Circumstellar and Interstellar Molecules

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Abstract

This paper details the current list of detected moledules in the interstellar medium (ISM) and circumstellar envelopes (CSEs). In tabulating these molecules, the methods used to detect them are also examined. These methods, almost exclusively, involve molecular spectroscopy. As of May 2013, there have been around 180 such molecules detected in the ISM or CSEs.

1 Atomic Spectroscopy

Atomic spectroscopy, also known as electronic spectroscopy, is a method of determining the chemical composition of some material (i.e. a gas cloud) by studying its light spectrum. These spectra will either be absorption or emission spectra. This phenomenon is entirely governed by the electron transitions of the valence electrons in the atoms occupying the material. If radiation of some kind is incident on an atom and has specific energy and wavelength the electron will transition to an excited state. If a source of continuous blackbody radiation is located behind a cold gas cloud, the atoms in the gas cloud will absorb some of the radiation at certain, specific wavelengths. This will then produce an absorption spectrum, essentially a continuous spectra with lines at certain wavelengths missing. A hot gas cloud will likely have many atoms with electrons already in an excited state. These electrons my spontaneously transition to a lower excited state, and in so doing emit a photon corresponding to the lost energy of the electron. This type of material will produce an emission spectrum, which only has lines at the specific wavelengths determined by the atoms within it. Atoms of different elements produce individually distinct spectra, allowing spectroscopy to identify the chemical compostion (the elements) contained in some cosmic material.

2 Molecular Spectroscopy

The detection and analysis of the spectra of molecules is not nearly as simple as that of single atoms. The introduction of more atoms adds greater complexity to the energy states in which the molecules reside, namely, the consideration of the nuclear motion as well as the electron motion. Using the simplification of the Born-Oppenheimer approximation, the motion of the electrons is considered with the nuclei fixed. Mathematically, this allows the wavefunctions for the electrons and nuclei to be separated (each dependent on their respective coordinates only):

$$\Psi_{\text{tot}} = \Psi_{\text{el}}(q_{\text{el}})\Psi_{\text{nuc}}(q_{\text{nuc}}). \tag{2.0.1}$$

In a similar manner, the nuclear wavefunction can also be separated into vibrational and rotational components. For molecules, vibrational motion is defined as the relative motion of the separation between the nuclei of the component atoms, whereas rotational motion is simply the change in orientation of the molecule as measured in the fixed laboratory frame. Experiments have shown empirically that the separation between vibrational energy levels is much larger than that of rotational energy levels, thus vibrational frequencies are also much larger than rotational frequencies. This allows the vibrational motion to be described by the rapidly moving electrons for a fixed molecular orientation. Or in other words, the three wavefunctions can be defined only in terms of their respective coordinates:

$$\Psi_{\mathrm{tot}} \approx \Psi_{\mathrm{el}}(q_{\mathrm{el}})\Psi_{\mathrm{vib}}(q_{\mathrm{vib}})\Psi_{\mathrm{rot}}(q_{\mathrm{rot}}). \tag{2.0.2}$$

Consequently, the total energy of the molecular system can be simply written as a sum of the energies of the three types of motion:

$$E_{\mathrm{tot}} = E_{\mathrm{el}} + E_{\mathrm{vib}} + E_{\mathrm{rot}}. \tag{2.0.3}$$

It is of enormous consequence that the Born-Oppenheimer separation leading to Equations 2.0.2 & 2.0.3, though just an approximation, albeit a very accurate approximation in most instances, gives a consistent and reliable description of the energy level scheme. This familiar energy level hierarchy ($\Delta E_{\mathrm{el}} \gg \Delta E_{\mathrm{vib}} \gg \Delta E_{\mathrm{rot}}$) is shown in Figure 1.

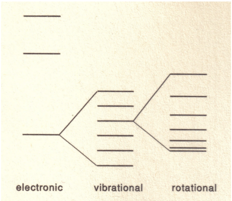

Figure 1: Molecular energy level diagram showing the Born-Oppenheimer classification. Each electron state contains a set of vibrational states, which in turn each contain a set of rotational states.[2]

As these three types of molecular motion are separable in this way, so too do these motions produce separate, and distinct spectra. These spectra are analyzed by the spectroscopy corresponding to each of the motions: electronic, vibrational, and rotational spectroscopy. They are also often named by the region of the electromagnetic spectrum that each examines: ultraviolet and visible, infrared, and microwave spectroscopy. In other words, electronic transitions absorb or produce photons in the ultraviolet and visible range, while vibrational transitions absorb or produce light in the infrared range, and finally rotational transitions absorb or produce photons in the microwave region. Though ideally, the spectra from the three types of motion could be analyzed separately, in real molecules the rotational and vibrational spectra tend to be analyzed together in "rovibrational" spectroscopy, sometimes vibrational and electronic spectra are analyzed together in "vibronic" spectroscopy, and sometimes all three spectra are measured simultaneoulsy in "rovibronic" spectroscopy.

3 Rotational Spectroscopy

Molecules in a gas will have some of their thermal energy stored in rotational energy. An isolated molecule will have this rotational energy quantized, where transitions between individual rotational levels gives rise to a rotational spectrum. These levels will remain well defined as long as the molecule remains isolated. Collisions with other molecules will likely change its rotational state and broaden the spectral lines. If the collision frequency is high enough compared to the rotation frequency, the lines will be broaden so much that the individual transitions would no longer be visible. Therefore, rotational spectroscopy is performed on gaseous samples at low pressures.

3.1 Classification of Molecular Rotors

The free rotation of a molecule is quantized, so that the rotational energy and the angular momentum can only take on certain fixed values related by the moment of inertia, I. Molecules have three moments of inertia, I_A, I_B, and I_C, about three mutually orthogonal axes, A, B, and C, with the origin at the center of mass of the system. Generally, the moments of inertia are defined as $I_A \leq I_B \leq I_C$. A convenient method of examining the rotations of the molecules is to divide them into four classes based on the symmetry of their structure: Spherical top molecules, linear molecules, symmetric top molecules, and asymmetric top molecules.

Spherical top molecules (spherical rotors) have all three moments of inertia equal to each other: $I_A = I_B = I_C$.

Linear molecules have their moments of inertia related by $I_A \ll I_B = I_C$. I_A can usuall be taken to be zero.

Symmetric top molecules (symmetric rotors) have two moments of inertia equal to each other $I_A = I_B$ or $I_B = I_C$. Thus symmetric rotors are broken down one tier further. Prolate symmetric tops (cigar shape) satisfy $I_A < I_B = I_C$, whereas oblate symmetric tops (disk shape) satisfy $I_A = I_B < I_C$.

Asymmetric top molecules (asymmetric rotors) have different values for all three moments of inertia.

3.2 Spherical Top Molecules

Spherical top molecules have no net dipole moment, therefore electric dipole transitions are forbidden, and pure rotational spectra cannot be observed by either absorption or emission spectroscopy.

3.3 Linear Molecules

Treating a diatomic molecule as a rigid rotor of two point masses, m_1, and m_2, separated by a distance r, then classicaly, its energy of rotation is equivalent to

$$E_{\text{rot}} = \frac{1}{2} I \omega^2 \tag{3.3.1}$$

where I is the moment of inertia of the rigid body and ω is its angular velocity (measured relative to a laboratory-fixed axis system). The moment of inertia for a diatomic molecule is given as

$$I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 \tag{3.3.2}$$

where μ is called the reduced mass. More generally, the moment of inertia is

$$I = \sum_i m_i r_i^2 \tag{3.3.3}$$

with m_i the mass of atom i at distance r_i from the center of mass.

Transforming Equation 3.3.1 from classical to quantum mechanics requires transforming the appropriate vectors to their operator representatives. It is unkown how velocity vectors transform, but transforming classical momenta is well established. In this case, the angular velocity vector $\boldsymbol{\omega}$ is changed to angular momentum $\boldsymbol{P}$. Equation 3.3.1 is thus rewritten as

$$E_{\text{rot}} = \frac{1}{2} \boldsymbol{P}^2 / I \tag{3.3.4}$$

where

$$\boldsymbol{P} = I \boldsymbol{\omega}.$$

In transforming to quantum mechanical operators, $\boldsymbol{P}$ is replace by $\hbar \boldsymbol{J}$. With this replacement, the energy expression is also transformed to an operator, the rotational Hamiltonian H_{rot},

$$H_{\text{rot}} = \frac{\hbar^2}{2I} \boldsymbol{J}^2 \tag{3.3.5}$$

Solving the hamiltonian for its corresponding eigenvalues and eigenfunctions, we find that $\boldsymbol{J}^2$ satisfies:

$$\boldsymbol{J}^2\Psi_{JM} = J(J+1)\Psi_{JM} \tag{3.3.6}$$

J is the rotational angular quantum number and takes integral values only, and Ψ_{JM} is the corresponding eigenfunction (and, as it turns out, rotational wavefunction). Therefore, the allowed energy levels of H_{rot} are

$$E_{\mathrm{rot}} = \frac{\hbar^2}{2I}J(J+1) \qquad \text{where } J = 0,\, 1,\, 2,\, \ldots \tag{3.3.7}$$

Clearly, the rotational energy levels increase quadratically with J, and depend inversely on I. The coeffecient of $J(J+1)$ determines how closely spaced the energy levels are, and is known as the rotational constant, B_{e}. In wavenumber units (cm^{-1}), the rotational constant is

$$B_{\mathrm{e}}/\mathrm{cm}^{-1} = \frac{\hbar^2}{2hcI} \tag{3.3.8}$$

And finally, in wavenumber units, the rotational energy levels are given by

$$\frac{E_{\mathrm{rot}}}{hc} = B_{\mathrm{e}}J(J+1) \qquad \text{where } J = 0,\, 1,\, 2,\, \ldots \tag{3.3.9}$$

Using the diatomic molecules allows the hamiltonian to be solved in this way, but these rotational energy levels in Equation 3.3.9 are true of any linear molecule.

3.4 Centrifugal Distortion

The above energy levels are an ideal case, but the simple motion of rotating creates a centrifugal force that wants to pull the atoms apart. The bonds between atoms are not infinitely stiff, but as the molecule rotates faster (J gets larger) the masses move apart, increasing the moment of inertia and reducing the rotational constant. Thus, a term is added to Equation 3.3.9 to account for this reduction. Using Hooke's law and treating stretching motion as a simple harmonic oscillator, then using a taylor expansion and taking the first order correction term, the centrifugal distortion term is found to be $-D_{\mathrm{e}}J^2(J+1)^2$. Consequently, the rotational kinetic energy is

$$\frac{E_{\mathrm{rot}}}{hc} = B_{\mathrm{e}}J(J+1) - D_{\mathrm{e}}J^2(J+1)^2. \tag{3.4.1}$$

D_{e} is the centrifugal distortion constant given by

$$D_{\mathrm{e}} = \frac{4B_{\mathrm{e}}^3}{\omega_{\mathrm{e}}^2} \tag{3.4.2}$$

where ω_e is the harmonic vibrational frequency (in cm^{-1}).

As only molecules that are centrosymmetric (i.e. homonuclear diatomic molecules) vibrate harmonically, most linear molecules vibrate anharmonically. If anharmonicity is to be taken into account, terms in higher powers of J (higher order correction terms from the above taylor expansion) should be added to the expression for the energy levels.

3.5 Symmetric Top Molecules

The rotational motion for symmetric top molecules is governed by two quantum numbers: the total angular momentum, J, and its projection on the symmetric axis, K. A prolate symmetric top has energy levels given by

$$\frac{E_{\text{rot}}}{hc} = BJ(J+1) + (A-B)K^2, \tag{3.5.1}$$

where the rotational constants A and B are equal to

$$A = \frac{\hbar^2}{2hcI_A}, \tag{3.5.2}$$

$$B = \frac{\hbar^2}{2hcI_B}, \tag{3.5.3}$$

and $A > B$. An oblate symmetric top has energy levels equivalent to

$$\frac{E_{\text{rot}}}{hc} = BJ(J+1) + (C-B)K^2, \tag{3.5.4}$$

where the rotational constant C is equal to

$$C = \frac{\hbar^2}{2hcI_C}, \tag{3.5.5}$$

and $C < B$.

3.6 Asymmetric Top Molecules

Since asymmetric top molecules have three different moments of inertia, there is no general formula describing the energy levels. With these three independent moments of inertia, two other independent quantum numbers need to be considered, however their values cannot be determined in closed form.

4 Vibrational Spectroscopy

4.1 Simple Harmonic Oscillator

Once again, begin with a diatomic molecule, as it is the simplest molecular form, and thus most logical place to start. Take the simplest vibrational coordinate

$$q = r - r_{\mathrm{e}} \tag{4.1.1}$$

where r and r_{e} are the instanteous and equilibrium bond lengths respectively. First, solving the simple harmonic oscillator, and reducing the problem to a one-body form, the Hamiltonian is given as a sum of the kinetic and potential energies (Hooke's Law)

$$\boldsymbol{H}_{\mathrm{vib}} = \frac{1}{2}\boldsymbol{p}^2/\mu + \frac{1}{2}k\boldsymbol{q}^2 \tag{4.1.2}$$

where $\boldsymbol{p}$ is the linear momentum vector, μ is the reduced mass, and k is the spring constant.

The energy eigenvalues that are solutions to Equation 4.1.2 are given as

$$E_{\mathrm{v}} = (v + \frac{1}{2})h\nu \tag{4.1.3}$$

or more appropriately

$$E_{\mathrm{v}} = (v + \frac{1}{2})hc\omega_{\mathrm{e}}. \tag{4.1.4}$$

v is the vibrational quantum number, which can only take integer values 0, 1, 2, 3, ...

4.2 Anharmonic Oscillator

Since most molecules are not ideal, their atoms do not simple vibrate harmonically. On the contrary, an anharmonic oscillator term needs to be added to the hamiltonian to account for this effect. This additional anharmonic term takes the form of the Morse potential function

$$U(q) = D_{\mathrm{e}}[1 - e^{-\beta q}]^2. \tag{4.2.1}$$

The energy eigenvalues that satisify this anharmonic hamiltonian are

$$\frac{E_{\text{vib}}}{hc} = (v + \frac{1}{2})\omega_{\text{e}} - (v + \frac{1}{2})^2 \omega_{\text{e}}\chi_{\text{e}}. \tag{4.2.2}$$

where χ_{e} is a positive quantity called the anharmonicity constant.

5 Rovibrational Spectroscopy

Molecular transitions most often occur with simultaneous transitions between rotational and vibrational energy levels. For heteronuclear diatomic molecules having a general formula AB the energy levels for the rovibrational spectrum are $E_{\text{rot-vib}} = G(v) + F_{\text{v}}(J)$. $G(v)$ is the anharmonic oscillator component given by

$$G(v) = \omega_{\text{e}}(v + \frac{1}{2}) - \omega_{\text{e}}\chi_{\text{e}}(v + \frac{1}{2})^2. \tag{5.0.3}$$

$F_{\text{v}}(J)$ is the rotational component given by

$$F_{\text{v}}(J) = B_{\text{v}}J(J+1) - DJ^2(J+1)^2. \tag{5.0.4}$$

The rotational constant, B_{v}, depends on the moment of inertia of the molecule I_{v}, which varies with the vibrational quantum number v,

$$B_{\text{v}} = \frac{\hbar^2}{2hcI_{v}}, \tag{5.0.5}$$

$$I_{\text{v}} = \frac{m_{\text{A}}m_{\text{B}}}{m_{\text{A}} + m_{\text{B}}} d_{\text{v}}^2. \tag{5.0.6}$$

The energy levels of the rovibrational states are finally, therefore, given by

$$E_{\text{rot-vib}} = \left[\omega_{\text{e}}(v + \frac{1}{2}) + B_{\text{v}}J(J+1)\right] - \left[\omega_{\text{e}}\chi_{\text{e}}(v + \frac{1}{2})^2 + DJ^2(J+1)^2\right]. \tag{5.0.7}$$

The first two terms correspond to the harmonic oscillator and rigid rotor, and the second two terms make a correction for anharmonicity and centrifugal distortion.

For homonuclear diatomic molecules, the electric dipole moment is zero, so the fundamental vibration transition is forbidden. However, weaker electric quadrapole transitions can sometimes be seen in these molecules.

6 Electronic Spectroscopy

Electronic spectroscopy for molecules is similar to that for single atoms. The component of the angular momentum vector of each electron along the internuclear axis can only take values $m_l = l, (l-1), (l-2), \ldots, -l$. The variable, λ, is the absolute value of m_l, where $\lambda = 0, 1, 2, \ldots$, correspond to σ, π, δ, …, analagous to atomic s, p, d, …, orbitals. For centrosymmetric molecules, parity under inversion is indicated by g for even and u for odd. The term symbols of electronic levels in diatomic molecules are characterized by the component of the total angular momentum along the intermolecular axis, $\Lambda = \sum_i \lambda_i$. Corresponding to $\Lambda = 0, 1, 2, \ldots$, diatomic molecules have designations Σ, Π, Δ, …, analagous to S, P, D, … for atoms. The degeneracy of the term is indicated by a superscript with the value $2S+1$, representing the orientation of the total spin angular momentum, Σ, with respect to the internuclear axis, where Σ can take the values $S, (S-1), (S-2), \ldots, -S$. The total angular momentum Ω is the sum of the orbital and spin angular momenta along the internuclear axis, $\Omega = \Lambda + \Sigma$. Molecular terms can then be designated by ${}^{2S+1}\Lambda_{u,\,g}$, where the subscripts only apply to centrosymmetric species. For Σ terms, a $\pm$ superscript indicates the behavior of the wave function under reflection in the plane containing the two nuclei.

For polyatomic molecules, electronic transitions are often connected to the excitation of specific types of electrons or electrons associated with a small group of atoms in the species.

7 Selection Rules

Finally, the selection rules in all of the above types of spectroscopy are integral in determining the transition frequencies and wavelengths of the absorbed or emitted photons. These selection rules describe which transitions are allowed, and therefore which energies these transitions can have. The first rule is that all of the molecules must have a permanent electric dipole moment. Those that do not can be observed through a magnetic dipole moment or an electric quadrapole moment, etc., but these are much weaker and thus harder to distinguish.

Linear homonuclear diatomic molecules, have no net electric dipole moment, but weak rotational quadrapole transitions with $\Delta J = \pm 2$ can be observed. Linear heteronuclear diatomic molecules have allowed transistions with $\Delta J = \pm 1$. In general, rotational transitions need to satisfy $\Delta J = 0, \pm 1$ and $\Delta K = 0$ or ± 1, and a parity transition of $+ \leftrightarrow -$.

Electric dipole rovibrational transitions must satisfy $\Delta v = \pm 1$ and $\Delta J = 0, \pm 1$, where $\Delta J = +1$ corresponds to what is known as the R branch, $\Delta J = 0$ to the Q branch, and $\Delta J = -1$ to the P branch. These branches are illustrated in Figure 2. $\Delta v = \pm 2$ is also allowed and is called an overtone. Electric quadrapole transitions must satisfy $\Delta J = 0, \pm 2$, where $\Delta J = +2$ corresponds to the S branch, $\Delta J = 0$ to the Q branch, and $\Delta J = -2$ to the O branch. Each must also satisify parity transitions of $+ \leftrightarrow -$.

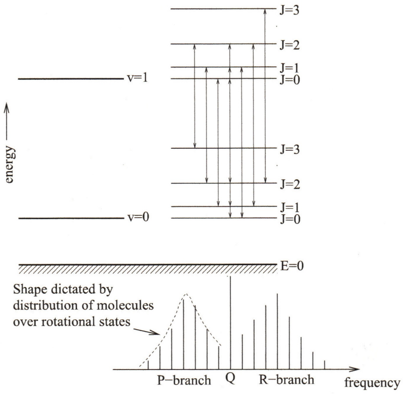

Figure 2: Rovibrational energy level diagram and emisson spectrum[1]

The selection rules for electronic transitions are $\Delta\Lambda = 0, \pm 1$, $\Delta S = 0$, $\Delta\Sigma = 0$, and $\Delta\Omega = 0, \pm 1$. The selection rules for symmetry are, for Σ terms, only $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$ are allowed. Lastly, for centrosymmentric species, only transitions with a change in parity (e.g. $u \leftrightarrow g$) are allowed.

8 Instellar and Circumstellar Molecules[5]

2 Atoms	3 Atoms	4 Atoms	5 Atoms	6 Atoms	7 Atoms
H_2	C_3	$c-C_3H$	C_5	C_5H	C_6H
AlF	C_2H	$l-C_3H$	C_4H	$l-H_2C_4$	CH_2CHCN
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H
C_2	C_2S	C_3O	$l-C_3H_2$	CH_3CN	HC_5N
CH	CH_2	C_3S	$c-C_3H_2$	CH_3NC	CH_3CHO
CH^+	HCN	C_2H_2	H_2CCN	CH_3OH	CH_3NH_2
CN	HCO	NH_3	CH_4	CH_3SH	$c-C_2H_4O$
CO	HCO^+	HCCN	HC_3N	CH_3NH^+	H_2CCHOH
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-
CP	HOC^+	HNCO	HCOOH	NH_2CHO	
SiC	H_2O	HNCS	H_2CNH	C_5N	
HCl	H_2S	$HOCO^+$	H_2C_2O	$l-HC_4H$	
KCl	HNC	H_2CO	H_2NCN	$l-HC_4N$	
NH	HNO	H_2CN	HNC_3	$c-H_2CCNH$	
NO	MgCN	H_2CS	SiH_4	H_2CCNH	
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-	
NaCl	N_2H^+	$c-SiC_3$	C_4H^-	HNCHCN	
OH	N_2O	CH_3	HC(O)CN		
PN	NaCN	C_3N^-	HNCNH		
SO	OCS	PH_3	CH_3O		
SO^+	SO_2	HCNO			
SiN	$c-SiC_2$	HOCN			
SiO	CO_2	HSCN			
SiS	NH_2	H_2O_2			
CS	H_3^+	C_3H^+			
HF	H_2D^+ HD_2^+				
HD	SiCN				
FeO	AlNC				
O_2	SiNC				
CF^+	HCP				
SiH	CCP				
PO	AlOH				
AlO	H_2O^+				
OH^+	H_2Cl				
CN^-	KCN				
SH^+	FeCN				
SH	HO_2				
HCl^+	TiO_2				
TiO					

8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	>12 Atoms
CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	$c{-}C_6H_6$	$HC_{11}N$
$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	$C_2H_5OCH_3$	C_{60}
CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	$n{-}C_3H_7CN$	C_{70}
C_7H	CH_3CH_2OH	CH_3CH_2CHO			
C_6H_2	HC_7N				
CH_2OHCHO	C_8H				
$l{-}HC_6H$	$CH_3C(O)NH_2$				
CH_2CHCHO	C_8H^-				
CH_2CCHCN	C_3H_6				
H_2NCH_2CN					
CH_3CHNH					

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