

Physics 272 Laboratory Experiments

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7 Spectroscopy of N_2

7.1 Introduction

Emission spectroscopy of molecular nitrogen is the final spectroscopy experiment of the semester. We examine a quantum system which comprises two atoms: the diatomic molecule. We will consider the “simplest” type of molecule, the homonuclear diatomic molecule. We will use familiar potential energy curves and quantized energy levels to understand physical characteristics of the diatomic molecule, such as the strength of the chemical bond, the fundamental vibrational frequency, and the mean distance between the atoms. Each of these characteristics depend on the electronic energy state of the molecule. Transitions between electronic states give rise to the spectra exhibited by homonuclear diatomic molecules, and we will try to connect these directly to the potential energy curves. The spectrum molecular nitrogen is shown in figure 1. It has a much richer structure than that typical of atoms.

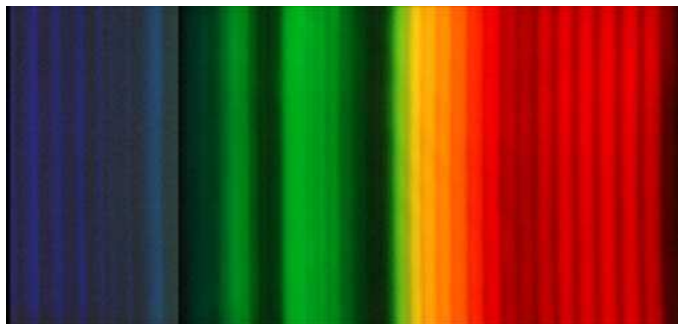


Figure 1: The visible emission spectrum of molecular nitrogen

But first things first. Why are molecules stable? What are the allowed excited states? And How does the emission spectrum reveal answers to such questions? We will attempt to understand the answers from a physics point of view. Its clear from the questions that physics and chemistry have overlapping interests. We are tempted to

wax lyrical about how all chemistry arises from the fundamentals of physics, and how biology arises from the fundamentals of chemistry, and so on, and so forth. But this reductionist point of view is too simple, and it almost blinds us to the possibility of unexpected emergent features arising in systems of increasing complexity, features that make it difficult to untangle physics and chemistry. Whats more, well find that the distinction between simplicity and complexity becomes blurred too. We will try to see that the simple study of diatomic molecules introduces us to a system of almost bewildering complexity, and that, even in the midst of that virtual forest of spectral features, we will meet the very first and simplest quantum system ever solved, that of the simple harmonic oscillator.

We will look for the simplicity within complexity. A simple way of thinking about how molecules form is depicted in figure 2. Two neutral atoms, say two hydrogen atoms, may attract each other weakly because they each electrically polarize the other, and so there is, potentially, a kind of electrostatic dipole-dipole force between the atoms. And since each dipole may reorient in the electric field of the other, the result is an attractive electrostatic potential. Their mutual electrical potential energy drops as the atoms get closer. But this process also suggests that if they get too close there will be electrical repulsion between the positively charged nuclei that raises the potential energy, and so, from a classical point of view, one may expect there to be an equilibrium distance between the atoms at the minimum of the potential energy. This is just a sketch of a classical heuristic argument, not a complete argument, nor a proof.

Nature, it turns out, does not act in this way over the distances that matter here. A guiding rule of thumb, not far wrong, is to suspect that quantum physics takes over when the wave functions of the atoms overlap. This is a kind of quantum heuristics. From a quantum point of view, for molecules to be stable, the electrons must be shared somehow by the separate atoms so as to complete a quantum energy shell (and subshell). This is at least one important way in which quantum physics creates what

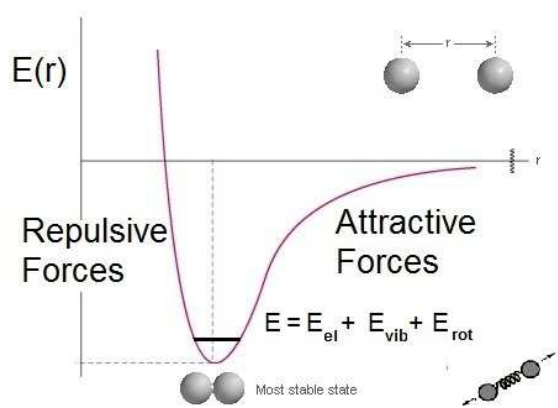


Figure 2: A classical cartoon of molecular formation from two of the same atoms. The picture of the little spheres is wrong in that they must overlap somehow, but artists, feeling the need to show the spring which accounts (classically) for the vibration spectrum, tend to draw the atoms as completely separate. Of course, quantum mechanically, they must overlap very significantly.

chemists call a chemical bond, in this case, the covalent bond.

For example, Carbon with its 6 nuclear protons possesses an electron configuration ($1s^2 2s^2 2p^2$) that is in want (so to speak) of 4 more electrons to complete the 2p subshell, and the second energy shell. Hydrogen atoms, in want of 1 electron to complete their 1s energy shell, four of them, can combine with Carbon by electron sharing to form the methane molecule (CH_4). In the same way, three hydrogen atoms can combine with Nitrogen ($1s^2 2s^2 2p^3$) to form ammonia (NH_3). The combination of two Hydrogen atoms to complete the first energy shell (H_2) would be even simpler. We are interested however in the homonuclear diatomic molecule Nitrogen (N_2), which is curiouser than molecular hydrogen, because, although nitrogen needs 3 electrons and has 3 to share, it must combine with itself in a different way than we are describing it is a triple bond, but one of the bonds has a different geometry associated with it than that which characterizes molecular hydrogens single covalent bond.

I want to add two comments about the physics of our problem. The quantum physics of this sharing of electrons leads to some surprising nonclassical behavior. It is known from NMR measurements that the protons (the Hydrogen nuclei) in long chain hydrocarbon molecules exist in a nearly magnetic field free environment. This means that the magnetic field due to spin of the shared electrons cancels out. The first thing to say is that this is what we expect from the constraints of the Pauli Exclusion Principle. The electrons will have opposite spins. But to say that the Pauli Exclusion Principle requires the two electrons be in opposite spin states does not exhaust

the description of its effects. Because electrons are indistinguishable, the principle also implies that the wavefunction describing the molecular orbital be symmetric with respect to the interchange of particle labels. This is a little bit complicated, but to put it simply, it also means that wherever the electron of the hydrogen atom can be, there also the shared electron can be, and just as often, with its spin upside down! This is not what we wouldve expected on the basis of classical physics. The requirements of quantum physics, and the constraints of the Pauli Exclusion Principle play an essential role in forming covalent bonds. The picture shown in figure 2 is meant to address our classical imagination. It relates to the actual reality only poetically. The nuts and bolts of reality however are found in the spectra, shown in figure 1.

At the risk of straining your powers of concentration just a little too much, I would like to give a kind of quantum version of the classical physical picture of what is going on in connection with the spectrum. We imagine that in a diatomic molecule, the total internal energy will have an electronic component and a nuclear component which is further subdivided into vibrational and rotational energies. I will pass over the very different times scales of these individual motions which permit this neat separation of energies (and wavefunctions). The electrostatic energy, which we associate with the electrons (by calling them electronic states, even though it is the electric potential energy of the entire system), depends now upon the relative distance between the nuclei, and so the electronic energy levels are not "level" levels as in solitary atoms, but instead dip at the equilibrium distance between the nuclei, giving us some feel for the actual size of the molecule. I will leave a discussion of the spectroscopic term designation for a footnote[2], except to say that the scheme is somewhat analogous to the scheme for atomic energy states, with addition of extra symmetry designations. Within this confining potential, the nuclei vibrate and rotate. The molecule then is one of nature's fundamental harmonic oscillators (note, I've left out the word "simple" - we will come back to that presently). The allowed energy levels within the electrostatic potential now are flat, independent of the internuclear distance. Transitions between such a level in one electronic state and another level in another electronic state account for molecular emission spectra for homonuclear diatomic molecules, as shown in figure 3. Transition between levels within an electronic state are possible for non-homonuclear molecules, and such molecules can absorb and emit radiation at much longer wavelengths. This fact has enormous implications for the problem of global warming. Can anyone guess how and why?

The most important potential energy curves, along with their electronic energy state descriptors as described above are shown later in figure 6. Have a look. Simple

is not the word that comes to mind. However, there is a deep simplicity in the behavior of quantum oscillators which I hope will become apparent as we actually acquire the data and analyze it. In the mean time, look again at the spectrum of molecular nitrogen (figure 1). Isn't it beautiful? It is an important contributor to the aurorae, which crown the earth above and below with a shimmering glow of awesome beauty. The sheets of luminous color in the upper atmosphere follow our tremulous magnetic field lines, most concentrated at the poles. They bless the earth! However, the earth is threatened by global warming, and we can begin to see how molecules play a role (although we will be happy to find that molecular nitrogen is not one of the culprits). It will occur to the student that the molecule ought also to absorb between vibrational levels *within an electronic state*. This is true only for nonhomonuclear diatomic molecules (like carbon monoxide!), and for more complicated molecules like methane, and even water molecules. These absorb very long wavelength radiation of the size of heat radiation which cools the earth, and so in order to strike a thermal equilibrium with its heat inputs and outputs, the earth must warm a little bit to account for the absorption of these greenhouse gas molecules (carbon monoxide, methane, water, etc.). A little bit of warming is good. A little bit more due to anthropogenic inputs holds the potential of truly altering the earth's equilibrium temperature, which could be very bad. What to do and how best to proceed occupies the thoughts of many people these days. We are getting familiar with some of the related physics in this laboratory experiment.

7.2 Procedure

We will use the USB4000 spectrometer to measure the emission spectrum of molecular nitrogen, in the same manner in which obtained the spectral lines associated with the Sodium doublet, and the Balmer series of Hydrogen atom. The setup is shown in figure 4. The light source is a simple nitrogen plasma discharge tube. An optical fibre conveys the emitted light from the source to the spectrometer. The resolution of this system was assessed in the second spectroscopy experiment and found to be a little better than what the manufacturer claims (about 0.5 nm). Make a nice plot of the spectrum with well labeled axes, and a figure caption. You will be asked to annotate the plot in a way described below.

Use the OceanView software to obtain the data files, being careful to record the filenames and scan parameters. Once you have obtained the data files, it's all analytical work after that!

9. Diatomic Molecules

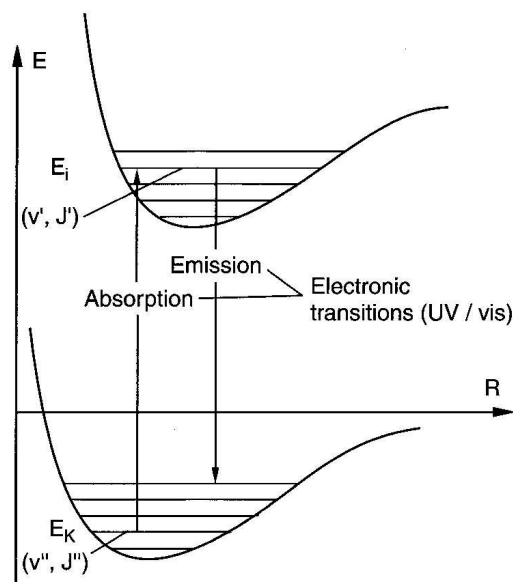


Fig.9.58. Schematic representation of the structure of molecular transitions

Figure 3: Absorption and emission transitions between electronic states in a molecule. For reasons passing understanding, molecular scientists (they are chemists!) use double primes for the lower state and single primes for upper states. The Greek letter ν denotes the vibrational states, the ones we'll examine in this experiment, and the Latin letter J marks the rotational states which are too closely packed to resolve in the set up that we will use. This is a 9.58 in Demtroder's excellent book. [1]

7.3 Questions

1. First, a couple of calculations to give you a feel for the vibrational figures of merit of the molecular nitrogen quantum oscillator. From the potential energy curve for the ground state[2], the $X^1\Sigma_g^+$ electronic potential energy curve shown in figure 6, estimate the effective spring constant of the chemical bond, k , expressed in N/m . You may do this in the following way: assume the curve is an ideal harmonic potential of the form $E = kx^2/2$, where $x = (r - r_e)$, where r_e is the equilibrium internuclear distance, which you may read right off the graph, *or look it up in Lofthus et al. [3]*. Then, making measurements directly on the paper (say, so many mm's horizontally is the measured x , and by way of calibration y mm is 0.4\AA). The same for the energy measurements, as depicted



Figure 4: We use the USB4000 integrated diffraction grating and CCD detector (Ocean Optics USB 4000) to observe (and capture to text file) light emitted from atomic and molecular source. Light is collimated by a fibre optic cable with which the light is directed via mirrors to reflective grating, and from there to a CCD detector. The detector is calibrated to readout intensity vs. wavelength

in the sketch shown in figure 5.

Compare the spring constant to that of other covalent bonds. Is the Nitrogen bond a relatively strong one? What implication does this have, say, for the building of chemical bombs? From a big picture point of view, how do ‘explosions’ work, or chemical burning for that matter. Give a simple physical argument.

2. From your estimate of k , calculate the fundamental resonance frequency for the ground state of the N_2 , from the simple expression,

$$\omega = \sqrt{\frac{k}{\mu}},$$

where μ is the “reduced mass” of the Nitrogen molecule. Compare both k and ω with accepted values shown in figure 7. Are you within 10%?

3. From table 29 on page 226 in reference [3], identify all the transitions observed in the spectra obtained from

the USB4000 between 350-450nm, annotating the spectral lines with the vibrational transitions that create them. The transitions are (for the most part) between the $v' = 0$ vibrational level in the $C^3\Pi_u$ electronic energy state and the vibrational levels in the $B^3\Pi_g$ electronic energy state. Identify as many of the transitions on your plot as you can, noting the vibration quantum numbers $v' - v''$. Table 29 refers to band heads[4], the wavelength of the leading edge of various smears of color as seen in the spectrum in figure 1.

4. From your *measured wavelengths*, make a table with three columns, as shown in table 1, with headings, $v' - v''$, $E_{v'} - E_{v''}$, and ΔE , where the third column is the difference between the energy in the row, column 2, and the same entry in the row above it. Interpret the meaning of column 3, and answer the following question: are these values consistent with that of a simple harmonic oscillator? It is well known that the energy levels of a simple harmonic oscillator is given by

$$E_n = (n + \frac{1}{2})\hbar\omega_o,$$

where ω_o is the fundamental resonance frequency. Estimate ω_o . Is it greater or less than that estimated for the ground state? Does this make sense? How? How does your data look? Is it basically that sort of thing expected for the progression of energy levels for a simple harmonic oscillator, or is there some discrepancy? If there is a discrepancy, is the discrepancy between uniform spacing between the energy levels ‘big’ or ‘small’ (‘small’ relative to the energy gap between adjacent vibrational levels)? Try to sum this up with an educated opinion: firstly, would you say that the confining potential is that of an harmonic oscillator, to a first approximation, and secondly, what is your opinion as to whether the perturbation, if it exists for the nitrogen molecule *from a perfectly harmonic potential* is small or large?

Table 1: Energy gaps between vibrational energy levels in the $B^3\Pi_g$ electronic state of N_2 . The numbers below are totally fictional :)

$v' - v''$	$E_{v'} - E_{v''} (eV)$	$\Delta E (eV)$
1	4	0.20
2	3.8	0.21
3	-	-
4	-	-

5. To make a connection with the potential energy curves and the data that you’ve taken, identify two

transitions on your annotated data set produced by the OceanView software from the spectrum recorded by the USB4000. Then, on figure 6, draw in the horizontal lines which denote the vibrational levels (and vertical lines of the transitions) connected by the identified spectral emission lines, *and measure the associated energies directly off the figure, just as you did for the calculation in problem 1 above.* From these energies, calculate the wavelength—compare with the measured value of the wavelength. Are you within 10%?

6. Is the effect spring constant of the $B^3\Pi_g$ electronic potential as stiff as that of the ground state? Estimate it in the two ways given above (with ruler and the paper copy of the potential curve, make measurements and estimates as you did for problem #1, and then from ω'_e , the fundamental frequency.
7. Consider again the emission spectrum shown in figure 3. All the excited states are populated by collisions with electrons (principally) in plasma discharge tube. Now imagine instead we tried to obtain an absorption spectrum of molecular nitrogen, in much the same way that we obtain the absorption spectrum of Rb in our previous lab. Imagine that we could tune a laser from very blue wavelengths to very red wavelengths, or, imagine a very bright flashlamp that was a very white, very broadband, continuum source of light. Would we get essential the same spectrum as the emission spectrum? Would it differ in some important respects? Please explain, using simple physical arguments.
8. Finally, there are 2 sets of bands between 500 and 750 nm. What transitions account for these? Try to figure this out using Lofthus as a guide.

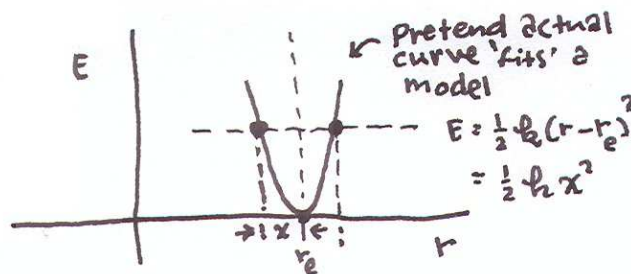


Figure 5: This sketch marks points you might draw on the potential energy curve to aid in making measurements directly on the figure (fig. 6). Use a ruler to measure the displacement from equilibrium to the position associated with the energy (which you are also measuring). Convert the length in mm's, say, from the ruler measurement, to its associated values in Åunits with a conversion factor (gotten by measuring the in mm's, say, the distance between 1.2 and 2.0 Å). Do the same sort of thing for the energy. Use the model formula and the measurements to solve for k

References

- [1] W. Demtroder, *Atoms, Molecules, and Photons*, (Springer, Berlin, 2005), fig.9.58, p364.
- [2] The naming scheme for the electronic states differs a little bit from the scheme used for atoms as expected because of the increased complexity of the system. The ground state is historical usage called and X state. The next excited states are not denoted by 2, 3, 4, etc., but rather by A, B, C, with perhaps, an a and a, b and b thrown in. Then, since the nuclei are in different locations, the neutralizing electrons do not move in a spherically symmetric potential, and so there is no conservation of angular momentum in general. There is instead conservation of the projection of angular momentum along the axis along which the nuclei vibrate. These axial components of the angular momenta for a single electron are designated as before, l_z , and s_z , for the orbital and spin momenta, respectively. Delineating the quantum numbers for angular momenta gets a little tricky. Greek letters are used to designate the quantum number instead of Latin letters as was the case for atomic angular momentum states, so, instead of using S,P, and D, and so forth to mark 0, 1, and 2 in units of \hbar , it is σ , π , and δ . But one also sees this written as $l_z = \lambda\hbar$, and $s_z = \sigma\hbar$, leading to the unavoidable confusion of using σ to refer to $\lambda = 0$ states, and to all of the spin projection states. However, one essentially never sees the lower case Greek letters designating electronic energy states, because the spectroscopic term designation depends in some way (there are multiple ways) on adding the angular momenta to arrive at total angular momenta. The total orbital angular momentum \mathbf{L} is added to the total spin angular momentum \mathbf{S} to give the total angular momentum \mathbf{J} , where again, there are multiple ways in which this needs to be done, and only the component along the axis along the nuclei matters, and one sees $L_z = \Lambda\hbar$, $S_z = \sigma\hbar$, and $J_z = \hbar$. The same confusion arising from the dual use of σ obtains. The designation of the spectroscopic term attaching to the electronic energy level is almost complete, and it is much like the case of atomic term schemes, $^{2S+1}\Lambda_\Omega$, only the subscript for the total angular momenta is not typically displayed. Instead, two more designations are preferred: that for two kinds of symmetry. If the electronic state possesses reflection symmetry about a plane passing through the axis along which the nuclei vibrate, whether even (+) or odd (-), this is denoted by a plus or minus sign as a superscript, and, further, for the special case of homonuclear diatomic
- molecules, there can be inversion symmetry about the origin (center of mass) for all non zero angular momentum states, and states even in this inversion are said to be gerade and the odd states, ungerade, after the German, for those words, and they appear as subscripts denoting the angular momentum states. Okay? Got it? Easy as Π .
- [3] A. Lofthus, and P.H. Krupenie, *The Spectrum of Molecular Nitrogen*, J. Phys. Chem. Ref. Data, **6** pp. 113-307 (1977).
- [4] It will come as a shock to experts in molecular physics that the words ‘band head’ comes into the discussion as a footnote. When you read the table entries in the reference above, you’ll read in the figure caption, ‘Table 29. Band heads and origins of the $C^3\Pi_u - A^3\Pi_g$, ...’, you’ll wonder what the heck a Band head is. Well, it’s complicated. It has to do with all the rotational transitions allowed between two vibrational states which are in different electronic states. The potential energy curves correspond to electronic energy states. Because the rotational states are very, very closely spaced, the vibrational transitions do not look like atomic spectral lines, but rather look rather broader, even blurry on one side or the other, but typically there is a sharp side to the spectral feature. This is called the Band head, and the ‘band’ includes all the electronic transitions associated with a given pair of vibrational state quantum numbers, v'' in the lower electronic state, and v' in the upper electronic state, and all the allowed changes in rotational kinetic energy. In our experiment, we cannot resolve the band into its separate lines arising from different rotational states, it is a kind of fine structure beyond the reach of our instrument. The student might find references that discuss the rotational spectrum of the HCl molecule to be pertinent here. You might then ask: what sort of resolving power will we need to neatly separate or ‘resolve’ the lines of that spectrum, and bear in mind that since HCl is not a homonuclear diatomic molecule, the rotational absorption spectrum may be measured directly with a broad band light source (heat!) with a long enough wavelength, and, note that the same feat would be much harder to pull off at visible wavelengths.
- [5] D.C. Harris and M.D. Bertolucci, *Spectroscopy and Symmetry, an introduction to Vibrational and Electronic Spectroscopy*, (Dover 1989), table 3.3, p105.

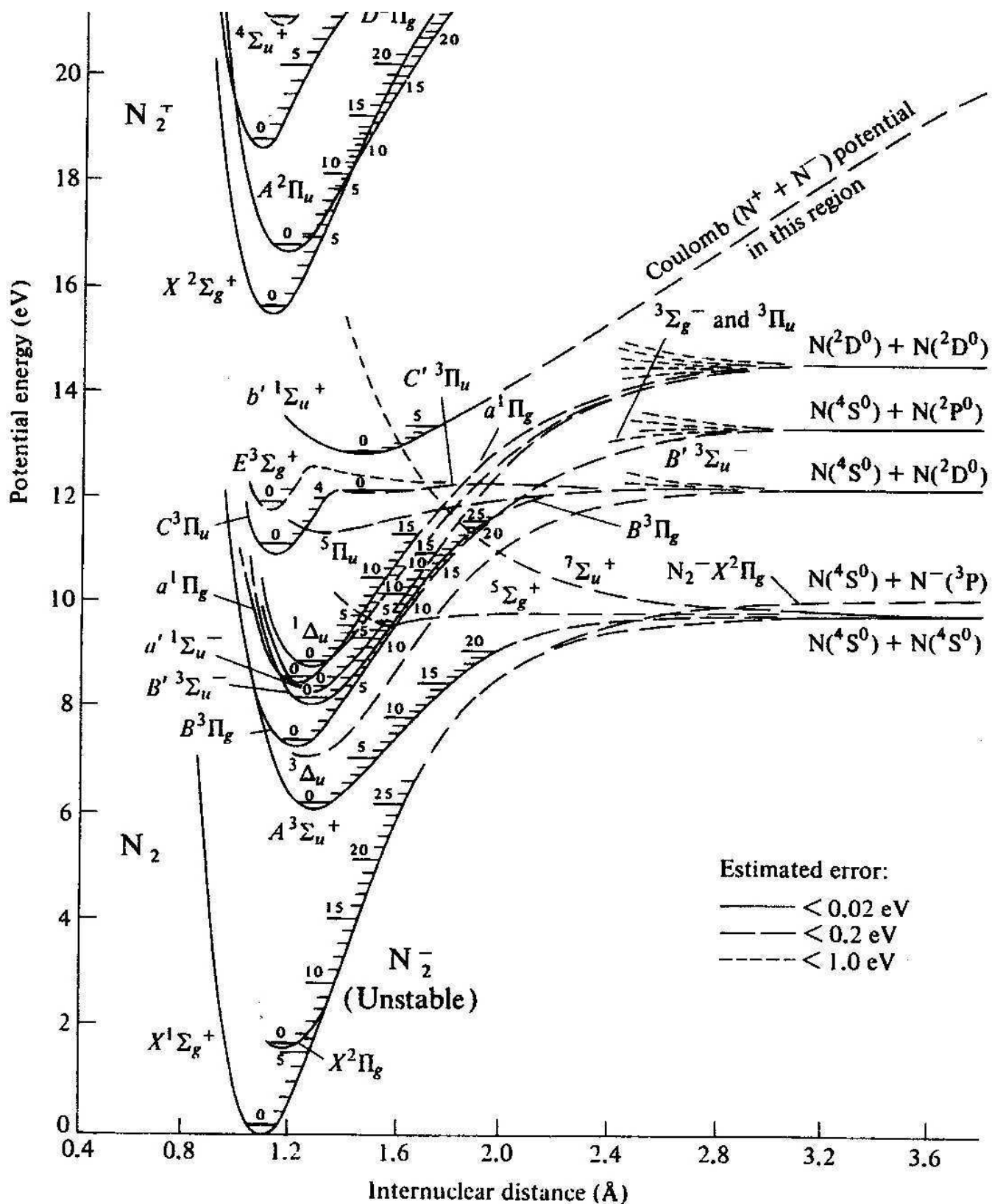


Figure 6: This is a 'clean' version of the potential energy curves, Figure 1, in Lofthus and Krupenie's work [3]

Table 3-3. Vibrational Constants of Diatomic Molecules

Molecule ^a	(cm ⁻¹)	$\bar{\omega}_e$ (cm ⁻¹) ^b	$\bar{\omega}_e x_e$ (cm ⁻¹) ^b	k_e (N m ⁻¹) ^c	kJ/mol	kcal/mol	kJ/mol	kcal/mol
H ₂	4159.5	4395.3	117.90	573.4	436	104.2	406	97.2
D ₂	2990.3	3118.5	64.10	576.9	—	—	—	—
HF	3958.4	4138.52	90.069	965.5	563	134.6	533	127.5
HCl	2885.7	2988.90	51.60	515.74	432	103.2	404	96.5
HBr	2559.2	2649.67	45.21	411.6	366	87.5	339	81.0
HI	2230.0	2309.5	39.73	314.1	299	71.4	272	65.0
CO	2143.3	2170.21	13.461	1902	1076	257.3	1040	248.6
NO	1876.1	1904.03	13.97	1594	630	150.5	599	143.1
F ₂	892	—	—	440	153	36.6	119	28.4
Cl ₂	556.9	564.9	4.0	328.6	243	58.0	211	50.4
⁷⁹ Br ⁸¹ Br	321	323.2	1.07	245.8	193	46.1	162	38.6
I ₂	213.4	214.57	0.6127	172.1	151	36.1	121	28.9
O ₂	1556.2	1580.361	12.0730	1177	495	118.4	460	110.0
N ₂	2330.7	2359.61	14.456	2297	945	225.9	911	217.7
Li ₂	346.3	351.44	2.592	25.5	111	26.5	86.9	20.8
Na ₂	157.8	159.23	0.726	17.2	75.3	18.0	52.3	12.5
KCl	278	280	0.9	85.9	427	102.1	402	96.0

^aData refer to the most abundant isotope of each element.

^bValues of $\bar{\omega}_e$ and $\bar{\omega}_e x_e$, defined in Section 3-3-C, were taken from G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand Reinhold, N.Y., 1950.

^c k_e is calculated from $\bar{\omega}_e$ using the relation $k_e = (200\pi c \bar{\omega}_e)^2 \mu$. For F₂, $\bar{\omega}$ was used instead of $\bar{\omega}_e$. The almost universal unit of force constant is mdyne/Å. The SI unit, Newton/m, is equal to 0.01 mdyne/Å. The force constant for H₂, for example, is 573.4 N/m = 5.734 mdyne/Å.

^dBond enthalpies and free energies were taken from H.A. Bent, *The Second Law*, Oxford University Press, N.Y., 1965.

Figure 7: Blurry table of molecular constants from Harris's book [5].