mass changed. In quantum mechanics mass enters the frequency—and frequency enters the energy of standing still.

Observation 1.3

The way of measuring is fixed first. The C--H stretch is taken as a representative 3000 cm^{-1} and treated harmonically—anharmonicity is ignored, so these are indicative rather than precise values.

Question: Why does changing only the mass move the rate?

2. The Frequency Ratio Is 0.734230, Not $1/\sqrt{2}$

Setting: A diatomic stretch has $\nu \propto \sqrt{k/\mu}$, with k the force constant (set by the electrons) and $\mu = m_1 m_2 / (m_1 + m_2)$ the reduced mass. Isotopic substitution leaves k alone, so the ratio of ν is fixed by reduced masses only.

Calculation 2.1: Compute for C--H and C--D (computed in this paper).

Quantity	Value
C--H stretch (representative)	3000.00 cm^{-1}
Frequency ratio $\sqrt{\mu_{CH}/\mu_{CD}}$	0.734230
C--D stretch	2202.6900 cm^{-1}
The naive $1/\sqrt{2}$	0.707107

Observation 2.2

0.734230 is not $1/\sqrt{2} = 0.707107$. The mass doubled, so one wants $1/\sqrt{2}$ —but it is not only the hydrogen that vibrates; the carbon moves a little too.

Observation 2.3

The reduced mass turns that “a little” into a number. $\mu_{CH} = 0.929740$ and $\mu_{CD} = 1.724636$, a ratio of 1.854965 and not 2—the 12 of carbon dilutes a doubling of mass into a factor of 1.854965.

Observation 2.4

The heavier the partner, the closer to $1/\sqrt{2}$. O--H against O--D gives 0.728010, nearer $1/\sqrt{2}$ than the 0.734230 of C--H against C--D—because the 16 of oxygen moves less than the 12 of carbon.

Observation 2.5

Between heavy atoms the effect nearly vanishes. Carbon 12 against carbon 13 gives 0.980520—two per cent. The isotope effect is large for hydrogen because the mass ratio is a full factor of two.

3. The Core: What Makes the Difference Is the State of Rest Before the Reaction

Setting: In quantum mechanics vibration does not stop even at absolute zero. The lowest state still carries $E_0 = \frac{1}{2} h\nu$ —the zero-point energy.

Observation 3.1

This is the core of the paper. C--D has the lower frequency, hence the lower zero-point energy—which is to say that C--D starts deeper in the well. Breaking the bond means climbing that much further.

Calculation 3.2: Compute the zero-point difference (computed in this paper).

$$\Delta E_0 = \frac{1}{2} h c (\nu_{CH} - \nu_{CD}) N_A = 4.7690 \text{ kJ/mol}$$

Observation 3.3

This becomes the difference in activation energy. If that vibration is entirely lost at the transition state, the difference in barrier is exactly the zero-point difference—and the rate ratio is $k_H/k_D = \exp(\Delta E_0/RT)$.

Calculation 3.4: Rate ratios at three temperatures (computed in this paper).

Temperature	T [K]	k_H/k_D
0 °C	273.15	8.1650
25 °C	298.15	6.8468
100 °C	373.15	4.6512

Observation 3.5

A check—the room-temperature 6.8468 falls inside the usual six to eight for a primary isotope effect. A value derived from a representative 3000 cm^{-1} lands inside an independently known range.

Observation 3.6

4.7690 kJ/mol is small as chemistry goes. Typical activation energies run 50 to 150 kJ/mol—a difference under 5 kJ/mol moves the rate sevenfold. Because it sits inside an exponential.

Observation 3.7

And the difference is not “along the way”. The path of the reaction and the shape of the transition state are set by the electrons and do not change with the isotope—what changed is only the height of the starting point. The same mountain is climbed, and one party starts lower.

4. Temperature Matters Because the Difference Is Inside an Exponential

Observation 4.1

From 0 °C to 100 °C the effect falls from 8.1650 to 4.6512. A factor of 1.7555—raise the temperature and 4.7690 kJ/mol becomes relatively smaller.

Observation 4.2

At high temperature the effect disappears. Once RT is well above ΔE_0 , $\exp(\Delta E_0/RT) \rightarrow 1$ —the isotope effect lasts only until the quantum effect is buried in heat.

Observation 4.3

At low temperature it grows. But measurements can exceed what this formula predicts—tunnelling takes over, and the formula here cannot account for it. These values are the tunnel-free case.

Observation 4.4

This is the boundary to state honestly. A k_H/k_D far above 7 cannot come from zero-point energy alone—that a number exceeds the bound is itself evidence of another mechanism. The 6.8468 here is what provides that bound.

Observation 4.5

Where this stands relative to Paper 283. Paper 283 wrote that the same “double the Q ” gives 5.69×10^{18} in alpha decay, 32 in beta and 8 in gamma—there too a small input difference passed through an exponential into an enormous output difference. Nucleus and chemical bond are seventeen decades apart and the shape is the same.

5. The Separator: Does the Light Atom Sit on the Bond That Breaks?

Observation 5.1

The separator—whether the substituted atom sits on the bond broken in the rate-determining step.

	Position of substitution	Zero-point difference	k_H/k_D
Primary isotope effect	on the breaking bond	4.7690 kJ/mol	6.8468
Secondary isotope effect	elsewhere	much smaller	about 1.1

Observation 5.2

So the isotope effect becomes an instrument for reading mechanism. Measure k_H/k_D and find it above six, and that hydrogen is being broken in the rate-determining step—where in the molecule the reaction happens can be named from outside.

Observation 5.3

This is Paper 314 turned around. Paper 314 wrote that only one kind of constant can be asked whether it has changed—there the problem was moving a constant. Here the constants (the electrons) do not move and only the mass of the specimen is exchanged. What may be varied is different.

Observation 5.4

The separator can be moved. Deuterate a different position of the same molecule and the effect falls from 6.8468 to about 1.1—the answer depends on where the substitution was made.

Observation 5.5

To be stated honestly—this assumes the vibration is entirely lost at the transition state. In practice it is only partly lost, so 6.8468 is an upper bound and not a prediction—measured values are usually smaller.

Observation 5.6

One last thing—what moved here is a quantity from outside chemistry. Nuclear masses are settled where chemistry does not look—inside what chemistry calls “the same element” there remains a difference chemistry does not explain, and it moves the rate sevenfold.

6. The Census and the Close

1. Frequency ratio **0.734230** (Calculation 2.1): C--D at **2202.6900** cm^{-1} .
2. Not $1/\sqrt{2} = 0.707107$ (Observation 2.2): **the carbon moves too**.
3. Reduced masses in ratio **1.854965**, not **2** (Observation 2.3): **the 12 of carbon dilutes it**.
4. O--H/O--D gives **0.728010** (Observation 2.4): **heavier partner, nearer $1/\sqrt{2}$** .
5. Carbon 12/13 gives **0.980520** (Observation 2.5): **two per cent**.
6. Zero-point difference **4.7690** kJ/mol (Calculation 3.2): **it becomes the barrier difference**.
7. $k_H/k_D = 6.8468$ at room temperature (Calculation 3.4): **inside the usual six to eight**.
8. Under 5 kJ/mol moves the rate sevenfold (Observation 3.6): **inside an exponential**.
9. **8.1650** at 0 °C, **4.6512** at 100 °C (Calculation 3.4): **a factor of 1.7555**.
10. Far above 7 means tunnelling (Observation 4.4): **exceeding the bound is the evidence**.

Closing: Replace hydrogen with deuterium and with the same atomic number, the same charge and the same electrons, the rate moves sevenfold—only the mass changed. Mass enters the frequency— $\nu \propto \sqrt{k/\mu}$, and isotopic substitution leaves k alone, so the ratio comes from reduced masses only. C--D is **2202.6900** cm^{-1} , a ratio of **0.734230**. One wants $1/\sqrt{2} = 0.707107$ for a doubled mass and does not get it—because the carbon moves too, so the reduced masses stand in ratio **1.854965** and not 2. The heavier the partner the closer to $1/\sqrt{2}$ (O--H/O--D at 0.728010), and between heavy atoms the effect nearly vanishes (carbon 12/13 at 0.980520). And what makes the difference is not the passage of the reaction—vibration does not stop at absolute zero, and $E_0 = \frac{1}{2}h\nu$ remains. C--D, having the lower frequency, has the lower zero-point energy and starts deeper in the well. The difference is **4.7690** kJ/mol, and it becomes the difference in activation barrier. The path and the transition state are set by the electrons and do not change with the isotope; only the height of the starting point changed. The same mountain is climbed, and one party starts lower. **4.7690** kJ/mol is small as chemistry goes—typical activation energies run 50 to 150. A difference under 5 kJ/mol moves the rate sevenfold because it sits inside an exponential. $k_H/k_D = 6.8468$ at room temperature, **8.1650** at 0 °C, **4.6512** at 100 °C — raise the temperature and RT swallows the difference, and the isotope effect fades. One thing separates them—whether the substituted atom sits on the bond broken in the rate-determining step. On that bond it is **6.8468**; elsewhere about 1.1—so measuring k_H/k_D names, from outside, where in the molecule the reaction is happening. To be said honestly—this assumes the vibration is entirely lost at the transition state, so **6.8468** is an upper bound and not a prediction; measured values are usually smaller. And a value far above 7 cannot come from zero-point energy at all, which makes exceeding the bound itself the evidence of tunnelling. One last thing—what moved here is a quantity from outside chemistry. Nuclear masses are settled where chemistry does not look. Inside what chemistry calls “the same element” there remains a difference chemistry does not explain, and it moves the rate sevenfold.

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