Stretching Vibrations of the Hydrogen Bond in HOHOH^{-}

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(Joint work with Stephanie Gamble)

Outline

1. The Standard Born–Oppenheimer Approximation.

2. The Modified Approximations.

3. "Symmetric" Hydrogen Bonds.

4. Results for $HOHOH^-$.

The Standard Born–Oppenheimer Approximation

In 1927, Born and Oppenheimer developed an approximation for molecular energy levels.

The nuclear masses were scaled as ϵ^{-4} so the Hamiltonian had the form $-\dfrac{\epsilon^4}{2}\,\Delta_X \,+\, h(X),$ where X denoted the nuclear configuration. They concluded

$$E(\epsilon) \;=\; E_0 \;+\; \epsilon^2\,E_2 \;+\; \epsilon^4\,E_4 \;+\; O\!\left(\epsilon^5\right).$$

E_0 was the electron energy at a minimum of the potential energy surface.

E_2 was the energy of the nuclear vibrations.

E_4 was the rotational energy, an anharmonic correction to the vibrations, and the "diagonal Born–Oppenheimer correction."

Almost everything we know about molecules comes from this approximation. It works exceptionally well for many molecules and ions.
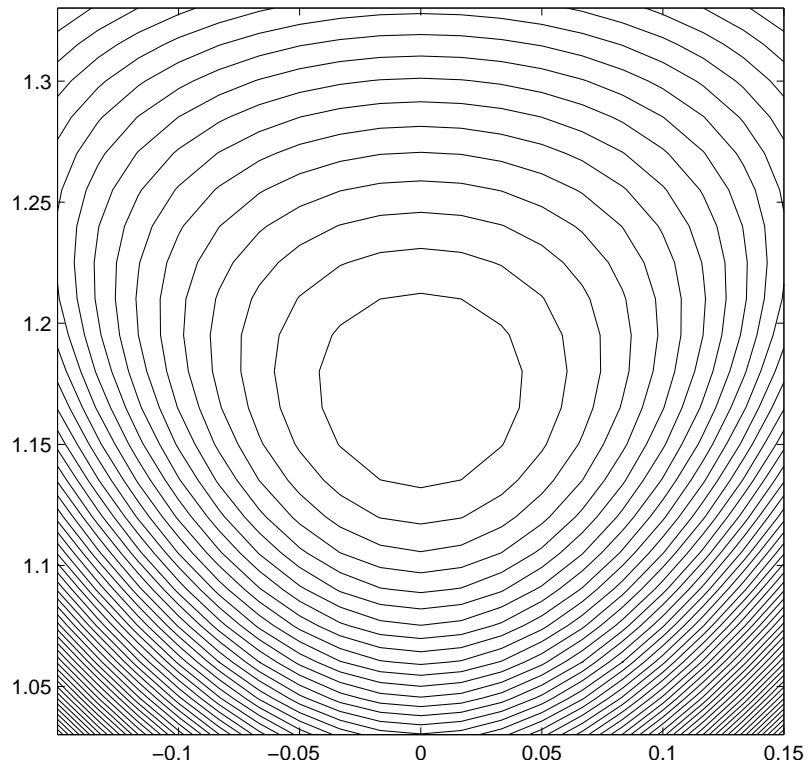
A successful example is CO_2.

The next slide has a contour plot of the potential energy surface for stretches near its minimum.

It is well approximated by a positive quadratic.

Frequencies

Computed	Experiment	
1340 cm^{-1}	1333 cm^{-1}	Symmetric Stretch
2374 cm^{-1}	2349 cm^{-1}	Asymmetric Stretch

The CO2 Potential Energy Surface

The Modified Approximations

Alain Joye and I published two papers about Hydrogen bonds
in 2007 and 2009.

The first paper was for "symmetric" Hydrogen bonds.
The second was for "non–symmetric" Hydrogen bonds.

More or less simultaneously,
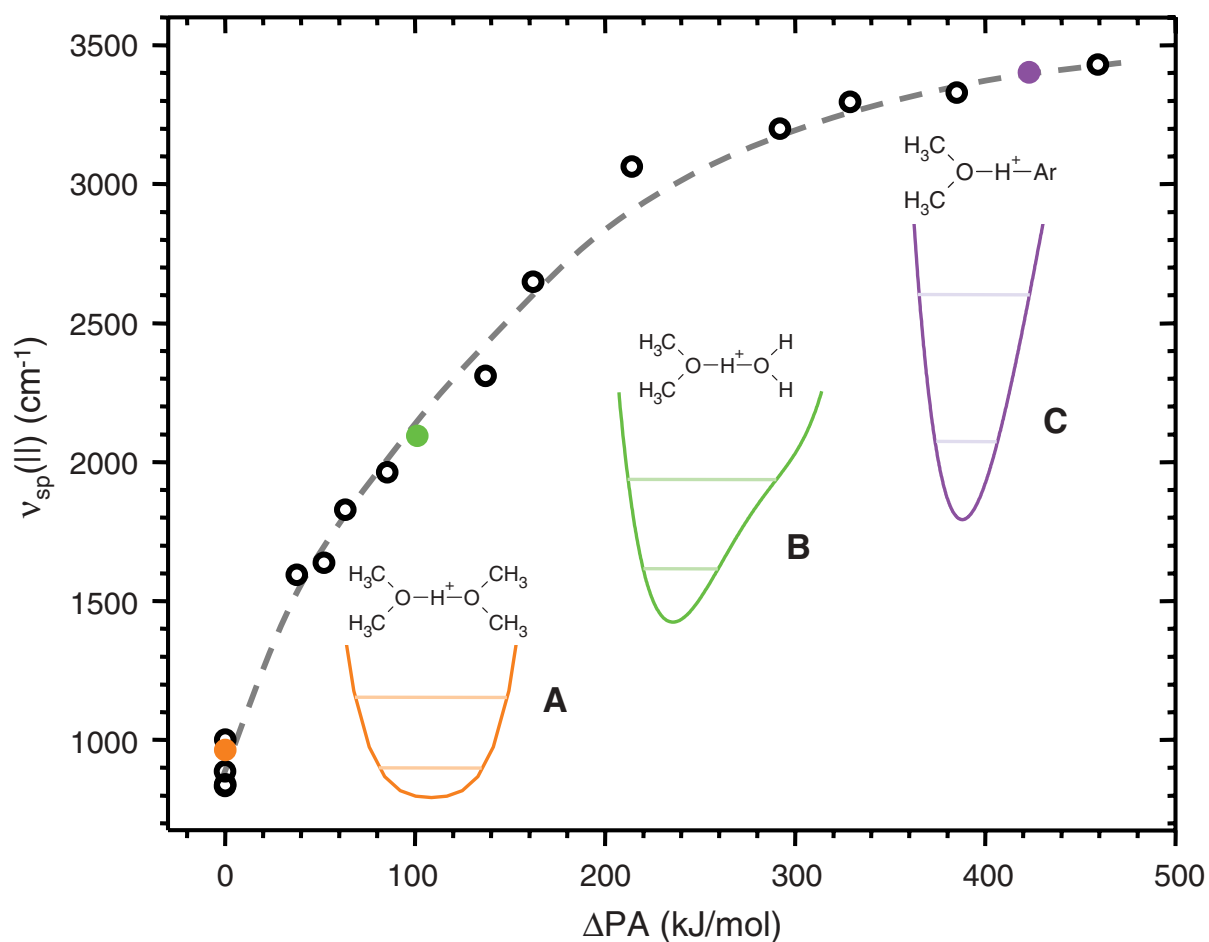people found exceptions to this classification...

Fig. 2. Dependence of the $\nu_{sp}(\|)$-derived band locations on the difference in proton affinities (ΔPA) for all systems reported in Table 1 (*25*). (**A** to **C**) Calculated potential curves (MP2/aug-cc-pVDZ) generated by scanning the shared proton between the heavy atoms while fixing the exomolecular structures at the equilibrium geometry of the complex (*28*). Energy levels were derived by solving the one-dimensional Schrödinger equation for the first two vibrational eigenstates. The potential curves are color-coded to match colored points on the graph.

the analogous modes in the protonated ether. Similarly, the band between these two can be assigned to the C-O stretch primarily localized on

Table 1. Observed centroids (cm^{-1}) of shared-proton asymmetric stretching bands, $\nu_{sp}(\|)$, and relative (gas-phase) proton affinity (ΔPA) values for [A·H$^+$·B] complexes (*25*).

Complex	$\nu_{sp}(\|)$ (cm^{-1})	ΔPA (kJ/mol)
Et$_2$O·H$^+$·OEt$_2$	843	0
Me$_2$O·H$^+$·OMe$_2$	952	0
EtOH·H$^+$·HOEt	840	0
MeOH·H$^+$·HOMe	887	0
H$_2$O·H$^+$·OH$_2$	1002	0
Me$_2$O·H$^+$·HOMe	1595	38
Et$_2$O·H$^+$·HOEt	1638	52
MeOH·H$^+$·OH$_2$	1828	63
EtOH·H$^+$·OH$_2$	1964	85
Me$_2$O·H$^+$·OH$_2$	2094	101
Et$_2$O·H$^+$·OH$_2$	2310	137
H$_2$O·H$^+$·NH$_3$	2649	162
CO$_2$·H$^+$·HOMe	3064	214
Me$_2$O·H$^+$·Xe	3200	292
Et$_2$O·H$^+$·Xe	3296	329
MeOH·H$^+$·Ar	3330	385
Me$_2$O·H$^+$·Ar	3403	423
Et$_2$O·H$^+$·Ar	3431	459

The Symmetric Case

I don't have time to describe the non–symmetric case.

We chose the numerical value of ϵ to be determined by the
Carbon 12 nuclear mass: $\quad \epsilon_0 = (12 \times 1836)^{-1/4}$.

Then the proton mass is $1.015\ \epsilon_0^{-3}$, so we represented it by $1.015\ \epsilon^{-3}$.

Next, guided by calculations for the stretches of FHF^-,
we noted that one of the Taylor series coefficients of the potential
energy surface was of order ϵ_0.
So, we replaced the coefficient by ϵ/ϵ_0 times its value.

This led to a new expansion. We proved that the energy again had an asymptotic expansion to all orders in powers of ϵ.

The stretching vibrations again were of order ϵ^2, but they were not described by a harmonic oscillator, but by a Hamiltonian with a fourth order Normal Form potential.

Our prototypical example, FHF^- had a single well minimum, but our theory could handle some double wells.

Results for $HOHOH^-$.

Recently Stephanie Gamble has been studying $HOHOH^-$, which has a double well that satisfies our conditions.

We use clustered Jacobi coordinates:
x is the distance from one terminal OH to the other terminal OH.
y is the component of the vector from the center of mass of these two OH's to the central proton in the direction between the two OH's.

We have computed the potential energy surface at 25 points using CCSD(T) with the aug-cc-pvtz basis set.

The leading order potential energy surface is represented as

$$E_0 + a_1\, x^2 + a_2\, \epsilon_0\, y^2 + a_3\, x\, y^2 + a_4\, y^4 + b_1\, x^3 + b_2\, x^2 y^2 + b_3\, x^3 y^2$$

$$+ b_4\, x^4 y^2 + b_5\, y^4 + b_6\, x\, y^4 + b_7\, x^2 y^4 + b_8\, x^3 y^4 + b_9\, x^4 y^4.$$

The Normal Form potential is

$$E_0 + a_1\, x^2 + a_2\, y^2 + a_3\, x\, y^2 + a_4\, y^4.$$

If distances are measured in Angstroms and energies in Hartrees, then

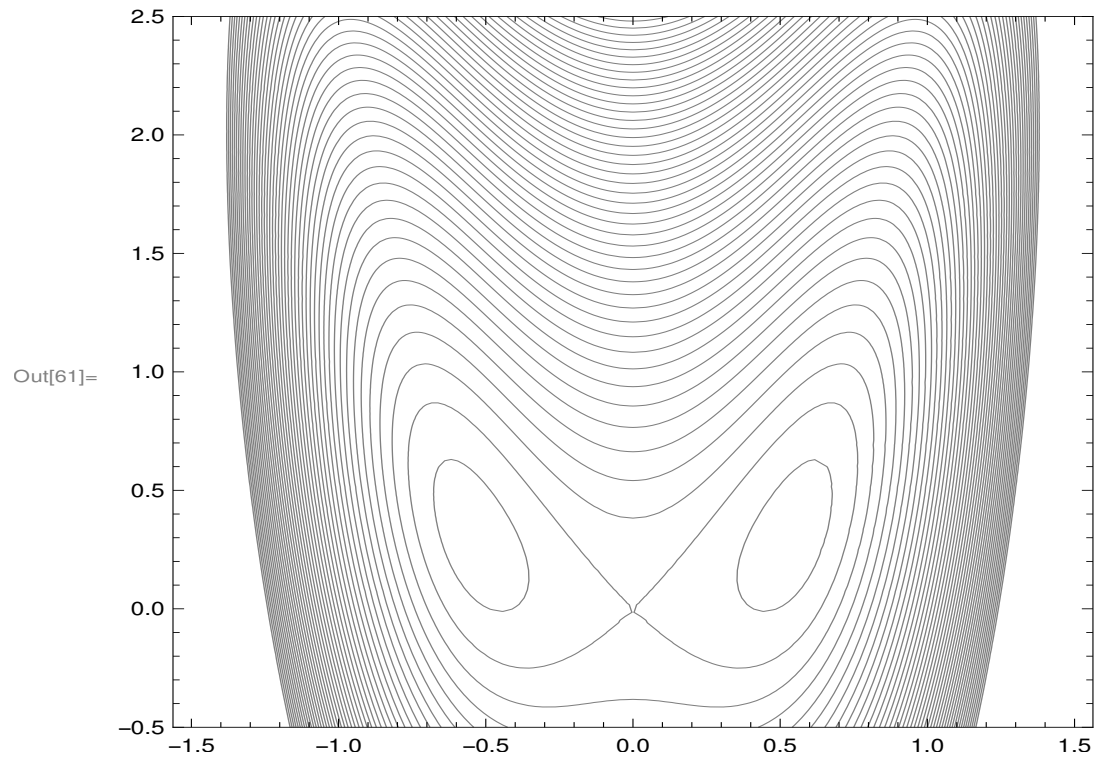$E_0 = -152.095$

$a_1 = 0.211625$

$a_2 = -0.316133$

$a_3 = 0.449109$

$a_4 = 0.779835.$

We then solve numerically for the low-lying eigenvalues of the Normal Form Hamiltonian.

The predicts the lowest symmetric stretch excitation energy
to be 597 cm^{-1},
and the lowest asymmetric stretch excitation energy
to be 744 cm^{-1}.

We have no experimental data for the symmetric stretch,
but the asymmetric stretch excitation energy
has been measured to be 697 cm^{-1}.

The 47 cm^{-1} discrepancy is perhaps a bit disappointing, but this is just a leading order calculation.

However, this is MUCH better than anything we can obtain from Born–Oppenheimer:

Born–Oppenheimer, expanding around the saddle point yields an imaginary result: $644i$ cm^{-1}.

If one expands around a minimum of the potential energy surface, one obtains 1699 cm^{-1}.

Possible Sources of Error

- Perhaps we should do a higher order calculation,
  but that would probably be complicated.
- Electron Structure Calculations not sufficiently accurate
  (We have been told to expect errors $\approx 100\,\mathrm{cm}^{-1}$
  with this basis set.)
- Fitting the potential energy surface with too few points
- Wrong two–dimensional subspace for these vibrations
- Wrong reduced mass for these vibrations
- Experimental Error (not likely!)

The paper we found with the experimental data,
J. Phys. Chem. A **109** 1487–1490, mentioned
calculations that were orders of magnitude more sophisticated,
but our emphasis was on simplicity.

Thank you!