1 ROTATIONAL STRUCTURE OF CARBON MONOXIDE

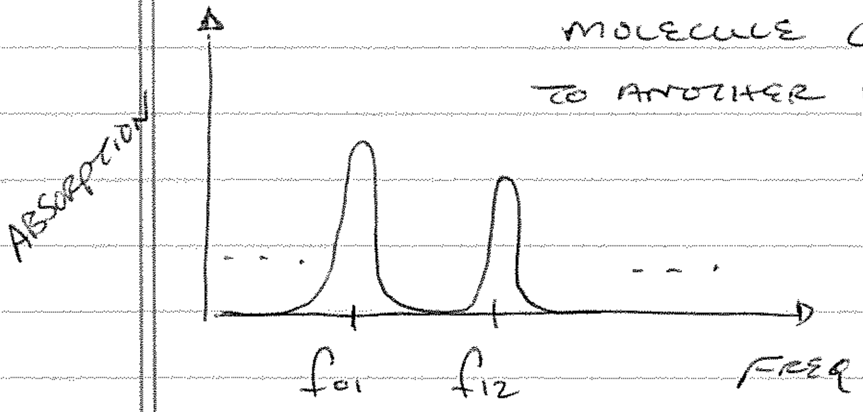
IN THIS EXAMPLE WE LOOK AT AN APPLICATION OF 2ND ORDER PERTURBATION THEORY TO GAIN SOME INSIGHT INTO THE MICROWAVE SPECTRUM OF CARBON MONOXIDE (CO).

MICROWAVES ~~RADIATION~~ ARE ELECTROMAGNETIC RADIATION WITH FREQUENCIES (WAVELENGTHS) ROUGHLY BETWEEN 300 MHZ (100 cm) AND 300 GHZ (.1 cm). RADIATION IN THIS RANGE IS GENERALLY ~~ASSOCIATED~~ ABSORBED AND EMITTED WITH CHANGES IN THE ROTATIONAL STATE OF MOLECULES.

Q1 GIVE A SEMI-CLASSICAL ARGUMENT WHY WE MIGHT EXPECT AN INTERACTION BETWEEN MOLECULAR ROTATION AND MICROWAVE RADIATION [AS OPPOSED TO, SAY, X-RAYS OR VISIBLE RADIATION].

HINT: TYPICAL BOND LENGTHS IN MOLECULES ARE A COUPLE ANGSTROMS (Å OR 10^{-10} m) AND TYPICAL NUCLEAR MASSES ARE 20 $\frac{GeV}{c^2}$ (A PROTON OR NEUTRON WEIGHS ABOUT 1 GeV) WHAT IS THE BOHR RULE OF ANGULAR MOMENTUM? i.e. WHAT IS THE SMALLEST AMOUNT A MOLECULE'S ANGULAR MOMENTUM CAN CHANGE BY?

QUANTUM MECHANICALLY, WE IDENTIFY PEAKS IN THE MICROWAVE SPECTRUM WITH TRANSITIONS FROM ONE ROTATIONAL STATE OF THE MOLECULE TO ANOTHER. LET'S SOLVE FOR THE ENERGY LEVELS OF A ROTATING MOLECULE AND COMPARE IT TO DATA OBTAINED FROM MICROWAVE SPECTROSCOPY:



MOLECULE GOES FROM ONE STATE TO ANOTHER BY ABSORBING PHOTON!

$$f_{01} = \frac{E_1 - E_0}{h}$$

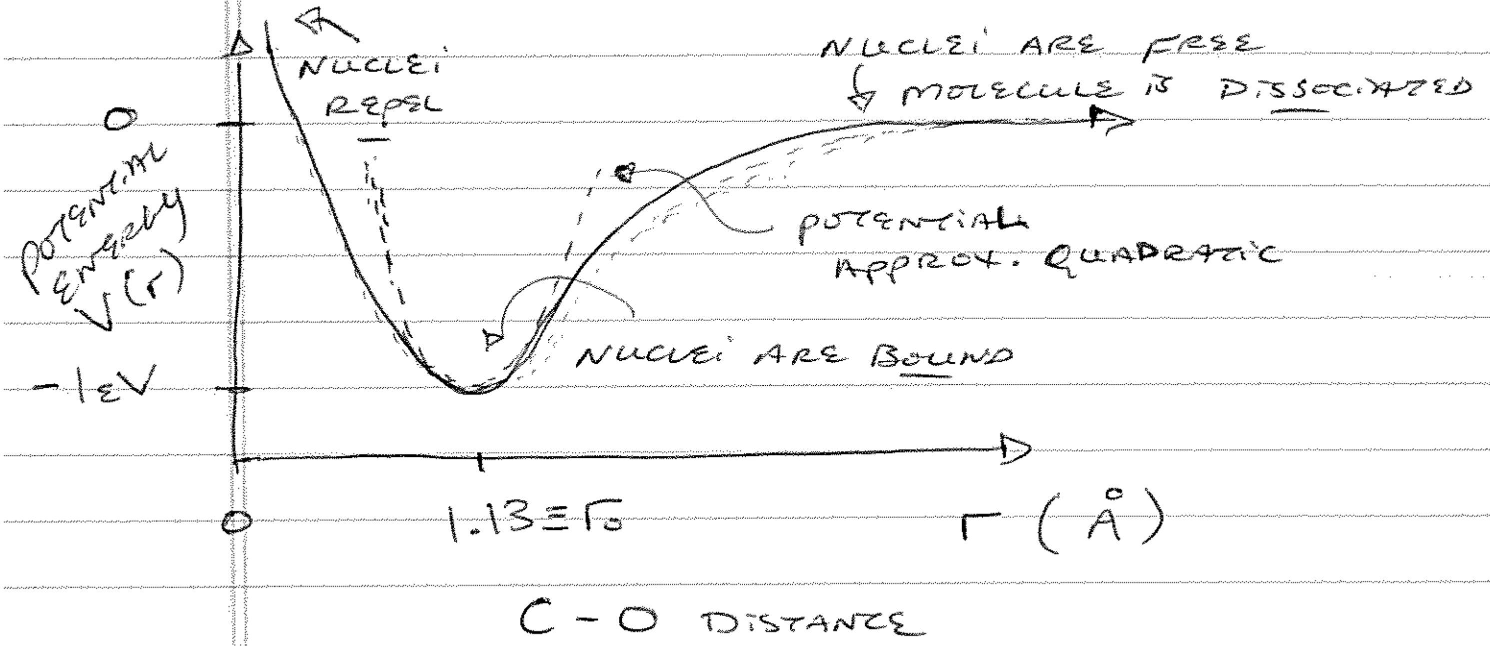
$$f_{12} = \frac{E_2 - E_1}{h}$$

ETC.

A DIATOMIC MOLECULE LIKE CO CAN UNDER SOME CIRCUMSTANCES BE TREATED LIKE A TWO-BODY SYSTEM, JUST LIKE A HYDROGEN ATOM. JUST LIKE THE H-ATOM, THE FORCE BETWEEN THE CARBON AND OXYGEN NUCLEI ~~POINTS~~ IS RADIAL, POINTING ALONG THE BOND AXIS. IN OTHER WORDS, THE POTENTIAL BETWEEN THE NUCLEI DEPENDS ONLY ON THE DISTANCE BETWEEN THEM.

UNLIKE THE H ATOM, THE POTENTIAL IS

NOT A COULOMB POTENTIAL, BUT SOMETHING MORE LIKE:



~~NEAR THE BOTTOM OF THE WELL~~

~~IF WE ONLY CONSIDER ENERGIES MUCH LOWER THAN THE DISSOCIATION ENERGY (≈ 1 eV),~~ ~~THEN~~ THE SCHRÖDINGER EQUATION FOR TWO BODIES SEPARATES INTO CENTER-OF-MASS MOTION, WHICH WE'RE IGNORING, AND RELATIVE MOTION. SINCE THE POTENTIAL HAS NO ANGULAR DEPENDENCE WE KNOW WE CAN CAN USE $Y_m^l(\theta, \phi)$ AS SOLUTIONS TO THE ANGULAR EQUATION. THIS LEAVES US WITH THE RADIAL EQUATION:

$$\left[\frac{p^2}{2m} + V(r) + \frac{\hbar^2 l(l+1)}{2m\, r^2}\right] u_{nl} = E_{nl}\, u_{nl}$$

RADIAL WAVE FUNCTION

WHERE $u_{n\ell}(r)$ IS THE n^{TH} RADIAL WAVE FUNCTION WITH ANG. MOM. QUANTUM NUMBER ℓ, AND m IS THE REDUCED MASS OF THE CARBON + OXYGEN ~~AN~~ NUCLEI: $m = \frac{M_c M_o}{M_c + M_o}$, AND p IS THE MOMENTUM OPERATOR $-i\hbar\frac{\partial}{\partial r}$

$$M_c = 12\,GeV/c^2$$

$$M_o = 16\,GeV/c^2$$

$$m \simeq 7\,GeV/c^2$$

AS INDICATED ON THE PREVIOUS DIAGRAM, WE CAN APPROXIMATE THE RADIAL POTENTIAL AS A PARABOLA CENTERED ABOUT THE EQUILIBRIUM BOND LENGTH r_o:

$$u(r) \simeq u_o + \frac{1}{2}\frac{d^2}{dr^2}u(r_o)\left[r - r_o\right]^2$$

$$\text{or: } \simeq u_o + \frac{1}{2}u''(r_o)\,\Delta r^2 \quad \left[\Delta r \equiv r - r_o\right]$$

$$\text{or: } \simeq u_o + \frac{1}{2}m\omega^2\Delta r^2 \quad \left[m\omega^2 \equiv u''(r_o)\right]$$

NEGLECTING CONSTANTS, WE CAN NOW WRITE THE RADIAL EQUATION AS*:

$$\left[\hbar\omega\left(a_+a_- + \frac{1}{2}\right) + \frac{B\ell(\ell+1)}{\left(1+\frac{\Delta r}{r_o}\right)^2}\right]u_{n\ell}(r)$$

$$= E_{n\ell}\,u_{n\ell}(r)$$

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* $a_\pm$ ARE THE STANDARD ~~RAIS~~ RAISING + LOWERING OPERATORS, i.e.

$$a_\pm = \frac{1}{\sqrt{2}}\left[\frac{\Delta r}{x_0} \mp i\frac{p}{p_0}\right], \quad x_0 \equiv \left(\frac{\hbar}{m\omega}\right)^{1/2}, \quad p_0 = \left[m\hbar\omega\right]^{1/2}$$

WHERE $B = \frac{\hbar^2}{2 m r_0^2}$ (THE "ROTATIONAL CONSTANT" OF CO)

FOR LOW ENERGIES WE EXPECT THE NUCLEI TO NOT STRAY TOO FAR FROM THE EQUILIBRIUM BOND LENGTH r_0, SO THAT $\Delta r \ll r_0$. THIS SUGGESTS A TAYLOR APPROXIMATION TO THE "CENTRIFUGAL TERM"

Q2

$$B\ell(\ell+1) \Big/ \left(1+\frac{\Delta r}{r_0}\right)^2$$

~~EXPAND~~ APPROXIMATE THE CENTRIFUGAL TERM AS A TERM CONSTANT W.R.T. Δr AND A TERM LINEAR IN Δr

Q3

WRITE DOWN THE SOLUTION TO THE RADIAL WAVE EQUATION, NEGLECTING THE TERM LINEAR IN Δr; IE WRITE DOWN THE ENERGY EIGENVALUES $E_{n\ell}$ AS A FUNCTION OF n & ℓ QUANTUM NUMBERS.

WHAT IS THE ENERGY DIFFERENCE BETWEEN STATES IN THE GROUND VIBRATIONAL LEVEL ($n = 0$) AND ROTATIONAL STATES $\ell + 1$ AND ℓ? i.e. $E_{0,\ell+1} - E_{0,\ell} = ?$

TRANSITIONS OBSERVED IN MICROWAVE SPECTROSCOPY ARE ~~PRECISELY~~ BETWEEN ADJACENT LEVELS $\Delta\ell = 1$. THIS CAN BE UNDERSTOOD AS

ABSORPTION OF A SINGLE MICROWAVE PHOTON

[illegible] (PHOTONS HAVE $\hbar$ ANGULAR MOMENTUM WHICH IS TRANSFERRED TO THE MOLECULE WHEN ABSORBED, TAKING $\ell \rightarrow \ell' = \ell + 1$).

SO OUR APPROXIMATIONS SO FAR PREDICT A CONSTANT SPACING OF ~~4B~~ 2B BETWEEN ABSORPTION LINES:

$$\Delta V_\ell \equiv \Delta E_{\ell+1} - \Delta E_\ell = \cancel{4B} \; 2B$$

$$\Delta E_\ell \equiv E_{0,\ell+1} - E_{0,\ell}$$

Ⓠ④ COMPUTE THIS SPACING 2B IN UNITS OF [illegible] MHz (i.e. $\frac{2B}{h}$) TO SIX DIGITS OF PRECISION

HELPFUL NUMBERS:

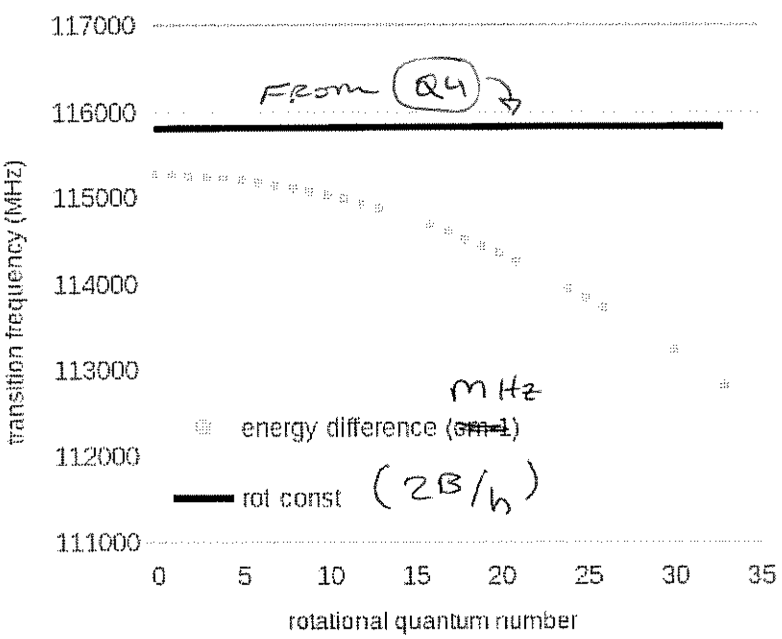
$\hbar c = 197.327$ eV nm

$r_0 = .112823$ nm

$m = 6.38651786$ GeV / c^2

$c = 2.99792458$ m/s

THE PRECISION OF MICROWAVE SPECTROSCOPY IS STUPID: UP TO A COUPLE PARTS IN A HUNDRED MILLION! THAT PRECISION IS WAY MORE THAN ENOUGH TO REVEAL ERRORS FROM OUR APPROXIMATION:



DEVIATIONS ARE <u>SMALL</u>, ON THE ORDER OF A PERCENT, BUT CLEARLY NOT EXPLAINED BY UNCERTAINTY

THE DOTS ARE EXPERIMENTAL DATA FROM 1992*

(Q5) TREAT THE LINEAR TERM AS A PERTURBATION AND FIND THE LOWEST ORDER CORRECTION TO $\Delta\nu_\ell \equiv \Delta E_{\ell+1} - \Delta E_\ell$. IS IT STILL CONSTANT W.R.T. ℓ? EXPRESS LIKE BEFORE IN UNITS OF MHz.

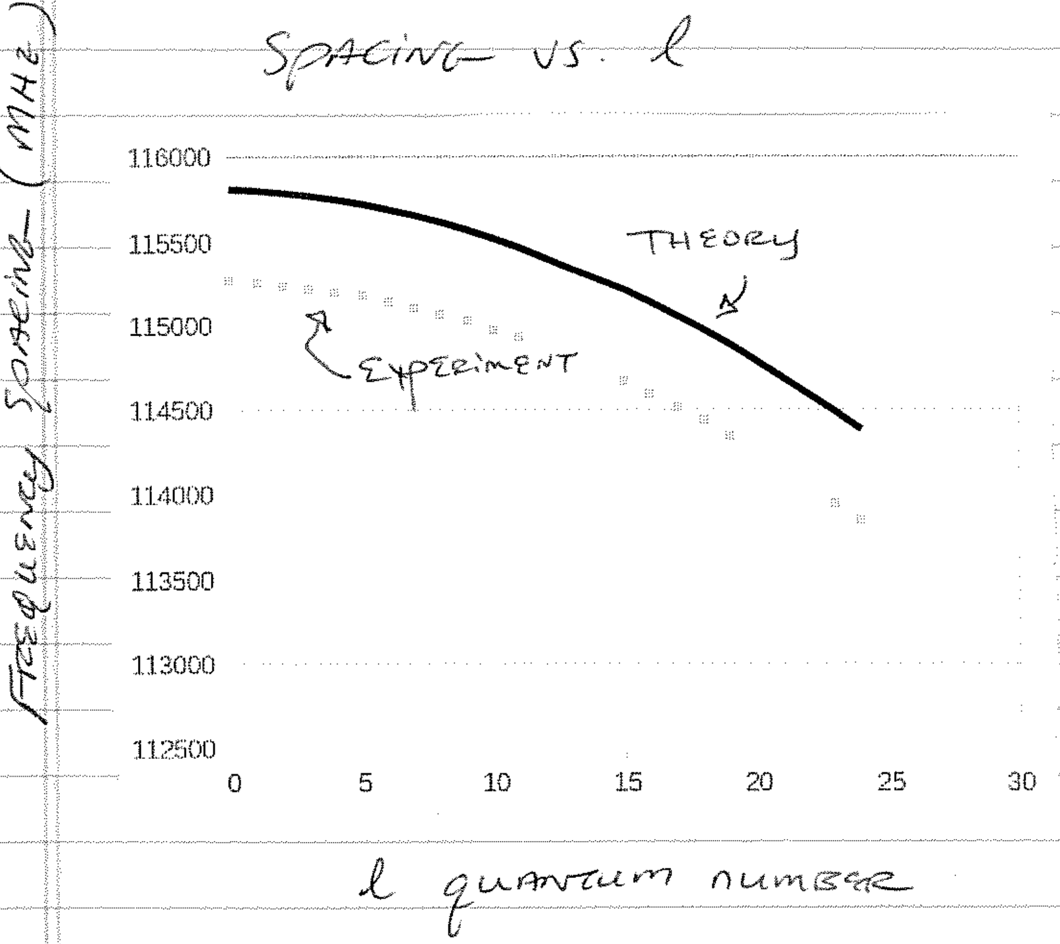
FROM INFRARED SPECTROSCOPY ("VIBRATIONAL SPEC.") WE ~~KNOW~~ CAN ESTIMATE

$\hbar\omega = .269015\,\text{eV}$

*BELOV, ASTROPHYS J. 393, 848 (1992)

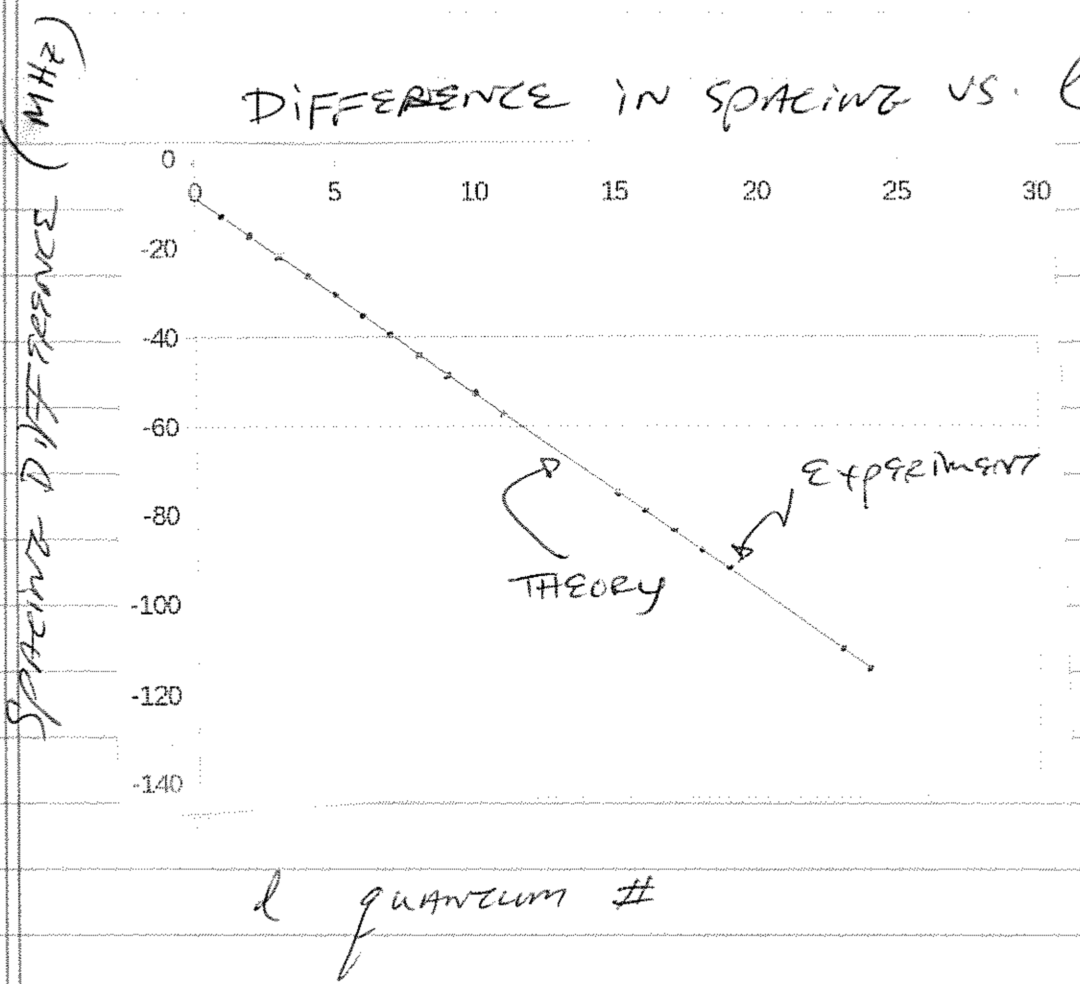
SO HOW DID WE DO?

SPACING VS. l

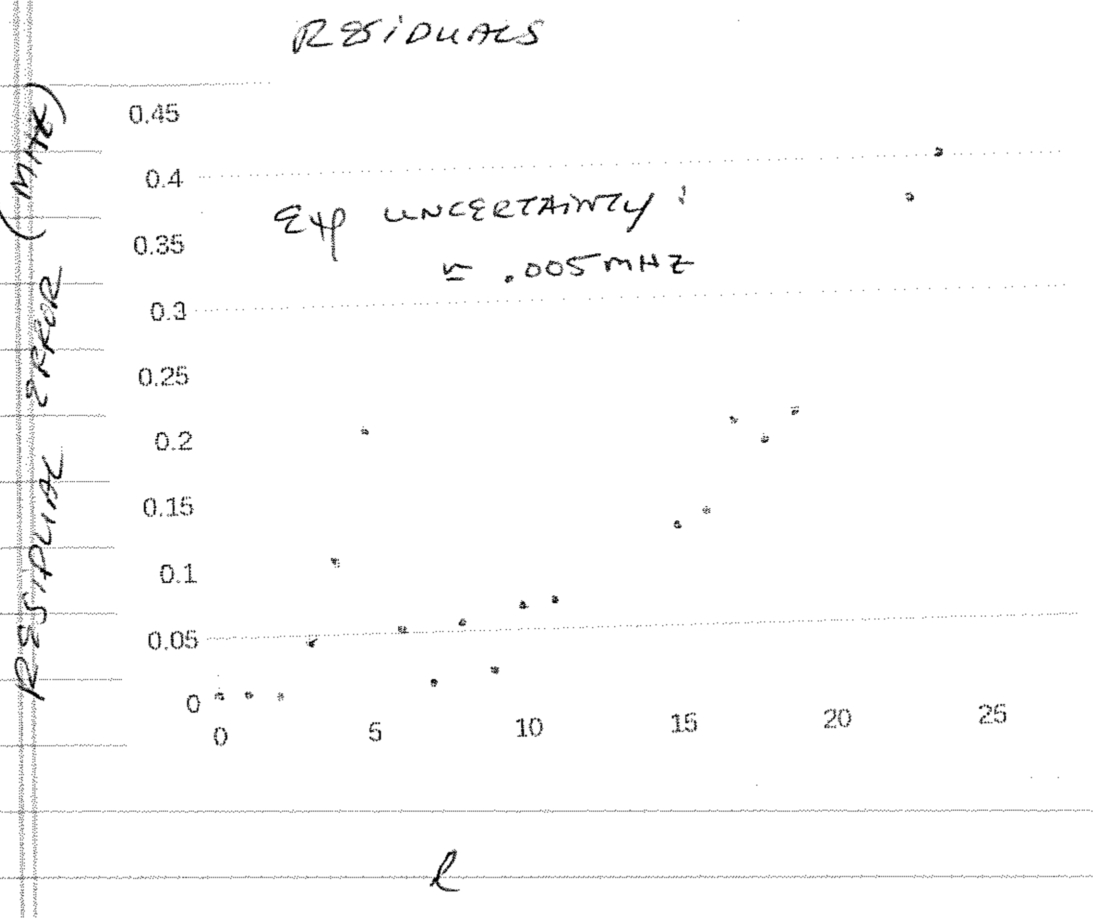


LOOKS OK, BUT THERE SEEMS TO BE AN OFFSET. WE CAN COMPARE THE DERIVATES W.R.T. l TO SEE HOW ACCURATE OUR CORRECTION E^2_{0l} IS:

DIFFERENCE IN SPACING VS. l



~~HERE~~ WE SEE THAT OUR CENTRIFUGAL STRETCHING CORRECTION PERFECTLY EXPLAINS THE OBSERVED DEVIATION FROM CONSTANT SPACING! FOR LOW l, THEORY AGREES WITHIN EXPERIMENTAL ERROR!



FOR LARGER ℓ THE PERTURBATION BECOMES STRONGER AND HIGHER ORDER CORRECTIONS BECOME NECESSARY. ALL THE SAME THIS SIMPLE EXAMPLE SHOWS HOW PERTURBATION THEORY CAN BE EMPLOYED TO YIELD FANTASTICALLY ACCURATE RESULTS. NOTICE THAT WE USED NO FITTING!

Q6 CAN YOU DERIVE A SEMICLASSICAL EXPLANATION FOR "CENTRIFUGAL STRETCHING" (THE DEVIATION FROM ℓ^2 DEPENDENCE ON ROTATIONAL ENERGY LEVELS)?