

24. Atomic Spectra, Term Symbols and Hund's Rules

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Suggested Reading: Chapters 8-8 to 8-11 of the text.

Introduction

Electron configurations, at least in the forms used in general chemistry are ambiguous. For example for carbon $1s^2 2s^2 2p^2$, where to the two electrons in the p orbitals reside? In which of the three p orbitals, p_{-1} , p_0 , p_{+1} ? What is the spin on the electrons.

As we saw in the last lecture, all of the various quantum numbers affect the energy of the state, not just the principle quantum number, in multi-electron systems. We need a new way to designate a state unambiguously. The scheme presented here is based on the total angular momentum, J, formed by adding the total orbital angular momentum, L, and the total spin angular momentum, S. The symbol used to designate a state by this means is called a term symbol and is of the form

$$^{2S+1}L_J \quad (24-1)$$

The scheme is called Russell-Saunders coupling and is performed as follows: The total orbital angular momentum is given by

$$\vec{L} = \sum_j \vec{l}_j \quad (24-2)$$

a vector addition. The total spin angular momentum is given by

$$\vec{S} = \sum_j \vec{s}_j \quad (24-3)$$

another vector addition. The z components of \vec{L} and \vec{S} are given by the scalar sums

$$L_z = \sum_i l_{z,i} = \sum_i m_i = M_L \quad (24-4)$$

and

$$S_z = \sum_i s_{z,i} = \sum_i m_{s,i} = M_S \quad (24-5)$$

Thus there are $2L + 1$ values of M_L spanning $-L, -L+1, -L+2, \dots, L-1, L$ and $2S + 1$ values of M_S for S spanning $-S, -S+1, -S+2, \dots, S-1, S$.

The leading $2S+1$ superscript in the term symbol is called the spin multiplicity.

Table 24-1: Names for the leading superscripts of atomic term symbols.

$2S+1$	Name
1	singlet
2	doublet
3	triplet

The value of L is substituted as in the hydrogen-like orbitals but with a capital letter. That is,

Table 24-2: Letter conversions for atomic term symbols.

Value of L	Letter
0	S
1	P
2	D
3	F
4	G
5	H

The value of J is kept as a number. Thus for example:

3S_1 - "triplet S one"

1D_3 - "singlet D three"

Examples

Hydrogen: $H 1s^1$, The maximum value of M_S is

$$\begin{aligned}M_{S, max} &= \sum_i m_{s, i} \\ &= \frac{1}{2}\end{aligned}\tag{24-6}$$

to give $S = 1/2$. The maximum value of L is

$$\begin{aligned}M_{L, max} &= \sum_i m_i \\ &= 0\end{aligned}\tag{24-7}$$

thus $L = 0$ and $J = L + S = 1/2$. The term symbol for the ground state of hydrogen is

$${}^2S_{\frac{1}{2}}\tag{24-8}$$

The ground state of He, $1s^2$:

$$\begin{aligned}M_{S, max} &= \sum_i m_{s, i} \\ &= \frac{1}{2} - \frac{1}{2} \\ &= 0\end{aligned}\tag{24-9}$$

$$\begin{aligned}
 M_{L, max} &= \sum_i m_i \\
 &= 0 + 0 \\
 &= 0
 \end{aligned}
 \tag{24-10}$$

Therefore, the term symbol is

$${}^1S_0
 \tag{24-11}$$

An excited state of He, $1s^1 2s^1$:

$$\begin{aligned}
 M_{S, max} &= \sum_i m_{s, i} \\
 &= \frac{1}{2} + \frac{1}{2} \\
 &= 1
 \end{aligned}
 \tag{24-12}$$

therefore $M_S = 1, 0, -1$ but what value of S?

$$\begin{aligned}
 M_{L, max} &= \sum_i m_i \\
 &= 0 + 0 \\
 &= 0
 \end{aligned}
 \tag{24-13}$$

Microstates

To answer our question above, there are two methods. One involves inspection of the problem and works quickly but is not reliable, the second is

perhaps tedious, but always works. It is this second methods that is given in the text and will be used here.

Lets create a table

M_L	M_S		
	1	0	-1
0	$(0^+,0^+)$	$(0^+,0^-), (0^-,0^+)$	$(0^-,0^-)$

The notation $(0^+,0^+)$ means that $(m = 0, m_s = +1/2; m = 0, m_s = +1/2)$ for the two electrons. $(0^+,0^-)$ and $(0^-,0^+)$ are not equivalent because the two electrons are in separate orbitals. The four entries are called microstates. Lets loot at $L = 0, S=1,$

$$L = 0 \rightarrow M_L = 0$$

$$S = 1 \rightarrow M_S = 1, 0, -1$$

This corresponds to the microstates $(0^+,0^+), (0^+,0^-)$ and $(0^-,0^-)$. We have one unaccounted for microstate, $(0^-,0^+)$. This microstate has $S = 0, L = 0$.

Thus there are two possible states for He $1s^1 2s^1$:

$${}^3S_1 \quad {}^1S_0 \quad (24-14)$$

The allowed values of J are $J = L+S, L+S-1, L+S-2, \dots, |L-S|$.

Beryllium $1s^2 2s^2$:

$$\begin{aligned}M_{S, max} &= \sum_i m_{s, i} \\ &= \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} \\ &= 0\end{aligned}\tag{24-15}$$

therefore $M_S = 0$.

$$\begin{aligned}M_{L, max} &= \sum_i m_i \\ &= 0 + 0 + 0 + 0 \\ &= 0\end{aligned}\tag{24-16}$$

therefore the term symbol is

$${}^1S_0\tag{24-17}$$

Filled subshells have total angular momentum of zero and make no contribution to the determination of the term symbol.

Back to carbon. We have six possible spin orbitals in which to place the two electrons

$$2p_0\alpha, 2p_0\beta, 2p_{-1}\alpha, 2p_{-1}\beta, 2p_1\alpha, 2p_1\beta$$

This is “6 choose 2”

$$\begin{aligned}\binom{6}{2} &= \frac{6!}{2!4!} \\ &= \frac{6(5)}{2} \\ &= 15\end{aligned}\tag{24-18}$$

There will be 15 microstates to deal with. In general, if we have j spin orbitals and need to place k electrons we have

$$\binom{j}{k} = \frac{j!}{k!(j-k)!}\tag{24-19}$$

microstates. For example $3d^2$ has

$$\begin{aligned}\binom{10}{2} &= \frac{10!}{2!8!} \\ &= 45\end{aligned}\tag{24-20}$$

microstates. How about $3d^8$?

$$\begin{aligned}\binom{10}{8} &= \frac{10!}{8!2!} \\ &= 45\end{aligned}\tag{24-21}$$

microstates. d^{10-j} has the same number of microstates as d^j .

Back to carbon:

The two electrons may go in the $m = -1, 0, 1$ orbitals. Thus M_L ranges from 2 to -2. The spins may be paired or unpaired, hence $M_S \rightarrow 1, 0, -1$.

M_L	M_S		
	1	0	-1
2		$(1^+, 1^-)$	
1	$(0^+, 1^+)$	$(1^+, 0^-), (0^+, 1^-)$	$(0^-, 1^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-), (-1^+, 1^-), (0^+, 0^-)$	$(1^-, -1^-)$
-1	$(0^+, -1^+)$	$(-1^+, 0^-), (0^+, -1^-)$	$(0^-, -1^-)$
-2		$(-1^+, -1^-)$	

Since the electrons are in the same shell $(1^+, 1^-)$ and $(1^-, 1^+)$ are indistinguishable and hence only one is included. Combinations that are excluded by the Pauli Principle do not make up the table entries.

The largest value of M_L is 2 and has $M_S = 0$, therefore $L = 2, S = 0, J = 2$ to give

$${}^1D_2 \quad (24-22)$$

This state has $M_S = 0, M_L = 2, 1, 0, -1, -2$ for five microstates.

The next largest value of M_L remaining is $M_L = 1$. The largest value of M_S associated with this is $M_S = 1$. Therefore $L = 1, S = 1$

$${}^3P \quad (24-23)$$

with $M_L = 1, 0, -1$ and $M_S = 1, 0, -1$ for nine microstates. The possible values of J are $J = (1+1), (1+1-1), (1-1)$ or $J = 2, 1, 0$ hence we have ${}^3P_2, {}^3P_1$ and 3P_0 with 5, 3, and 1 microstates respectively.

This leaves a single microstate remaining with $M_L = 0$ and $M_S = 0$ to give

$${}^1S_0 \quad (24-24)$$

Thus the states for the ground state configuration of carbon are

$${}^1D_2, {}^3P_2, {}^3P_1 \text{ and } {}^3P_0, {}^1S_0$$

The degeneracy of each state is $2J+1$ for 5, 1, 3, 5, 1 for 15 microstates.

The term symbols for a given electron configuration correspond to that with the same number of holes. For example $2p^2$ and $2p^4$ or $3d^4$ and $3d^6$ (see Table 8.4 in the text).

Hund's Rules

Each of the states designated by a term symbol corresponds to a determinantal wave function that is an eigenfunction of \hat{L}^2 and \hat{S}^2 . Thus each state corresponds to a given energy.

The spectroscopist Fredrich Hund worked out a set of empirical rules to order the energies of the states.

1. The state with the largest value of S is the most stable (has the lowest energy) and stability decreases with decreasing S .
2. For states with the same value of S , the state with the largest value of L is the most stable.
3. If the states have the same value of L and S , then for a subshell that is less than half filled, the state with the smallest value of J is the most stable. For a subshell that is more than half filled, the state with the largest value of J is the most stable.

For example for carbon, 3P_0 is the lowest energy state.

[As an exercise work out the state for d^2 using the microstate method.]

The term symbols are used to describe atomic spectra. Thus far in our development of the Hamiltonian operator for atoms we have included kinetic energy and electrostatic potential energy terms. That is,

$$\hat{H} = -\frac{1}{2} \sum_j \nabla_j^2 - \sum_j \frac{Z}{r_j} + \sum_{i < j} \frac{1}{r_{ij}} \quad (24-25)$$

We need to include spin and magnetic terms as well. The most important is the “spin-orbit interaction term” which results from the interaction of the magnetic moment associated with the spin of an electron with the magnetic field generated by the electric current produced by the electron’s own orbital motion. Other terms include spin-spin and orbit-orbit interaction (in multi-electron systems) but spin-orbit interactions are the most important.

$$\hat{H} = -\frac{1}{2} \sum_j \nabla_j^2 - \sum_j \frac{Z}{r_j} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_j \xi(r_j) \vec{l}_j \cdot \vec{s}_j \quad (24-26)$$

If the effect of the spin-orbit coupling is small, as it is for light atoms (approximately $Z < 30$) the effect may be treated as a perturbation. For heavier atoms, the effect is not small and must be dealt with explicitly.

Selection Rules for Atomic Spectra

Transitions involving light are allowed with atoms for the following

$$\begin{aligned} \Delta L &= \pm 1 \\ \Delta S &= 0 \\ \Delta J &= 0, \pm 1 \end{aligned} \quad (24-27)$$

expect that a transition from a state with $J = 0$ to another state with $J = 0$ is not allowed (forbidden).

Suggested Reading for Next Lecture: Chapter 9 of the text.

Term symbol

In [quantum mechanics](#), the **term symbol** is an abbreviated description of the [angular momentum quantum numbers](#) in a multi-[electron atom](#). It is related with the energy level of a given [electron configuration](#). [LS coupling](#) is assumed. The ground state term symbol is predicted by [Hund's rules](#).

The term symbol has the form

$$^{2S+1}L_J$$

where

S is the total [spin quantum number](#). $2S+1$ is the **spin multiplicity**: the maximum number of different possible states of J for a given (L,S) combination.

L is the total [orbital quantum number](#) in [spectroscopic notation](#). The symbols for $L = 0, 1, 2, 3, 4, 5$ are S, P, D, F, G, H respectively.

J is the [total angular momentum quantum number](#).

When used to describe electron states in an atom, the term symbol usually follows the [electron configuration](#), e.g., in the case of [carbon](#), the ground state is $1s^2 2s^2 2p^2 \ ^3P_0$. The 3 indicates that $2S+1=3$ and so $S=1$, the P is spectroscopic notation for $L=1$, and 0 is the value of J .

The term symbol is also used to describe compound systems such as [mesons](#) or atomic nuclei, or even molecules (see [molecular term symbol](#)). In that last case, Greek letters are used to designate the (molecular) orbital angular momenta.

For a given electron configuration

- The combination of an S value and an L value is called a **term**, and has a statistical weight (i.e., number of possible microstates) of $(2S+1)(2L+1)$;
- A combination of S , L and J is called a **level**. A given level has a statistical weight of $(2J+1)$, which is the number of possible microstates associated with this level in the corresponding term;
- A combination of L , S , J and M_J determines a single **state**.

As an example, for $S = 1$, $L = 2$, there are $(2 \times 1 + 1)(2 \times 2 + 1) = 15$ different microstates corresponding to the 3D term, of which $(2 \times 3 + 1) = 7$ belong to the 3D_3 ($J=3$) level. The sum of $(2J+1)$ for all levels in the same term equals $(2S+1)(2L+1)$. In this case, J can be 1, 2, or 3, so $3 + 5 + 7 = 15$.

Term symbol parity

The parity of a term symbol is calculated as

$$P = (-1)^{\sum_i l_i},$$

where l_i is the orbital quantum number for each electron. In fact, only electrons in odd orbitals contribute to the total parity: an odd number of electrons in odd orbitals (those with an odd l such as in p, f,...) will make an odd term symbol, while an even number of electrons in odd orbitals will make an even term symbol, irrespective of the number of electrons in even orbitals.

When it is odd, the parity of the term symbol is indicated by a superscript letter "o", otherwise it is omitted:

$${}^2\text{P}_{1/2}^{\circ} \text{ has odd parity, but } {}^3\text{P}_0 \text{ has even parity.}$$

Alternatively, parity may be indicated with a subscript letter "g" or "u", standing for *gerade* (German for 'even') or *ungerade* ('odd'):

$${}^2\text{P}_{1/2,u} \text{ for odd parity and } {}^3\text{P}_{0,g} \text{ for even.}$$

Ground state term symbol

It is relatively easy to calculate the term symbol for the ground state of an atom. It corresponds with a state with maximal S and L .

1. Start with the most stable [electron configuration](#). Full shells and subshells do not contribute to the overall [angular momentum](#), so they are discarded.
 - o If all shells and subshells are full then the term symbol is ${}^1\text{S}_0$.
2. Distribute the electrons in the available [orbitals](#), following the [Pauli exclusion principle](#). First, we fill the orbitals with highest m_l value with one electron each, and assign a maximal m_s to them (i.e. +1/2). Once all orbitals in a subshell have one electron, add a second one (following the same order), assigning $m_s = -1/2$ to them.
3. The overall S is calculated by adding the m_s values for each electron. That is the same as multiplying $1/2$ times the number of **unpaired** electrons. The overall L is calculated by adding the m_l values for each electron (so if there are two electrons in the same orbital, then we add twice that orbital's m_l).
4. Calculate J as:
 - o if less than half of the subshell is occupied, take the minimum value $J = |L - S|$;
 - o if more than half-filled, take the maximum value $J = L + S$;
 - o if the subshell is half-filled, then L will be 0, so $J = S$.

As an example, in the case of [fluorine](#), the electronic configuration is: $1s^2 2s^2 2p^5$.

1. Discard the full subshells and keep the $2p^5$ part. So we have five electrons to place in subshell p ($l = 1$).

2. There are three orbitals ($m_l = 1, 0, -1$) that can hold up to $2(2l+1) = 6$ electrons. The first three electrons can take $m_s = 1/2$ (\uparrow) but the Pauli exclusion principle forces the next two to have $m_s = -1/2$ (\downarrow) because they go to already occupied orbitals.

	m_l		
	+1	0	-1
m_s :	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow

3. $S = 1/2 + 1/2 + 1/2 - 1/2 - 1/2 = 1/2$; and $L = 1 + 0 - 1 + 1 + 0 = 1$, which is "P" in spectroscopic notation;

4. As fluorine 2p subshell is more than half filled, $J = L + S = 3/2$. Its ground state term symbol is then ${}^{2S+1}L_J = {}^2P_{3/2}$.

Term symbols for an electron configuration

To calculate all possible term symbols for a given [electron configuration](#) the process is a bit longer.

- First, calculate the total number of possible microstates N for a given electron configuration. As before, we discard the filled (sub)shells, and keep only the partially-filled ones. For a given orbital quantum number l the total number of electrons that can be fitted is $t = 2(2l+1)$. If there are e electrons in a given subshell, the number of possible microstates is

$$N = \binom{t}{e} = \frac{t!}{e!(t-e)!}$$

As an example, let's take the [carbon](#) electron structure: $1s^2 2s^2 2p^2$. After removing full subshells, there are 2 electrons in a p-level ($l = 1$), so we have

$$N = \frac{6!}{2!4!} = 15$$

different microstates.

- Second, draw all possible microstates. Calculate M_L and M_S for each microstate, with

$$M = \sum_{i=1}^e m_i$$

where m_i is either m_l or m_s for the i -th electron, and M represents the resulting M_L or M_S respectively:

	m_l			M_L	M_S
	+1	0	-1		
all up	↑	↑		1	1
	↑		↑	0	1
		↑	↑	-1	1
all down	↓	↓		1	-1
	↓		↓	0	-1
		↓	↓	-1	-1
one up	↑↓			2	0
	↑	↓		1	0
	↑		↓	0	0
	↓	↑		1	0
one down		↑↓		0	0
		↑	↓	-1	0
	↓		↑	0	0
		↓	↑	-1	0
		↑↓	-2	0	

- Third, count the number of microstates for each M_L — M_S possible combination

		M_S		
		+1	0	-1
M_L	+2		1	
	+1	1	2	1
	0	1	3	1
	-1	1	2	1
	-2		1	

- Fourth, extract smaller tables representing each possible term. Each table will be $(2L+1)(2S+1)$, and will contain "1"s as entries. The first table extracted corresponds to M_L ranging from -2 to $+2$ (so $L = 2$), with a single value for M_S (implying $S = 0$). This corresponds to a 1D term. The remaining table is 3×3 . Then we extract a second table, removing the entries for M_L and M_S both ranging from -1 to $+1$ (and so $S = L = 1$, a 3P term). The remaining table is a 1×1 table, with $L = S = 0$, i.e., a 1S term.

$$S=0, L=2, J=2$$

$$\begin{array}{c}
 {}^1D_2 \\
 M_s \\
 \mathbf{0} \\
 \hline
 +2 \quad \left| \begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{array} \right. \\
 +1 \\
 M_l \quad \mathbf{0} \\
 -1 \\
 -2
 \end{array}$$

$$S=1, L=1, J=2,1,0$$

$$\begin{array}{c}
 {}^3P_2, {}^3P_1, {}^3P_0 \\
 M_s \\
 \mathbf{0} \\
 \hline
 +1 \quad \left| \begin{array}{ccc} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{array} \right. \\
 +1 \\
 M_l \quad \mathbf{0} \\
 -1
 \end{array}$$

$$S=0, L=0, J=0$$

$$\begin{array}{c}
 {}^1S_0 \\
 M_s \\
 \mathbf{0} \\
 \hline
 M_l \quad \mathbf{0} \quad \left| \begin{array}{c} 1 \end{array} \right.
 \end{array}$$

- Fifth, applying [Hund's rules](#), deduce which is the ground state (or the lowest state for the configuration of interest.) Hund's rules should not be used to predict the order of states other than the lowest for a given configuration.

Dunham expansion

From Wikipedia, the free encyclopedia

In [quantum chemistry](#), the **Dunham expansion** is an expression for the rotational-vibrational [energy levels](#) of a [diatomic molecule](#):^[1]

$$E(v, J) = \sum_{k,l} Y_{k,l} (v + 1/2)^k [J(J + 1)]^l,$$

where v and J are the [vibrational](#) and [rotational quantum numbers](#). The constant coefficients $Y_{k,l}$ are called **Dunham parameters** with $Y_{0,0}$ representing the electronic energy. The expression derives from a [semiclassical](#) treatment of a [perturbational approach](#) to deriving the energy levels.^[2] The Dunham parameters are typically calculated by a [least-squares](#) fitting procedure of energy levels with the quantum numbers.

Relation to conventional band spectrum constants [\[edit\]](#)

	$Y_{0,1} = B_e$	$Y_{0,2} = -D_e$	$Y_{0,3} = H_e$	$Y_{0,4} = L_e$
$Y_{1,0} = \omega_e$	$Y_{1,1} = -\alpha_e$	$Y_{1,2} = -\beta_e$		
$Y_{2,0} = -\omega_e x_e$	$Y_{2,1} = \gamma_e$			
$Y_{3,0} = \omega_e y_e$				
$Y_{4,0} = \omega_e z_e$				

This table adapts the sign conventions from the book of Huber and Herzberg.^[3]

Rotational and vibrational energy levels of diatomic molecules

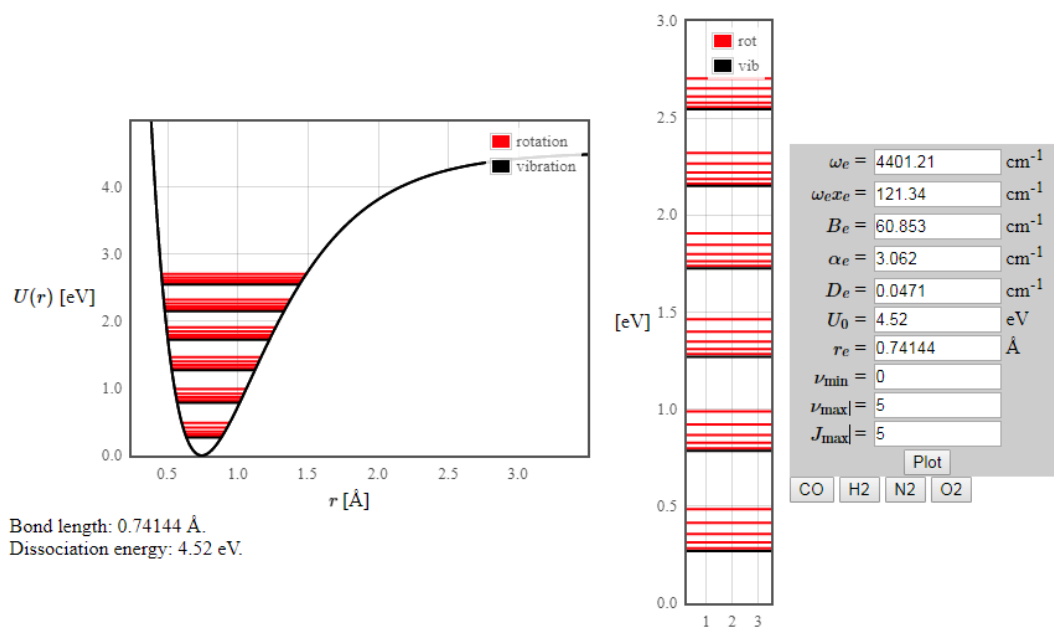
The rotational and vibrational energy levels of diatomic molecules can be approximated as,

$$E_{\text{vib}} = hc\omega_e(\nu + 1/2) - hc\omega_e x_e(\nu + 1/2)^2,$$

$$E_{\text{rot}} = hc(B_e - \alpha_e(\nu + 1/2))J(J + 1) + D_e(J(J + 1))^2),$$

where ω_e , x_e , B_e , α_e , and D_e are spectroscopic constants. The quantum numbers ν and J can take on integer values, $\nu, J = 0, 1, 2, \dots$. Here h is Planck's constant and c is the speed of light in vacuum. The units of all of the spectroscopic constants are cm^{-1} except for x_e which is unitless. The rotational and vibrational energy levels $E_{\nu J} = E_{\text{vib}} + E_{\text{rot}}$ are plotted in the bond potential on the left. An enlargement of the energy level spacing is shown on the right. The rotational levels have a degeneracy of $(2J + 1)$.

Vibration-rotation energy levels of H₂



State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	v_{00}	
$F^2\Sigma^+$	[47677.3]				[0.5088]			[2.15E-6]		[1.816 ₄]	F \rightarrow A R	41843.5 ₂ Z	
	↳missing citation												
													41972.3 ₆ Z
$E^2\Delta_1$	45562 1	(503)			[0.4951]			[1.9E-6]		[1.844 ₄]	E \leftrightarrow A R	39979.81 Z	
	↳Coheur and Rosen, 1941; Tyte, 1967; missing citation; missing citation												
	45431	(503)			[0.4919]			[1.9E-6]		[1.844 ₄]	E \leftrightarrow A R	39977.17 Z	
↳Coheur and Rosen, 1941; Tyte, 1967; missing citation; missing citation													
State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	v_{00}	
$D^2\Sigma^+4$	40266.7	819.6 Z	5.8		0.5652 2	0.0046	-0.00005	1.10E-6		1.723 ₄	D \rightarrow B 3 R	(19552)	
	↳Prasad and Narayan, 1969												
												D \leftrightarrow A V	34841.23 Z
	↳Coheur and Rosen, 1941; Tyte, 1967; missing citation												
												D \leftrightarrow A V	34970.09 Z
	↳Coheur and Rosen, 1941; Tyte, 1967; missing citation												
											D \leftrightarrow X R	40187.2 Z	
↳missing citation; Tyte, 1967; Singh and Narasimham, 1969; missing citation; Singh, 1972; Tawde and Tulasigeri, 1972; Singh and Saksena, 1973													
State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	v_{00}	
$C^2\Pi_4$	33153	856 H	6		5						(C \rightarrow B) 6 R _V	(12457)	
	↳Goodlett and Innes, 1959; missing citation												
	33079		6		5						(C \rightarrow B) 6 R _V	(12383)	
	↳Goodlett and Innes, 1959; missing citation												
												C \leftrightarrow X R	33092
	↳Coheur and Rosen, 1941; missing citation; Becart and Declerck, 1960; Tyte, 1967; missing citation; McDonald, Innes, et al., 1969												
											C \leftrightarrow X R	33018	
↳Coheur and Rosen, 1941; missing citation; Becart and Declerck, 1960; Tyte, 1967; missing citation; McDonald, Innes, et al., 1969													
State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	v_{00}	
$B^2\Sigma^+9$	20688.95	870.05 Z	3.52		0.6040 ₈ 7	0.0044 ₇		1.16E-6		1.6670	B \leftrightarrow X 8 R	20635.22 Z	
	↳Pomeroy, 1927; missing citation; missing citation; missing citation; missing citation; Shimauchi, 1958; Loginov, 1959; Nicholls, 1962; Tawde and Korwar, 1962; Becart and Mahieu, 1963; missing citation; missing citation; Sharma, 1967; Tyte, 1967; Prasad and Narayan, 1969; missing citation; Knight and Weltner, 1971; Gole and Zare, 1972; Liszt and Smith, 1972												
$A^2\Pi_1$	5470.6 10	728.5 H	4.15		[0.5374] 11 12			[1.1E-6]		[1.7708]	A \leftrightarrow X 13 R	5346	
	↳Knight and Weltner, 1971; Rosenwaks, Steele, et al., 1975												
	5341.7	728.5 H	4.15		[0.5333] 12			[1.1E-6]		[1.7708]	A \leftrightarrow X 13 R	5217	
↳Knight and Weltner, 1971; Rosenwaks, Steele, et al., 1975													
$X^2\Sigma^+9$	0	979.23 Z	6.97		0.6413 ₆ 14 15	0.0058 ₀		1.08E-6 16		1.6179 17			

TABLE V
Molecular Equilibrium Constants of H³⁵Cl, H³⁷Cl, D³⁵Cl, D³⁷Cl Obtained from Separate Fits

v_{ij}	H ³⁵ Cl	ΔY_{ij} [a]	H ³⁷ Cl	ΔY_{ij} [a]	D ³⁵ Cl	ΔY_{ij} [a]	D ³⁷ Cl	ΔY_{ij} [a]
v_{10}	2990.96638	3.9×10^{-3}	2988.7033	4.2×10^{-3}	2145.1523	6.7×10^{-3}	2142.0317	1×10^{-2}
v_{20}	-52.836415	2.9×10^{-3}	-52.756916	2.4×10^{-3}	-27.173645	3.7×10^{-3}	-27.114282	5.8×10^{-3}
v_{30}	0.230224	8×10^{-4}	0.229699	3.9×10^{-4}	8.39028×10^{-2}	5.8×10^{-4}	8.6674×10^{-2}	9×10^{-4}
v_{40}	-1.28228×10^{-2}	7.3×10^{-5}	-1.2784×10^{-2} [b]		-3.3927×10^{-3} [b]		-3.3728×10^{-3} [b]	
v_{01}	10.5933609	7.6×10^{-6}	10.577340	1.1×10^{-5}	5.448806	8.9×10^{-6}	5.432779	9.3×10^{-6}
v_{11}	-0.307178	1.9×10^{-5}	-0.306511	2.6×10^{-5}	-0.113297	2.1×10^{-5}	-0.112803	2.2×10^{-5}
v_{21}	1.76929×10^{-3}	9.2×10^{-6}	1.780805×10^{-2}	7.7×10^{-6}	4.663514×10^{-4}	6.9×10^{-6}	4.647162×10^{-4}	7.3×10^{-6}
v_{31}	-1.1959×10^{-4}	1.2×10^{-6}	-1.1914×10^{-4} [b]		-2.2694×10^{-5} [b]		-2.2527×10^{-5} [b]	
v_{02}	-5.318961×10^{-4}	5×10^{-8}	-5.297529×10^{-4}	1×10^{-7}	-1.404857×10^{-4}	9.2×10^{-8}	-1.396645×10^{-4}	7.6×10^{-8}
v_{12}	7.5215×10^{-6}	2.9×10^{-8}	7.2133×10^{-6}	3.5×10^{-8}	1.4049×10^{-6}	2×10^{-8}	1.4027×10^{-6}	1.6×10^{-8}
v_{22}	-3.9914×10^{-7}	7.1×10^{-9}	-3.9733×10^{-7} [b]		-5.4322×10^{-8} [b]		-5.3844×10^{-8} [b]	
v_{03}	1.7370×10^{-8}	1×10^{-10}	1.5852×10^{-8}	2.7×10^{-10}	1.5108×10^{-9}	3.7×10^{-10}	1.8078×10^{-9}	3.5×10^{-10}
v_{13}	-6.486×10^{-10}	1.3×10^{-11}						
v_{04}	-1.034×10^{-12}	7×10^{-14}						
σ	=1.0		σ =1.0		σ =1.5		σ =0.9	

[a] Value corresponding to one standard error

[b] Values introduced in the fit as a constraint. These values are calculated from the H³⁵Cl ones by using the approximate isotopic relation [3]

Ammonia Vibrational Energy Levels – NIST Webbook, from Shimanouchi (1972)

Symmetry: C_{3v} Symmetry Number $\sigma = 3$

Sym. Species	No	Approximate type of mode	Selected Freq. Value	Infrared Rating	Infrared Value	Raman Phase	Raman Value	Comments
a ₁	1	Sym str	3337	A	3336.2			symmetric level
a ₁	1	Sym str	3337	A	3337.2			antisymmetric level
a ₁	2	Sym deform	950	C	932.5			symmetric level
a ₁	2	Sym deform	950	C	968.3			antisymmetric level
e	3	Deg str	3444	A	3443.6			symmetric level
e	3	Deg str	3444	A	3443.9			antisymmetric level
e	4	Deg deform	1627	A	1626.1			symmetric level
e	4	Deg deform	1627	A	1627.4			antisymmetric level

CH₂ (methylene) – Radical species

State: 4p

Energy (cm ⁻¹)	Med.	Transition	λ_{\min} (nm)	λ_{\max} (nm)	References
T _o = 74254	gas				Irikura, Johnson, et al., 1992

State: D

Energy (cm ⁻¹)	Med.	Transition	λ_{\min} (nm)	λ_{\max} (nm)	References
T _o = 71592	gas	D-X	140	140	Herzberg, 1961 Irikura and Hudgens, 1992

State: C

Energy (cm ⁻¹)	Med.	Transition	λ_{\min} (nm)	λ_{\max} (nm)	References
T _o = 70917	gas	C-X	141	141	Herzberg, 1961 Irikura and Hudgens, 1992

State: 3d³A₂

Energy (cm ⁻¹)	Med.	Transition	λ_{\min} (nm)	λ_{\max} (nm)	References
T _o = 70634	gas	3d ³ A ₂ -X	142	142	Herzberg, 1961 Irikura and Hudgens, 1992

State: 3p

Energy (cm ⁻¹)	Med.	Transition	λ_{\min} (nm)	λ_{\max} (nm)	References
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T₀ = 64126 gas

Irikura, Johnson, et al., 1992

State: C

Energy (cm ⁻¹)	Med.	Transition	λ _{min} (nm)	λ _{max} (nm)	References
	gas	c-a	330	362	Herzberg and Johns, 1966 Kim, Komissarov, et al., 2005 Kim, Hall, et al., 2006

State: b

Energy (cm ⁻¹)	Med.	Transition	λ _{min} (nm)	λ _{max} (nm)	References
T ₀ = 11497 ± 10	gas	b-a	465	1400	Herzberg, 1961 Herzberg and Johns, 1966 McKellar, Bunker, et al., 1983 Petek, Nesbitt, et al., 1987 Green, Chen, et al., 1989 Hartland, Xie, et al., 1992 Hartland, Qin, et al., 1993 Garcia-Moreno and Moore, 1993 Qin, Hartland, et al., 1994 Chang, Wu, et al., 1994 Fockenberg, Marr, et al., 1998 Marr, Sears, et al., 1998 Kobayashi, Pride, et al., 2000 Kobayashi and Sears, 2001 Hall, Komissarov, et al., 2004 Kobayashi, Hall, et al., 2006 Chang, Wang, et al., 2011 Chang, Xin, et al., 2011

Vib. sym.	No.	Approximate type of mode	cm ⁻¹	Med.	Method	References
a ₁	2	Bend	570 T	gas	AB	Herzberg and Johns, 1966

State: **a**

Energy (cm ⁻¹)	Med.	Transition	λ_{\min} (nm)	λ_{\max} (nm)	References
T _o = 3147 ± 5	gas	b-a	465	1400	<p>Herzberg, 1961</p> <p>Herzberg and Johns, 1966</p> <p>McKellar, Bunker, et al., 1983</p> <p>Leopold, Murray, et al., 1985</p> <p>Bunker and Sears, 1985</p> <p>Bunker, Jensen, et al., 1986</p> <p>Petek, Nesbitt, et al., 1987</p> <p>Petek, Nesbitt, et al., 1987, 2</p> <p>Jensen and Bunker, 1988</p> <p>Xie, Harkin, et al., 1989</p> <p>Xie, Harkin, et al., 1990</p> <p>Hartland, Xie, et al., 1992</p> <p>Hartland, Qin, et al., 1993</p> <p>Garcia-Moreno and Moore, 1993</p> <p>Qin, Hartland, et al., 1994</p> <p>Chang, Wu, et al., 1994</p> <p>Hartland, Qin, et al., 1995</p> <p>Fockenberg, Marr, et al., 1998</p> <p>Marr, Sears, et al., 1998</p> <p>Kobayashi, Pride, et al., 2000</p> <p>Kobayashi and Sears, 2001</p> <p>Hall, Komissarov, et al., 2004</p> <p>Kobayashi, Hall, et al., 2006</p>

Vib. sym.	No.	Approximate type of mode	cm ⁻¹	Med.	Method	References
<i>a</i> ₁	1	CH s-stretch	2806.01 ± 0.07	gas	LF LD	<p>Feldman, Meier, et al., 1978</p> <p>Petek, Nesbitt, et al., 1983</p> <p>Hartland, Qin, et al., 1993</p>
	1	CH s-stretch	2806.01 ± 0.07	gas	IR	Petek, Nesbitt, et al., 1989
	2	Bend	1352.6	gas	AB LF	<p>Herzberg and Johns, 1966</p> <p>Petek, Nesbitt, et al., 1987</p>

b_2	3	CH a-stretch	2864.97 ± 0.02	gas	LD IR	Petek, Nesbitt, et al., 1987, 2 Hartland, Qin, et al., 1993 Petek, Nesbitt, et al., 1983 Petek, Nesbitt, et al., 1989
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State: **X**

Vib. sym.	No.	Approximate type of mode	cm^{-1}	Med.	Method	References
a_1	2	Bend	963.10	gas	LMR DL	Sears, Bunker, et al., 1981 Sears, Bunker, et al., 1982 McKellar, Yamada, et al., 1983 Marshall and McKellar, 1986
b_2	3	CH ₂ a-stretch	3190 ± 5	gas	IR	Petek, Nesbitt, et al., 1989