

The Potential Energy Surface (PES)

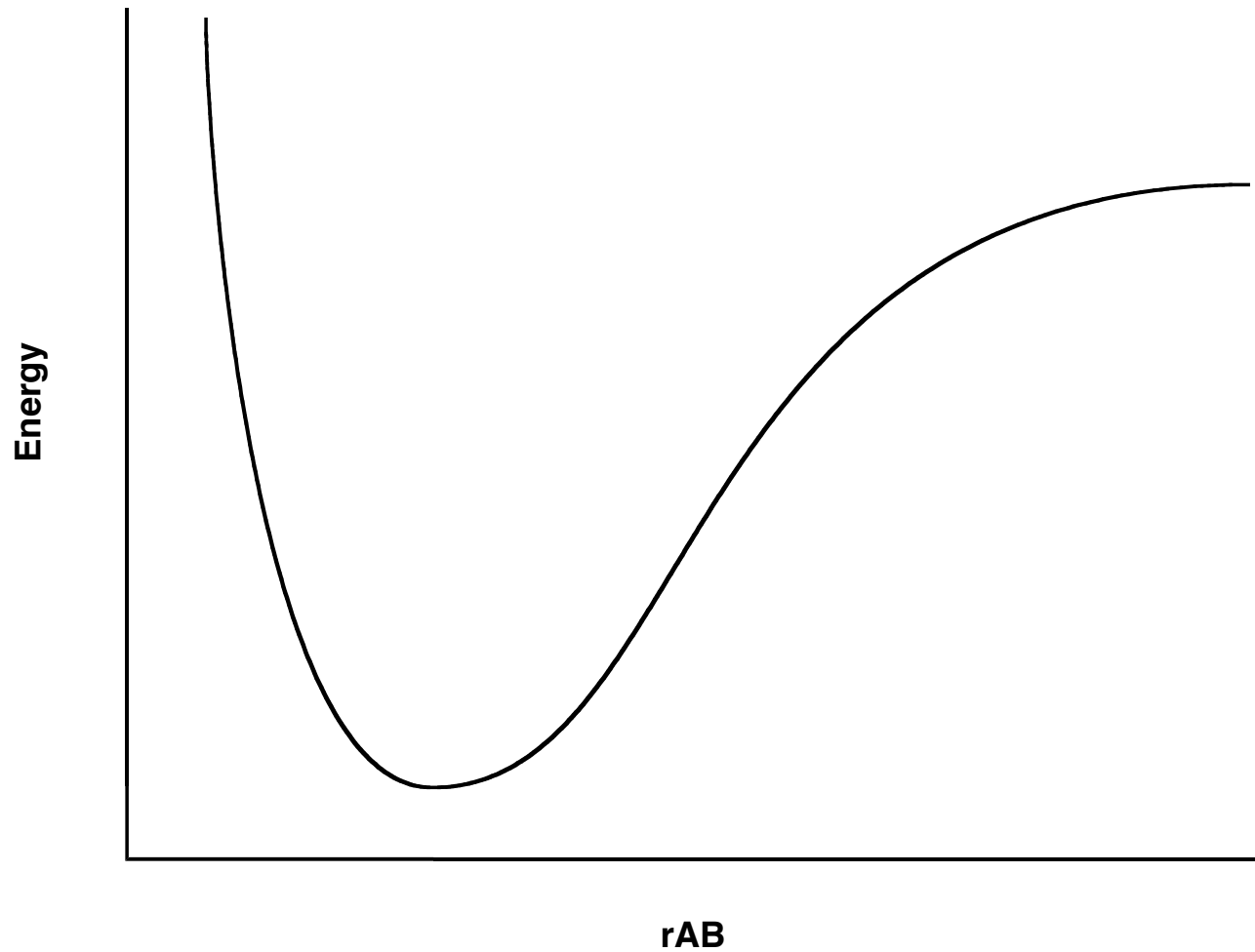
Preamble to the Basic Force Field

The Potential Energy Surface

- Captures the idea that each structure—that is, geometry—has associated with it a unique energy
- Since geometry changes are smooth, this idea creates a smooth energy “landscape”
- Chemistry becomes topology...

Simplest Example is One-dimensional

Standard Diatomic Bond Stretch

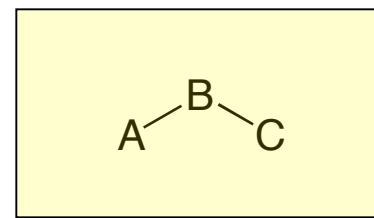
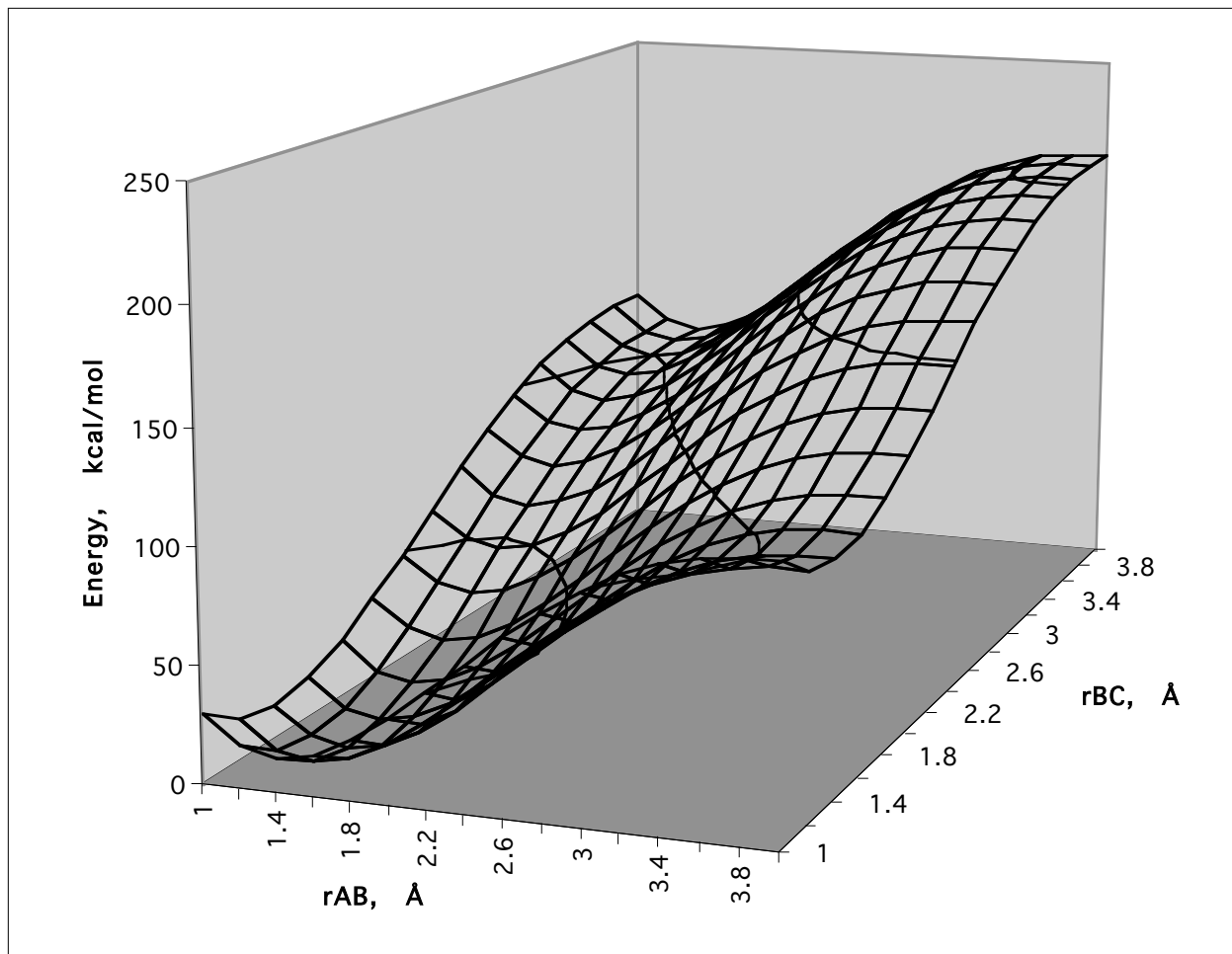


Dimensionality of the Generic PES

- How many dimensions are there, formally? To define an atom's location in 3-dimensional space in principle takes 3 coordinates (e.g., x , y , and z in some laboratory reference frame)
- But, the PES should not depend on the *absolute* location of the atoms, only on their location *relative to one another* (i.e., the molecular geometry)
- So, a typical PES has the same dimensionality as the number of *degrees of freedom* of the (not everywhere linear) molecule ($3N-6$, where $N = \#$ of atoms and $N > 2$)

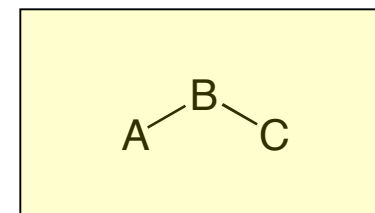
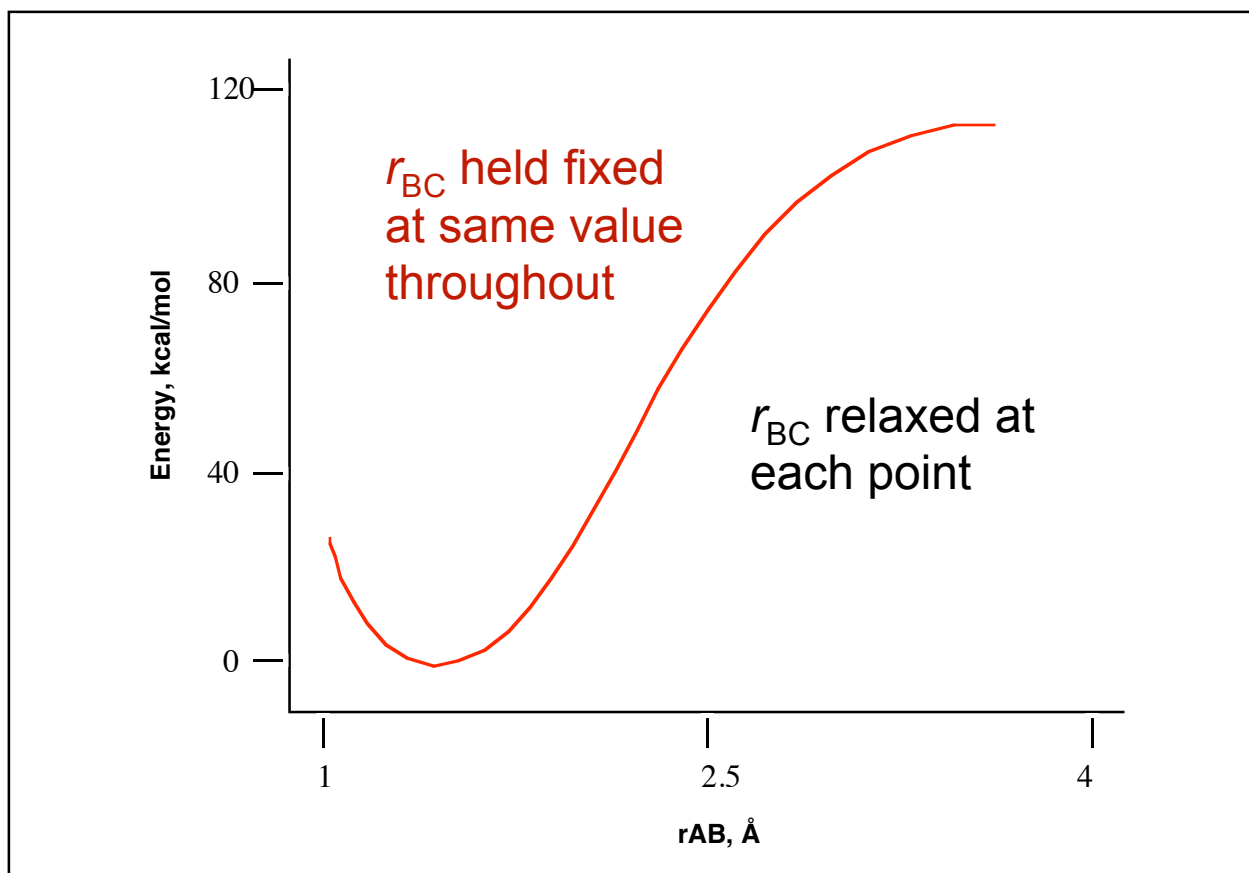
More Dimensions Don't Graph Well...

So, we usually take "slices" of the PES



Here, we take a two-dimensional slice (the most we can easily graph, since energy is the third coordinate) of a molecule with 3 degrees of freedom; it is the bond angle that is being held fixed that defines the slice.

Typical Reaction Coordinate is Really a One-dimensional Slice of a PES



This is a slice of the surface from the last slide now not only holding the ABC angle to some fixed value, but also controlling r_{BC} .

A *true* reaction coordinate implies that all other degrees of freedom are *relaxed*, not held fixed

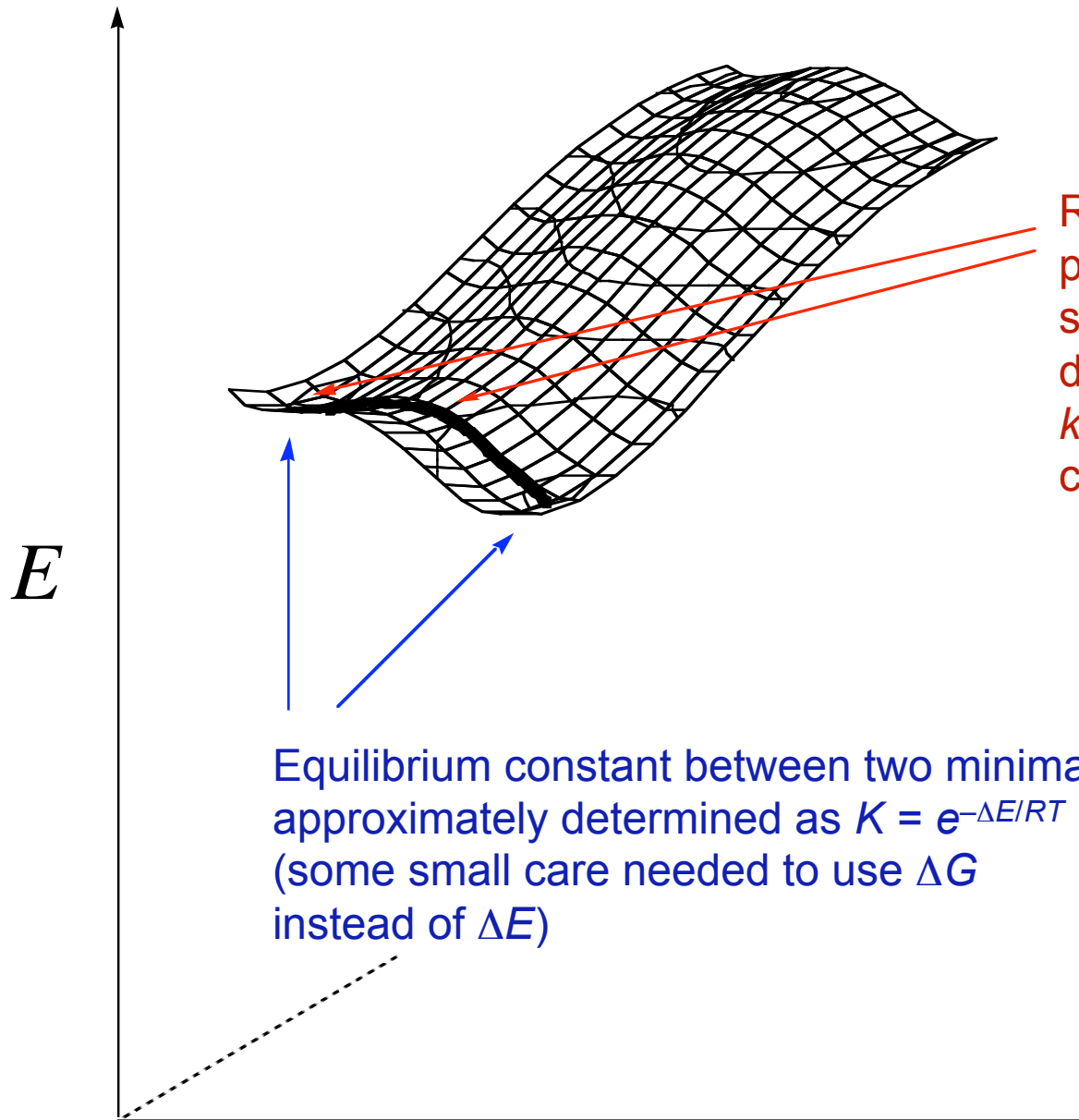
Deeper Aspects of the PES

- Depends in a fundamental way on the Born-Oppenheimer approximation
- Inherently a classical construct with respect to the nuclei (but quantum in the electronics)
- Corresponds to a single molecule; thinking about a *collection* of molecules requires us to bring in thermodynamics (which we'll discuss later)

More Deeper Aspects of the PES

- Does not show *kinetic* energy! So, everyone's favorite picture of a dynamic molecule being a ball rolling on the surface is misleading if you think of the energy decreasing as you go downhill. *Total* energy (PE + KE) is conserved at a constant value. Again, this is something we'll discuss later.
- At $T = 0$ K (no KE), the rules of our universe say that our molecule will want to be at the lowest possible potential energy, i.e., at a *minimum* on the PES. It sure would be nice to have ways of finding the locations of minima efficiently...
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a saddle point. In chemistry, we call that saddle point a transition-state structure. They'd be nice to find too...

Some Foreshadowing



Rate constant for a minimum passing through a transition state approximately determined as
 $k = (k_B T/h)e^{-\Delta E^\ddagger/RT}$ (same caveat about ΔG and ΔE)

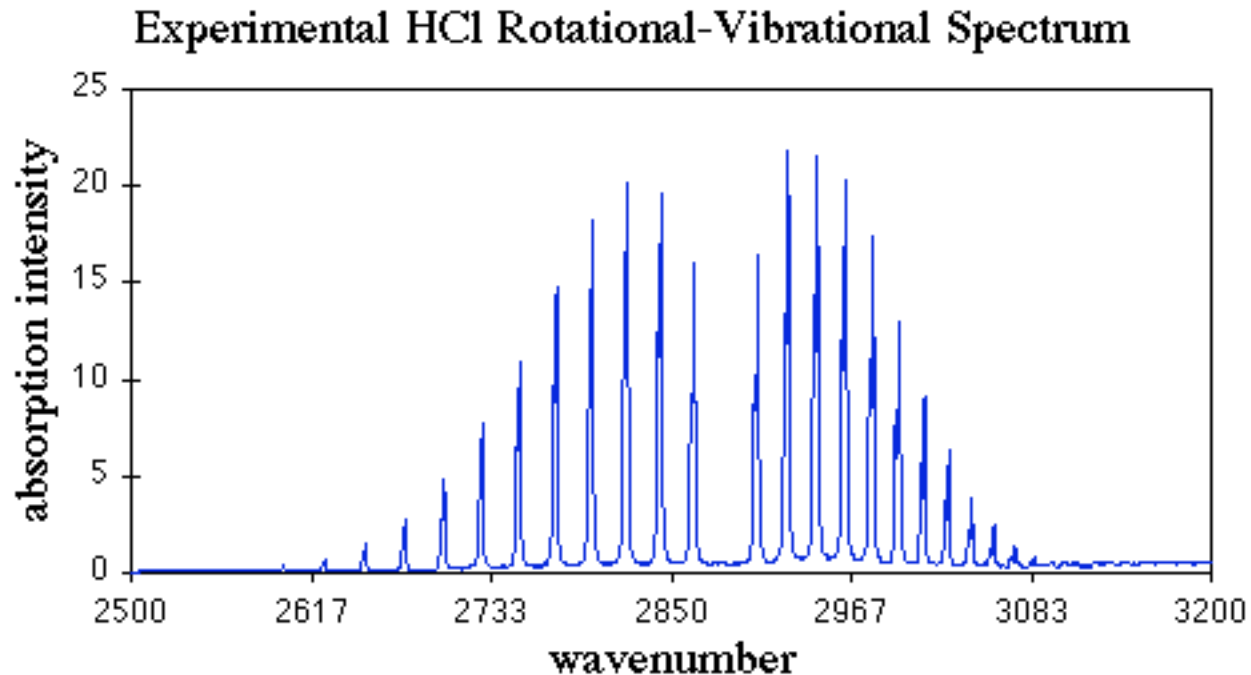
Equilibrium constant between two minima approximately determined as $K = e^{-\Delta E/RT}$ (some small care needed to use ΔG instead of ΔE)

Equilibrium and rate constants:
now we're talking real chemistry

Fundamental Points About Which to Be Thinking

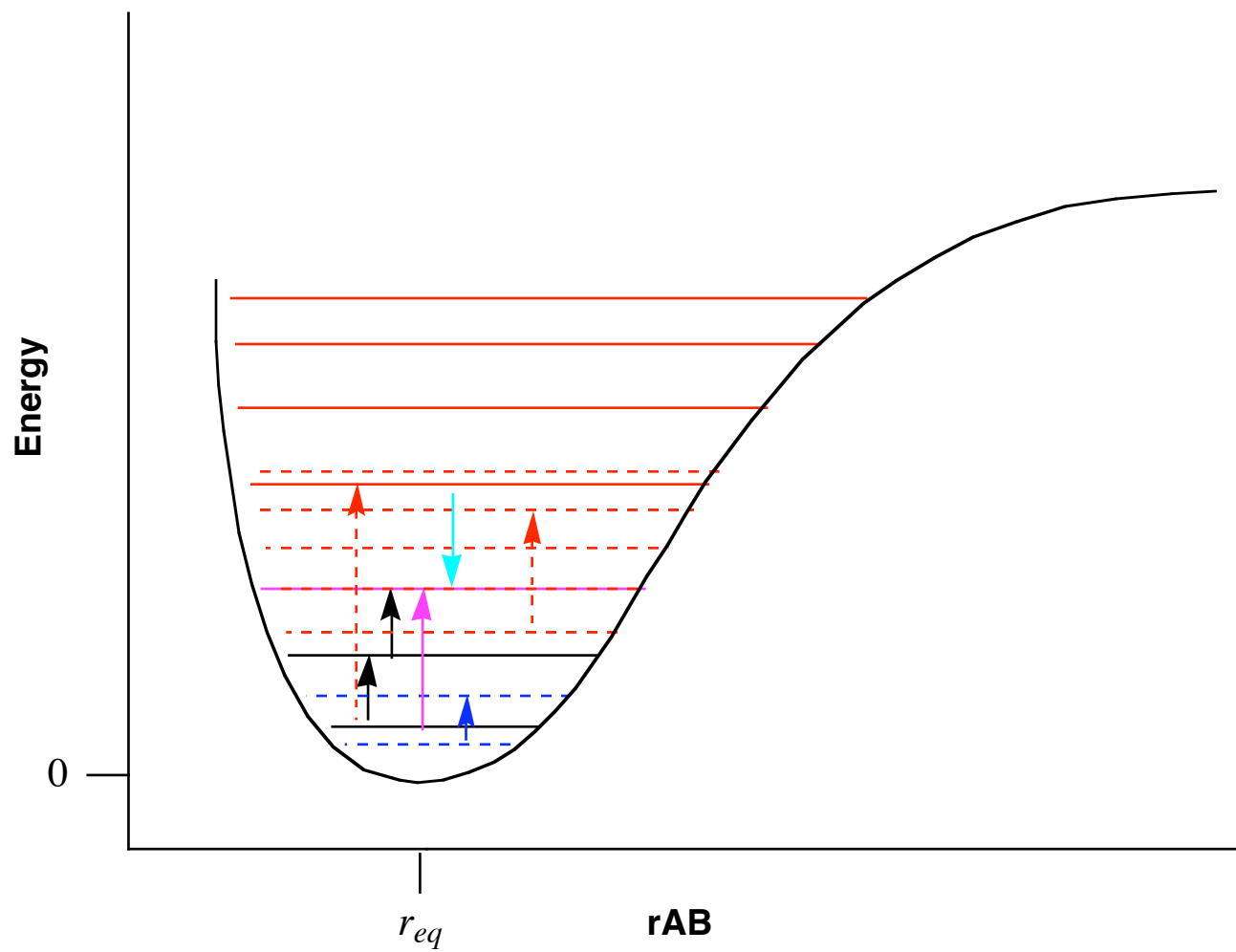
- It's clear the PES is useful, so how can I construct it for an arbitrary system (defined simply by the molecular formula)?
- It seems that for equilibrium and rate constants, I don't actually need to know the whole surface, only the energies of critical points (minima and saddle points)—is there a way to find these without mapping out the entire surface in detail?
- If I *don't* do the whole surface, can I be sure that I know about the locations of *all* the critical points and how they relate to one another?

An *Experimental* One-dimensional PES



Quantum mechanics tells us that vibrational energy levels are quantized, and that the energy separations between levels are dictated by the shape of the potential within which vibration takes place (i.e., the 1-D PES). By observing the allowed (above, with rotational information too) and forbidden (not shown) transitions of HCl and its isotopomers (which have different vibrational energy levels by virtue of having different reduced masses) the shape of the PES can be deduced over a large range.

In Practice



Breathless Appreciation