

Spectra of diatomic molecules

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1 Rotational energy levels and spectra

We have seen that the energy levels of a diatomic molecule in a Σ state may be written as

$$E_{s,v,r} = E_s(R_0) + E_v + E_r$$

where the three terms are the energies of the electron cloud, of nuclear vibration along the internuclear axis \mathbf{R} , and rotation of the nuclei about an axis normal to \mathbf{R} .

What is the situation when the electrons have non-zero orbital angular momentum \mathbf{L} ? In this case, if the orbital angular momentum of the nuclei is now denoted by \mathbf{N} , the total angular momentum \mathbf{J} is given by

$$\mathbf{J} = \mathbf{L} + \mathbf{N}.$$

Clearly \mathbf{N} is perpendicular to \mathbf{R} , so the projection of \mathbf{J} onto \mathbf{R} is the same as the projection L_R with eigenvalue $\Lambda\hbar$ of \mathbf{L} . (We now reserve z for a direction fixed in space, and use the subscript R for a component along \mathbf{R}). Because total angular momentum of an isolated molecule is constant, eigenfunctions of H when \mathbf{L} is non-zero will have the quantum numbers J , M_J , Λ , s (to describe the electronic state), and sn , the sign of Λ .

Because \mathbf{L} is non-zero, the electronic potential field in which the nuclei move is no longer really axisymmetric, and \mathbf{N} is no longer a good quantum number. However, we may approximate the main effect of non-zero \mathbf{L} on the nuclear wave functions by replacing the centrifugal term $\hbar^2 J(J+1)/2\mu R^2$ in the nuclear wave equation by one in the expectation value $\langle \mathbf{N}^2 \rangle$:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\langle \mathbf{N}^2 \rangle}{2\mu R^2} + E_s(R) \right] \mathcal{F}(R) = E\mathcal{F}(R).$$

Now

$$\langle \mathbf{N}^2 \rangle = \langle (\mathbf{J} - \mathbf{L})^2 \rangle = \hbar^2 J(J+1) - 2\langle \mathbf{J} \cdot \mathbf{L} \rangle + \langle \mathbf{L}^2 \rangle.$$

Because the system is in an eigenstate of L_R , the expectation value of a component of \mathbf{L} perpendicular to \mathbf{R} vanishes, and because $J_r = L_R$, we have

$$\langle \mathbf{J} \cdot \mathbf{L} \rangle = \langle J_R L_R \rangle = \Lambda^2 \hbar^2.$$

The total energy of the molecule is then approximately

$$E_{s,v,r} = [E_s(R_0) + \frac{1}{2\mu R_0^2}(\langle \mathbf{L}^2 \rangle - 2\Lambda^2 \hbar^2)] + E_v + \frac{J(J+1)\hbar^2}{2\mu R_0^2}.$$

The quantity in square brackets depends only on the electronic state, so we rename it $E'_s(R_0)$. All the dependence of $E_{s,v,r}$ on J (the total nuclear plus electronic orbital angular momentum) is in the term $BJ(J+1)$, where B is a constant. This looks very much like our previous result – except that now J must satisfy $J \geq \Lambda$, because J must be at least as big as the component L_R .

We now consider the rotational spectrum that should be emitted by a diatomic molecule. Classically, we expect that radiation could be emitted as a result of the rotation of the molecule *if* the molecule has a net electric dipole moment, which will be the case for example in a molecule with ionic bonding between different nuclei (e.g. CN or OH). On the other hand, a homonuclear molecule, one with two identical nuclei (H_2 , N_2 , O_2 , etc), has no overall electric dipole because the two ends are identical. Thus we expect that such molecules may be inhibited from emitting dipole radiation due to rotation.

Now look at the rotational emission problem quantum mechanically, first for a homonuclear molecule. In the dipole approximation, we expect that the transition amplitude between two rotational states (having the same vibrational and electronic wave functions) will be proportional to the matrix element of

$$\mathbf{D} = e \left(\sum_i Z_i \mathbf{R}_i - \sum_j \mathbf{r}_j \right).$$

The matrix element we are interested is that of the dipole operator between an initial state given approximately by

$$\Psi_a = \Psi_{s,v,J} \approx \Phi_s(\mathbf{R}, \mathbf{r}_i) (\psi_v(R)/R) \phi_J(\mathbf{R})$$

and a final state $\Psi_{s,v',J'}$ of the same form but with different quantum numbers v' and J' . To discover whether radiation can be emitted as a result of transitions between rotational levels, we must examine how these various terms in the matrix element change when the two nuclei are exchanged (i.e. \mathbf{R} is replaced by $-\mathbf{R}$). In a homonuclear molecule, the operator itself is unchanged by the exchange of the two nuclei, since there is still exactly the same arrangement of charged particles as before. We know that under exchange of the nuclei, the rotation states $\phi_J(\mathbf{R}) = Y_{J,M_J}(\Theta, \Phi)$ are unchanged, or change sign, depending on whether J is even or odd. The vibrational states, $\psi_v(R)/R$, which depend only on R but not on its direction, do not change sign. Finally, to see how the electronic states react, imagine carrying out the inversion of the nuclei in two steps. First, reflect *all* the particles through the origin, then reflect again only the electrons through the origin. The first operation is the parity operation, and since states of a homonuclear molecule have parity (in

molecular terminology: are positive or negative states), the result will be the same wave function with a plus or minus sign. In a homonuclear molecule, in which states are even or odd (g or u) to reflection of the *electron cloud*, the second operation also results in the same state again with a plus or minus sign. We conclude that overall, in a homonuclear molecule the states $\Phi_s(\mathbf{R}, \mathbf{r}_i)$ either remain unchanged or reverse sign: they are even or odd with respect to exchange of the two nuclei.

To summarize the effects of exchange of the nuclei:

- the dipole operator is unchanged
- a rotation state $\phi_J(\mathbf{R})$ is replaced by $(-1)^J \phi_J(\mathbf{R})$
- the vibrational state is unchanged
- the electronic state $\Phi_s(\mathbf{R}, \mathbf{r}_i)$ is replaced by $\pm \Phi_s(\mathbf{R}, \mathbf{r}_i)$.

Now, consider again the matrix element that determines the probability of radiation. For emission of radiation from rotational transitions alone, in the usual case of a molecular ground state with $\Lambda = 0$, i.e. a Σ state, we expect to have the selection rule $J' = J \pm 1$ between the radiating rotation states. The electronic and vibrational states remain unchanged while the rotational states change. If we exchange the two nuclei (an operation which cannot affect the value of the matrix element, since we are only changing the labeling of the nuclei), because of the selection rule $J' = J \pm 1$, one of the rotational states changes sign while the other does not. The operator and the vibrational states do not change sign, and if the electronic state changes sign, the effect cancels out because the electronic state appears squared in the matrix element. Thus an exchange of nuclei *changes the sign of the matrix element*. But since the value of the matrix element cannot depend on which nucleus is designated as the tail of the vector \mathbf{R} , the matrix element must vanish.

The same conclusion applies to radiation in which the vibrational state (but not the electronic state) changes, i.e. to purely vibrational transitions. Such radiation also requires the rotational state to change J by ± 1 , so again exchange causes the sign of the matrix element to change. We conclude that *a homonuclear molecule in the ground electronic state does not emit purely rotational or vibrational spectra by dipole radiation*. Such molecules can only emit dipole radiation if the electronic state changes; they can also emit quadrupole radiation or magnetic dipole radiation, but this is much weaker than the suppressed dipole radiation would be.

2 Rotational and vibrational-rotational spectra

Heteronuclear molecules can emit a purely rotational, or a vibrational-rotational spectrum. From the dependence of the energy of the eigenstates on J , as $E_r = BJ(J+1)$, we immediately see that that spectral lines due to rotational transitions satisfying $J' = J + 1$ will have frequencies (for $J \geq \Lambda$)

$$h\nu_{J+1,J} = E_r(J+1) - E_r(J) = 2B[(J+1)(J+2) - J(J+1)] = 2B(J+1).$$

The spectral lines will be uniformly spaced in frequency, with wavelengths of the order of 0.1 mm, in the far infrared or microwave region of the spectrum.

To have spectral lines arise through the change of vibrational levels, the matrix element

$$\mathbf{D}_{v',v;J',J} = \int \psi_{v'}^* \phi_{J,M,J}^*(\Theta, \Phi) \mathbf{D}(R) \phi_{J,M,J}(\Theta, \Phi) \psi_v d\Omega dR$$

must be non-zero (note that the factor $1/R^2$ from the definition of ψ_v cancels the R^2 factor from the volume element in spherical coordinates). The angular integral (over the rotational eigenfunctions) is just the one we have seen before in the one-electron problem; it is from this factor that one gets the selection rule $J' = J \pm 1$, and we see that this rule also holds for vibrational transitions (with $\Lambda = 0$). Now if \mathbf{D} were independent of R , the integral would vanish for $v' \neq v$ because of the orthogonality of the Hermite polynomials which are the solution of the (approximate) vibrational problem. Let us suppose that \mathbf{D} does depend on R , so that we may expand it as

$$\mathbf{D}(R) = \mathbf{D}(R_0) + (R - R_0) \left. \frac{d\mathbf{D}}{dR} \right|_{R=R_0} + \dots$$

We ignore higher terms since the vibration amplitude is small. Now the matrix element that matters is given by

$$I(v', v) = \int \psi_{v'}^*(R - R_0) \psi_v dR.$$

Using a recursion relation for the Hermite polynomials, this integral vanishes unless

$$\Delta v = v' - v = \pm 1.$$

(Because of the fact that the simple harmonic oscillator is only an approximation to the actual potential, transitions with $\Delta v = \pm 2, \pm 3, \dots$ can also occur, but these are usually considerably weaker than those for which $\Delta v = \pm 1$.)

Now for a given pair of vibration levels v and $v' = v + 1$, the transitions fall into two groups, those with $\Delta J = +1$ (the R branch) and those with $\Delta J = -1$ (the P branch). The frequencies for the R branch are given approximately by

$$h\nu_R = E(v + 1, J + 1) - E(v, J) = 2B(J + 1) + \hbar\omega_0, \quad J = 0, 1, 2, \dots$$

while the P branch are at frequencies

$$h\nu_P = E(v + 1, J - 1) - E(v, J) = -2BJ + \hbar\omega_0, \quad J = 1, 2, \dots$$

The two branches together make up a vibrational-rotational band. The lines are now in the infra-red (typical wavelengths of a few μm), and are evenly spaced in frequency (with spacing $2B$) except for a gap $4B$ wide at the position of $\nu_0 = \omega_0/2\pi$ caused by the fact that J must change by ± 1 . In actual spectra, the spacing of the lines is not quite uniform because the constant B is actually slightly different in the two vibrational bands.

For a molecule with $\Lambda \neq 0$, transitions with $\Delta J = 0$ (the Q branch) are also possible. If the two B values are essentially equal, all the Q branch lines occur at the frequency ν_0 , which instead of being absent is quite strong.

Another important effect involving vibrational and rotational levels is Raman scattering. In this effect, a photon is scattered by the molecule, effectively by an absorption immediately followed by an emission to a state near the original one, so that the frequency of the scattered photon is changed slightly. The absorption changes J by one, and the re-emission does so as well. Thus in the end, the final emission satisfies the selection rule $\Delta J = 0, \pm 2$. It is found that the Raman effect does *not* require a permanent electric dipole moment; the moment induced by the radiation field itself is enough to make the process occur. This means that the Raman effect provides a means of probing the vibrational-rotational levels in molecules such as O_2 and N_2 which normally have no intrinsic vibrational-rotational spectrum.

3 Electronic spectra

Electronic spectra arise from transitions in which the electronic state of the molecule changes – these are the transitions most nearly analogous to atomic transitions, and typically involve photons in the visible and ultraviolet parts of the spectrum. At low resolution, electronic spectra seem to be made up of series of more or less evenly spaced *bands*; at higher resolution, each band is made of many individual spectral lines.

To understand these spectra, recall that we have found that the energy of a single level of electronic state s , vibrational state v , and rotational level J may be written as a sum of these three energies, $E_{s,v,J} = E_s + E_v + E_J$, so that the frequency of a particular transition will be given by

$$h\nu = [E_{s'} - E_s] + [\hbar\omega'_0(v' + \frac{1}{2}) - \hbar\omega_0(v + \frac{1}{2})] + [B'J'(J' + 1) - BJ(J + 1)].$$

For a particular pair of electronic levels s, s' , this equation is very similar to that for vibrational-rotational spectrum, except in two respects. First, because two different electronic levels are involved, ω'_0 will be rather different from ω_0 and (more importantly) B' will be different from B (because different electronic states have different equilibrium positions R_0 and hence different moments of inertia); and secondly, the frequency of the transition is moved from the infrared into the visible or UV by the addition of the large term due to $[E_{s'} - E_s]$.

Selection rules control which electronic states can make strong transitions with each other; these are somewhat complicated and will not be treated here. There is no selection rule on the difference $\Delta v = v' - v$, since the two vibrational levels are not formed in the same electronic potential well, and values of Δv up to 5 or 6 are not uncommon. Since the rotational energies involve the same angular functions (the Y_{lm} 's) in both states, they continue to observe the selection rule $\Delta J = \pm 1$ between two Σ states, or $\Delta J = 0, \pm 1$ for states with $\Lambda \neq 0$.

For a given pair of electronic levels s, s' , each of the bands seen at low resolution corresponds to a particular value of Δv . Writing the part of the energy difference due to the vibrational levels as

$$\Delta E_{v',v} = \hbar[(\omega'_0 - \omega_0)(v + \frac{1}{2}) + \omega'_0 \Delta v],$$

we see that for a given Δv , various values of v will form an evenly spaced series of bands with spacing proportional to $(\omega'_0 - \omega_0)$, while different Δv values will produce more widely spaced sequences of such v series of bands, with spacing proportional not to $(\omega'_0 - \omega_0)$ but to ω'_0 . The equation describing this structure is known as the Deslandres formula.

Each series of bands for given values of v and Δv will have a large number of lines (*fine structure*) because of the rich structure of rotational levels possessed by each vibrational level. Two or three series of rotational lines will be present for each pair of vibrational levels, corresponding to $\Delta J = -1$ (the P branch), $\Delta J = +1$ (the R branch), and perhaps $\Delta J = 0$ (the Q branch). For transitions between two Σ levels, the frequency series for the P and R branches are given by

$$h\nu_P = h\nu_{s',s,v',v} + B'J(J-1) - BJ(J+1) = (B' - B)J^2 - (B' + B)J$$

and

$$h\nu_R = h\nu_{s',s,v',v} + B'(J+1)(J+2) - BJ(J+1) = (B' - B)J^2 + (3B' - B)J + 2B'.$$

Here both series of lines are clearly quadratic in J because $B' - B \neq 0$. Because the coefficient of J has opposite signs for the two series of rotational lines, the two series set out in opposite directions from $\nu_{s',s,v',v}$, but as the J^2 term dominates, with the same coefficient, one of the two series reverses direction and both go off towards higher frequency (if $B' - B > 0$) or lower (if $B' - B < 0$). This phenomenon places several lines at nearly the same frequency near the point where the direction changes, and gives each series in J a *band head*, while on the other side of $\nu_{s',s,v',v}$ the band gradually fades away. Because the values of B and B' vary only a little with v and v' , all the series of lines from a given pair of electronic states will have band heads on the the same (high or low frequency) side of the series. A plot of J versus frequency for a single band is called a Fortrat parabola.

4 Electronic spin: Hund's cases

In diatomic molecules we actually have four different kinds of angular momentum that combine in different ways. These are the orbital angular momentum of the electrons \mathbf{L} , the spin angular momentum of the electrons \mathbf{S} , the nuclear rotational angular momentum \mathbf{N} , and the nuclear spin \mathbf{I} , which can almost always be neglected except for its influence on symmetries in homonuclear molecules (see below). These may combine in a variety of fairly complicated ways.

Hund identified some of the most common ways in which the angular momentum combines, or *couples*. To appreciate this phenomenon, it is useful to have first studied many-electron atoms, which you have not yet done, so we will simply summarize a sample situation.

One possible situation is Hund's case (a), when \mathbf{L} couples strongly to \mathbf{R} , so that Λ is a good quantum number (i.e. is well-defined for each quantum state), and also couples strongly to \mathbf{S} , so that the projection of \mathbf{S} on \mathbf{R} , $\Sigma\hbar$, is also a good quantum number. Then the sum of these two components can take on the values

$$\Omega = |\Lambda + \Sigma| = |\Lambda - \Sigma|, |\Lambda - \Sigma| + 1, \dots, \Lambda + \Sigma,$$

and Ω is also a good quantum number. Each pair of numbers Λ and Ω define a different basic state that can have a series of rotational levels defined by the total angular momentum of the molecule \mathbf{J} , the vector sum of Ω (parallel to \mathbf{R}) and \mathbf{N} (perpendicular to \mathbf{R}), so that $J \geq \Omega$. The states with different pairs of Λ and Ω have slightly different energies because of the interaction energy of \mathbf{L} and \mathbf{S} .

Other cases arise as other kinds of coupling dominate.

5 The effects of nuclear spin

Nuclei have spin due to the intrinsic spins of protons and neutrons, which like electrons have spins of $\hbar/2$. These spins combine (couple) to form the total spin of the nucleus, which may be different for different excited states. The ground state of the nucleus always has a definite spin; for example, ^1H has spin $1/2$, while ^{16}O has spin 0 . The nuclear spin can couple with other angular momenta, but as mentioned above this coupling has no direct effect of importance on molecular spectra.

There are however important effects of nuclear spin in homonuclear molecules due to the operation of the Pauli exclusion principle. We know that the exclusion principle requires that the total wave function of a system be antisymmetric under exchange of identical fermions, or symmetric under exchange of bosons. Since electrons have spin $1/2$ and do not combine into aggregates, the wave function must always be antisymmetric under exchange of electrons, but since nuclei can act as bosons (if they have an even number of nuclei) or fermions (with an odd number of nucleons), both symmetries are possible for nuclear exchange. Let's look at one example of how this restriction affects molecular spectra of a homonuclear molecule.

We have seen that the total wavefunction (without nuclear spin) of a homonuclear molecule (we add in the electron spin function χ_{el})

$$\Psi_a = \Psi_{s,v,J} \approx \Phi_s(\mathbf{R}, \mathbf{r}_i)(\psi_v(R)/R)\phi_J(\mathbf{R})\chi_{\text{el}}$$

has definite symmetry under exchange of nuclei: Φ_s may be symmetric or antisymmetric, ψ_v is always symmetric, and ϕ_J is multiplied by $(-1)^J$, so that alternate levels have opposite symmetry. Now suppose for example that the nuclear spin is zero, as in $^{16}\text{O}_2$, so that the spin function is symmetrical under exchange of the nuclei. Then

the rest of the wave function must be symmetric under exchange too. Suppose Φ_s is also symmetric; in this case only the symmetric rotation functions ϕ_J can occur, and thus only the J values $0, 2, \dots$. If Φ_s is antisymmetric, J is restricted to the values $1, 3, \dots$. Thus in each case half the normal rotational levels are missing. This will be true also of excited electronic levels, and for a pair of electronic levels between which transitions are permitted, the absence of half the rotational levels will mean that half the rotational lines are missing from each band. In the almost identical molecule $^{16}\text{O}^{17}\text{O}$ this restriction does not apply, and the missing lines are restored.

This kind of effect in homonuclear molecules is very helpful in determining the spin of the nuclei, in spite of the fact that these nuclear spins have almost no interaction with the rest of the molecule.