THE MOLECULAR UNIVERSE

ASTROCHEMISTRY OR MOLECULAR ASTROPHYSICS A MULTIDISCIPLINARY FIELD

Lecturer III. Lecture I

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Molecules in the Cosmos : CHEMISTRY IN INTERSTELLAR AND CIRCUMSTELLAR CLOUDS









Position	Institution	Dates
Ph. D. Student	Observatorio Astronómico Nacional (Yebes, Spain)	1/9/78 - 11/1/79
Ph. D. Student	Paris Observatory (France)	11/1/79 -31/09/83
Research Scientist	CNRS. Obs. Grenoble. France -commissioning of the 30m and the PdBI-	1/10/83 - 31/12/88
Astronomer Co-Director	Obs. Astron. National 30m Radiotelescope	1/1/89 -30/4/96 1/1/89-31/03/92
Research Professor	Consejo Superior de Investigaciones Científicas -ISO, ALMA, Herschel-	1/5/96 – present
Mission Scientist Herschel	ESA	1/1/1998-present
Vicediretor	Center for Astrobiology	1/10/2010- 1/10/2011

Interstellar and circunstellar media. Stellar evolution.

- i. Cold dark clouds. Precursors of stellar formation.
- ii. Star forming regions. Low mass protostars. High mass star formation
- iii. Line Surveys
- iv. Research of new molecular species (≈50 molecules found in space)
- v. Chemistry
- vi. Radiative Transfer
- vii. Infrared Astrophysics
- viii. Radiotelescopes. Instrumentation
- ix. Evolved stars (AGB-PPN-PN)
 - Physical Conditions
 - Astrochemistry. Spectral surveys.
 - Circunstellar masers.
- x. Star formation in external galaxies.
- xi. Remote sensing (Earth atmosphere and surface. ATM package)
 - P/T soundings.
 - Minor Gases.
 - Scattering and Polarization due to hydrometeors.
 - Calibration in Radioastronomy

MOLECULAR ASTROPHYSICS. AN INTRODUCTORY COURSE

I. Introduction

- A) Why Molecular Astrophysics
 - Where molecules are found?
- What information can be obtained from the observation of molecular lines?
- Molecular Astrophysics : What we need to interpret molecular observations?
- B) Molecular emission/absorption at all Wavelength Domains
 - Basic concepts of molecular spectroscopy
 - Rotational transitions. Examples
 - Vibrational transitions. Examples
 - Electronic transitions. Examples
- II. The Formation of Molecules in the Interstellar Medium
 - An overview of the needs for specific chemical models of the ISM
 - Basic chemical processes in the ISM. The role of cosmic rays
 - Formation of Molecular Hydrogen on the dust grains
 - Photodissociation

III. Chemistry in Dense Clouds

Basic chemical networks -Isotope Fractionation in cold dark clouds -Shocks in star forming regions. -The chemistry of high temperature region.

- IV. Chemistry in the Circumstellar Envelopes of Evolved Stars
 - Molecule formation under thermal equilibrium
 - The chemical evolution of circumstellar envelopes
 - Post-AGB objects
 - Planetary Nebula
- V. The interpretation of molecular spectra
- Radiative transfer in the ISM and the CSM
 - Collisional and Radiative excitation
 - LVG models
 - The need for non-local radiative transfer codes

UNIDENTIFIED INTERSTELLAR LINES IN THE YELLOW AND RED*

PAUL W. MERRILL AND O. C. WILSON

ABSTRACT

Six unidentified interstellar lines (Table 1) are discussed. Following a brief history of previous observations, Tables 2 and 3 give widths and central absorptions of three of the lines. The total intensity of λ 6284, which, in the mean, equals the average for the detached lines D1 and D2, shows a somewhat stronger correlation with stellar color excess than does the intensity of the D lines. The widths of the unidentified lines, which are rather diffuse and not sharp like the D lines, and other facts make an atomic origin improbable. The lines may be portions of molecular bands, as yet unidentified. Several facts, however, suggest that the lines are produced by small solid particles, perhaps closely related to those that cause space reddening.

CARNEGIE INSTITUTION OF WASHINGTON MOUNT WILSON OBSERVATORY August 1937



NOTES

CONSIDERATIONS REGARDING INTERSTELLAR MOLECULES

ABSTRACT

An attempt has been made to compute the numbers of certain molecules in interstellar space. The results obtained are unfavorable to Saha's identification of one of Merrill's interstellar lines with Na_2 . A search for the bands of CH, OH, NH, CN, and C_2 would appear to be promising.

> P. Swings L. Rosenfeld

Department of Astrophysics University of Liége, Belgium May 1937

CONSIDERATIONS REGARDING COMETARY AND INTERSTELLAR MOLECULES*

P. Swings¹

ApJ 1942, 95, 270

ABSTRACT

The presence of CH^+ molecules in comets is demonstrated by the attribution of three cometary lines, $\lambda\lambda$ 4231, 4238.5, and 4254.4, to the first transitions of the three branches of the (0, 0) band. There is also good evidence for the presence of the (1, 0) band of CH^+ . The CH^+ molecules are observed in the head and in part of the tail.

The spectral region $\lambda\lambda$ 3560-3600 of cometary spectra is discussed. It seems very probable that some of the features are not due to the $\Delta v = +1$ sequence of CN and to the (8, 0) band of CO^+ and that the (0, 0) band of OH^+ plays some role. But spectrograms of higher resolving-power are required to settle this matter.

Additional evidence is given for the presence of the isotopic bands of C_2 in cometary spectra; the $C^{12}C^{13}$ molecule is observed in the three transitions (1, 0), (2, 1), and (3, 2).

The problems of molecular formation, dissociation, and ionization are quite different in interstellar space and in comets. In interstellar space the main source of molecular formation is by two-body encounters with simultaneous emission of radiation. In comets the diatomic molecules result from the liberation of occluded gases and from the photodissociation of more complex molecules.

The dissociation equilibrium of CH^+ in interstellar space is discussed. Account has to be taken of the fact that practically all the CH^+ molecules are on the lowest rotational level. Thus the photodissociation may arise only from this lowest level, whereas the formation by capture may lead to any excited level. The corresponding correction factor has a value of the order of 10³. The computed abundance of CH^+ is in agreement with the observations.

The ionization equilibrium of CH^+ and CH is considered. It is suggested that the electron density in the regions of molecular absorption is about 10⁻¹ electron per cubic centimeter.

The dissociation and ionization equilibrium of CN cannot yet be discussed because of the absence of essential physical data, especially the ionization potential of CN. The abundance of C_2 molecules must be much lower than that of CN or CH; moreover each (v', o) band of the interstellar C_2 molecules would possess a large number of absorption lines, instead of three or less as in the case of CH, CH^+ , and CN. From these considerations it is concluded that interstellar lines of C_2 must be very much weaker than those of CH, CH^+ , and CN.

THE INTERSTELLAR λ 4430 BAND

Jesse L. Greenstein and Lawrence H. Aller

Mount Wilson and Palomar Observatories and Observatory of the University of Michigan Received December 9, 1949

ABSTRACT

Measured equivalent widths of the interstellar λ 4430 band made on spectrograms taken at the Mc-Donald Observatory are given in Table 1. The profile is found symmetric and smooth. Correlations of λ 4430 with other interstellar features are given in Table 2. The band is most strongly correlated with the interstellar λ 6284, fairly well correlated with interstellar reddening, and may be well correlated with interstellar polarization. Diffuse absorption bands occur in the solid and liquid states in molecules which have incomplete inner shells of electrons. Such substances are often paramagnetic, as in the case of iron alums and salts of the rare earths. It is possible that the compounds responsible for the diffuse interstellar bands also are active in the orientation of small, elongated paramagnetic grains and thus produce the interstellar polarization.

THE ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

VOLUME 113

MAY 1951

NUMBER 3

THE DENSITY OF MOLECULES IN INTERSTELLAR SPACE

DAVID R. BATES* AND LYMAN SPITZER, JR. University College, London, and Princeton University Observatory Received January 22, 1951

ABSTRACT

Analysis of Adams' visual estimates indicates that the interstellar lines $CH^+ \lambda 4232$ and $CH \lambda 4300$ originate in two types of regions—in the normal obscuring clouds responsible for selective extinction and in circumstellar clouds near stars of late B types. In stars of types O and early B, the intensities of $\lambda 4232$ and $\lambda 4300$ are closely correlated with color excess, E_1 ; the mean particle densities of these molecules, averaged over the volume in and between the clouds, is about 10^{-8} cm⁻³. Among stars of later B types, many unreddened stars ($E_1 \leq 0.05$) show strong molecular lines; the number of molecules per square centimeter in the line of sight averages about 3×10^{12} cm⁻² for types B2–B5. Of fifteen unreddened stars showing the molecular lines, the velocity difference, interstellar minus stellar lines, is positive in all but one case.

A theoretical analysis shows that many of the rate coefficients affecting the equilibrium abundance of CH and CH^+ molecules have different values from those assumed hitherto. In particular, the formation of CH by radiative association is markedly slower than previously believed, and there is some possibility that dissociative recombination $(CH^+ + e \rightarrow C + H)$ is very rapid. If best estimates are adopted for all the rate coefficients, the observed molecular densities can be explained only if the clouds are extremely concentrated, with a central density $n_0(H)$ of neutral H about 10³ cm⁻³. If, however, the *f*-value for $CH \ \lambda 4300$ is increased by a factor of 30 above the theoretical figure, an increase for which there is some observational evidence, agreement is obtained with $n_0(H)$ equal to about 80. Alternatively, the molecules may be formed at the surface of the grains.

The molecules observed in circumstellar clouds may originate from the sublimation of CH_4 from the grains, a process which should occur when the internal temperature of the grains rises much above some 25° K. The CH_4 molecules will dissociate, forming a hemispherical shell of CH^+ molecules on the side of the star from which the cloud is advancing. This hypothesis explains why the circumstellar molecular lines in an unreddened star show a greater radial velocity than do the stellar lines, and quantitative agreement with the number of observed CH^+ molecules is obtained with reasonable values for the unfortunately rather uncertain physical parameters. However, once again, agreement with the observed abundance of CH can be obtained only if the *f*-value for λ 4300 is taken to be 30 times that indicated by quantal calculation.

MOLECULAR SPECTRA

and

MOLECULAR STRUCTURE

I. SPECTRA OF DIATOMIC MOLECULES

BY

GERHARD HERZBERG, F.R.S. National Research Council of Canada

With the co-operation, in the first edition, of J. W. T. SPINKS, F.R.S.C.

Nobel prize in Chemistry

1950

SECOND EDITION

The observation that in interstellar space only the very lowest rotational levels of CH, CH⁺, and CN are populated is readily explained by the depopulation of the higher levels by emission of the far infrared rotation spectrum (see p. 4 ±) and by the lack of excitation to these levels by collisions or radiation. The intensity of the rotation spectrum of CN is much smaller than that of CH or CH⁺ on account of the smaller dipole moment as well as the smaller frequency [due to the factor ν^4 in (I, 48)]. That is why lines from the second lowest level (K = 1) have been observed for CN. From the intensity ratio of the lines with K = 0 and K = 1 a rotational temperature of 2.3° K follows, which has of course only a very restricted meaning.

What is the scope of Molecular Astrophysics/Astrochemistry ?

- Molecules as tracers of physical and chemical conditions
- Molecular Clouds
- Pre-stellar cores
- Low/high mass star forming regions
- Solar System
- Protoplanetary disks
- Planetary disks
- Galaxies (ISM)
- Cosmology (High z molecules)





ASTROCHEMISTRY: Where Astrophysics becomes Chemistry

MOLECULAR ASTROPHYSICS: Where Astrophysics becomes Molecular Spectroscopy

Where molecules are found ?

Is the observation of molecules a mandatory step to understand the chemical evolution of the Universe ?

What we need to use molecules as working tools ?

In Galaxies

© European Southern Observatory





ESO PR Photo 20c/99 (30 April 1999











In high redshift quasars ...





Detection of an object at z=4.7 in the emission of CO (PdB interferometer)



In dark clouds

The external layers of the clouds are illuminated and heated by the

galactic UV field. The dust grains absorb the UV photons and protect the inner regions of the clouds





Jets from Young Stars

HST · WFPC2

PRC95-24a · ST Scl OPO · June 6, 1995 C. Burrows (ST Scl), J. Hester (AZ State U.), J. Morse (ST Scl), NASA



Visible • WFPC2

Diagram of HH 30 Circumstellar Disk & Jet Proto-Star Accretion Disk-Jet

HH111 Hubble Space Telescope WFPC2 • NICMOS

NASA and B. Reipurth (CASA, University of Colorado) • STScI-PRC00-05



Stellar jets







War<u>m Molecula</u>r Clouds

















Trifid nebula in the optical (top left panel) and in the mid-IR observed with ISO. The central object is a bright O7 star.

300

200

100

600

400

200

300

200

100

0

The distribution of the molecular gas molecular is shown in the right bottom panel (CO J=3-2 emission observed with the CSO telescope).





wavelength (μm)





 $V_{LSR} (kms^{-1})$



In Planets and Moons




Fig. 20.— Integrated HDO line emission from the atmosphere of Mars. The brightest emission is centered on the north pole, indicating that sublimation of seasonal water deposits in the north polar cap has begun.

In Comets ...



Even in impact of Comets





Impact of Fragment A of Comet Shoemaker-Levy 9 on Jupiter Infrared image in the 2.3 micron methane band taken using MAGIC on the 3.5-m telescope, Calar Alto Observatory, Spain, 16/07/94











FIG. 1.—A part of the spectrum of the 0–0 band of the δ system ($b^{1}\Pi$ – $a^{1}\Delta$) of TiO. (a) Laboratory spectrum; (b) sunspot spectrum; (c) photosperic spectrum.





ATMOS (SKYLAB) SOLAR SPECTRUM



All frequencies can be computed with a few constants !

Molecules in evolved stars



The far-IR spectrum of IR+10216 (C-rich) is dominated by the pure rotational lines of CO and HCN (in all v_1 , v_2 , and v_3 states)







In Planetary Nebula





Hourglass Nebula · MyCn18

HST · WFPC2

PRC96-07 · ST Scl OPO · January 16, 1996 R. Sahai and J. Trauger (JPL), the WFPC2 Science Team and NASA



HST · WFPC2 **Planetary Nebula NGC 7027** PRC96-05 · ST Scl OPO · January 16, 1996 · H. Bond (ST Scl) and NASA

Egg Nebula · CRL 2688 PRC96-03 · ST Scl OPO · January 16, 1996 R. Sahai and J. Trauger (JPL), the WFPC2 Science Team and NASA

HST · WFPC2

Number of Atoms												
2	3	4	5	6	7	8	9					
H_2	H_2O	NH ₃	SiH ₄	CH ₃ OH	CH ₃ CHO	CH ₃ CO ₂ H	CH ₃ CH ₂ OH					
OH	H_2S	H_3O^+	CH ₄	NH ₂ CHO	CH ₃ NH ₂	HCO ₂ CH ₃	(CH ₃) ₂ O					
SO	SO ₂	H ₂ CO	CHOOH	CH ₃ CN	CH ₃ CCH	CH ₃ C ₂ CN	CH ₃ CH ₂ CN					
SO+	HN_2^+	H ₂ CS	HC ≡CCN	CH ₃ NC	CH ₂ CHCN	C ₇ H	H(C≡C) ₃ CN					
SiO	HNO	HNCO	CH ₂ NH	CH ₃ SH	HC₄CN	H_2C_6	$H(C \equiv C)_2 CH_3$					
SiS	SiH ₂ ?	HNCS	NH ₂ CN	C ₅ H	C ₆ H		C ₈ H					
NO	NH_2	CCCN	H ₂ CCO	HC ₂ CHO	$c-CH_2OCH_2$							
NS	H_3^+	HCO_2^+	C₄H	$CH_2 = CH_2$	C ₇ ?		10					
HCI	NNO	CCCH	$c-C_3H_2$	H ₂ CCCC								
NaCl	HCO	c-CCCH	CH ₂ CN	HC ₃ NH ⁺			CH ₃ COCH ₃					
KCI	HCO+	ccco		ecent detec	tion of anio	ns•	$CH_3(C \equiv C)_2 CN?$					
AICI	ocs	CCCS	SiC ₄			11.5.						
AIF	CCH	HCCH	H ₂ CCC	$\mathbb{N}^{-}, \mathbb{C}_{3}\mathbb{N}^{-}, \mathbb{C}_{3}$	5 ¹ N ⁻ ,		11					
PN	HCS ⁺	HCNH ⁺	HCCNC C	₄ H ⁻ ,C ₆ H ⁻ .C ₈	H-							
SiN	c-SiCC	HCCN	HNCCC				H(C≡C)₄CN					
NH	cco	H ₂ CN	H ₃ CO ⁺	5 actions								
СН	CCS	c-SiC ₃		15 cations			13					
CH+	C ₃	CH ₃										
CN	MgNC	CH ₂ D ⁺ ?	>]	00 Carbon	Molecules		H(C≡C)₅CN					
co	NaCN											
CS	CH_2		10		• • •							
C_2	MgCN	CH		Nietai-bea	ring Molec	ules						
SIC	HOC+	CH,	6	rings + C_{60}	$\& C_{70} + PA$	Hs						
CP	HCN	CN										
CO+	HNC	1040		70 00	00 0000							
HF	SICN 1940 50 60 70 80 90 2000											
	KCN12			rear								

MODELING ASTROPHYSICAL DATA





LVG multishell models



MODELING

LVG multishell models



MODELING

 T_A^* (K)

0.1

0.05

0

LVG multishell models



 $V_{\rm LSR}$ (km s⁻¹)

0

Molecules as probes of T and n_H



Based on figure by R. Genzel (1991)

ASTROCHEMISTRY AS A MULTISDICIPLINAR FIELD



THE POWER OF SINGLE DISHES and SMALL INTEREFEROMETERS

-

-

1

1214

THE FUTURE : ALMA

THE FIRST STEP TOWARDS CHEMISTRY : MOLECULAR ORBITALS AND THE STABILITY OF MOLECULES

The Molecular Bond

The problem of molecular stability has to be addressed in a strict quantum frame.

In atoms the electrons are described by their atomic orbitals.

Each atom has a number of configurations corresponding to the different ways the electrons fill the energy levels.

All atomic properties are perfectly defined by the atomic orbitals describing the electronic density around the nucleus.

The main difference between atoms and molecules is that in atoms electrons are submitted to a central potential while in molecules the electrons are submitted to a potential arising from all nuclei, i.e., each electron moves under the action of all nuclei.

The goal of molecular physics is to find the wave function $\psi(r,\theta,\phi)$ for each electron in the molecule and the different energy levels of the molecule (rotation, vibration, and electronic levels).

 ψ^2 represents the density of electronic cloud in each point around the nuclei. Very sofisticated methods have to be used to obtain the energy levels with the accuracy required in molecular spectroscopy (Earth or Space) Assuming a molecule can be described from our experience in atomic physics :

1) Each molecular orbital will contain two electrons with opposite spins.

2) In the ground state electrons start to fill orbitals from the lowest energy to the highest levels

3) In the ground state and in the simplest approximation the electronic energy is obtained by addind the energies of the individual electrons (no interaction at all between electrons).

4) The wave function is the product of the mono-electronic wave functions.

With these simple assumption let us consider molecular hydrogen (H_2) , i.e., the simplest molecule, and the most abundant one in the space.

Let H_A and H_B be two atoms of hydrogen and let ψ_A and ψ_B the wave functions of the electron in atoms H_A and H_B when both atoms are far away.

Obviously these wave functions do not represent the electrons when the two atoms are very close and forming, perhaps, molecular hydrogen.

However, the electron of atom H_A when H_A is far from H_B will be reasonably well represented by ψ_A and when the same electron is close to atom H_B by ψ_B . It is reasonable to think that the wave function describing the electrons in the molecule of hydrogen can be given by

 $\Psi_{AB} = \psi_A + \lambda \psi_B$

The square of λ represents the contribution of each atomic orbital to the molecular orbital. In the case of H₂ it is obvious that $\lambda^2 = 1$ and $\lambda = \pm 1$

Hence, these very simple hypothesis let us to the following conclusions :

A) There are two possible states with different electronic energy. If the energy of the electrons 1s in the hydrogen atoms is E_0 , then one of these two levels will have energy $E_+ < E_0$ and the other will have an energy $E_- > E_0$.

B) The molecular orbital

 $\Psi_{+} = \Psi_{A} + \Psi_{B}$

will have the energy E₊ while the molecular orbital

 $\Psi_{-} = \psi_{\mathsf{A}} - \psi_{\mathsf{B}}$

will have the energy E_

C) The ground state of the molecule is obtained when two electrons are placed in the orbital E_+ . Obviously, both electrons should have opposite spins.

D) The orbital E₋ may be partially or fully used by the electrons. The associated states correspond to the excited states of the molecule. E) The electronic energy of the molecule, in this simple approximation, is the sum of the indivual energies of the electrons. In the ground state is, hence, 2E₊.

F) The wave function of the system, Φ , is the product of the individual wave functions of the electrons (1 y 2)

 $\Phi = \Psi_{+}(1) \Psi_{+}(2) = [\psi_{A}(1) + \psi_{B}(1)] [\psi_{A}(2) + \psi_{B}(2)]$

F) The dependency of the electronic energy of the system as a function of the internuclear distance will have the following shape



The function correspondind to the orbital Ψ_+ has a very well defined minimum for r = 0.85 A (experimental = 0.74 A !!!) and the bondind energy is 2.7 eV (experimental 4.7 eV !!!, the interaction between electrons has not been considered; also the fact that two protons interact with each electron has to be included).

The orbital Ψ_{-} shows a continuum increase of energy when the distance between the atoms decreases. It is an unbound state. The electronic density probability in both orbitals Ψ_{+} and Ψ_{-} is given by

 $\Psi_{+}^{2} = \psi_{A}^{2} + \psi_{B}^{2} + 2\psi_{A}\psi_{B}$ $\Psi_{-}^{2} = \psi_{A}^{2} + \psi_{B}^{2} - 2\psi_{A}\psi_{B}$

The electronic isodensity contours have the following shape



In Ψ_+ the electronic density has a maximum between the protons while in Ψ_- the electronic density is concentrated around each proton.





The dependency of the electronic energy of the system as a function of the internuclear distance has the following shape:





required (3rd body will carry out the excess of energy)



FIG. 200. Potential Curves of the Observed Electronic States of the CN Molecule. The magnitude of the heat of dissociation is not yet certain. If Gaydon's (34) high value for $D_0^0(CO)$ should turn out to be correct, a $D_0^0(CN)$ value of 7.6 e.v. would follow and the asymptotes in the figure would have to be altered correspondingly.

Overview of the entire spectrum

Chan Sr	ge of pin	Change of Orientation	Change of Configuration	Change of Electron Distribution		Change of Nuclear Configuration
nmr	esr	m wave	IR	vis-UV	X-ray	g-ray
			or		6	$\bigcirc \rightarrow \bigcirc$
10	-2 ·	1 1(00 10	0 ⁴ 10 cm ⁻¹	0 ⁶ 10 wavenumber) ⁸
10 m 100	cm 1	cm 100	m m 1 r	nm 10	nm 10 wavenumber	pm
$13 \cdot 10^6$ 3.	10 ⁸ 3 · ′	10 ¹⁰ 3 · 1	0 ¹² 3 · 1	10 ¹⁴ 3 · 1 Hz	I0 ¹⁶ 3 ⋅ 1 frequency	0 ¹⁸
10 ⁻³ 10) ⁻¹ 11	0 1	0 ³ 10	0 ⁵ 10 joules/mole	0 ⁷ 10 energy) ⁹

ROTATIONAL SPECTRUM OF LINEAR MOLECULES

From a "classical" point of view of quantum theory a molecule has a rotational energy proportional to the square of the angular momentum, J^2 . Hence the energy levels should have a dependency on J given by

$$E(J) \propto J(J+1)$$

The frequencies of the transitions could be given by

 $v(J = >J-1) \propto J$

From a classical point of view the angular momentum of the molecule is given by I ω , where I is the momentum of inertia of the molecule,

$$I = \mu r^2$$

where μ is the reduced mass, $\mu = M_1 M_2 / (M_1 + M_2)$, and r is the separation between the nuclei.

In this "classical" approximation for the energy of a rigid molecule the energies can be written as

E(J) = B J(J+1)

and the frequencies as

$$v = 2 B (J_1 + 1) = 2 B J_u$$

The constant B, the rotational constant, is given by

B = (h / 8 π^2 I) = 505379.05 / I(ua Å²) MHz

The rotational constant has units of Hz and is often given in MHz or in wavenumbers

 $1 \text{ cm}^{-1} = 29979.2459 \text{ MHz} \approx 30 \text{ GHz} \approx 1.4388 \text{ K}$
This simple expression for the energy works fine for heavy molecules. However, when the accuracy of the observations is large it is observed that the frequencies of successive rotational transitions do not follow this simple approximation.

¿WHY?

Because when molecules are rotating the nuclei are submitted to centrifugal forces which increase the distance between them and increase the momentum of inertia.

The distance between the nuclei is defined by the molecular orbitals. We need a potential U(r) describing the energy of the system as a function of the internuclear distance.

As the movement of the nuclei is much slower than those of the electrons we could consider that the electronic energy of the molecule is indepent of the vibration and of the rotation.

This approximation (Born-Oppenheimer) allows to separate the total energy into electronic, vibrational and rotational energies, i.e., the total energy of the molecule could be written as a sum of terms depending on $(m_e/M_N)^{\frac{1}{2}}$.

The problem is to find the potential energy of the molecules, U(r), describing in a reasonable way the variation of energy as a function of the internuclear distance.

Under this approximation the wave equation for a diatomic molecule is given by

$$\frac{1}{M_1} \nabla_1^2 \psi + \frac{1}{M_2} \nabla_2^2 \psi + \frac{8\pi^2}{h^2} [W - U(r)] \psi = 0$$

Where Ψ is the wave function describing the movement of the nuclei of mass M_1 y M_2 respectively, and

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$
 where $i = 1$ or 2

 x_i , y_i , z_i are the coordinates of the nucleus i

Using spherical coordinates r, θ , ϕ

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}\left[W - U(r)\right]\psi = 0$$

Where μ is the reduced mass of the system, $\mu = M_1 M_2 / (M_1 + M_2)$ and

$$\Psi = R(r)\Theta(\theta)\Phi(\phi)$$

 $\Theta(\theta)$ y $\Phi(\phi)$ are the same functions than those for the rigid molecule

The radial wave function obtained after separation of the different terms is given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left\{\frac{8\pi^2\mu}{h^2}\left[W - U(r)\right] - \frac{J(J+1)}{r^2}\right\}R = 0$$

The term J(J+1) has to be considered as a potential energy associated to the centrifugal forces produced by the rotation of the molecule. The wave equation for the radial movement of the nuclei could be simplified to the expression

$$\frac{d^2S}{dr^2} + \left\{ -\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2} \left[W - U(r) \right] \right\} S = 0$$

The solution of the wave equation depends on the shape of U(r).



Morse Potential :
$$U(r) = D(1 - e^{-a(r-r_e)})^2$$

D = dissociation energy of the molecule $r_e =$ equilibrium distance between nuclei a = a constant

The wave equation is then :

$$\frac{d^2S}{dr^2} + \left[-\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2} \left(W - D - De^{-2a(r-r_e)} + 2De^{-a(r-r_e)} \right) \right] S = 0$$

Making the following changes

$$y = e^{-a(r-r_e)}$$
 and $A = J(J+1) \frac{h^2}{8\pi^2 \mu r_e^2}$

We obtain :

$$\frac{d^2S}{dy^2} + \frac{1}{y}\frac{dS}{dy} + \frac{8\pi^2\mu}{a^2h^2}\left(\frac{W-D}{y^2} + \frac{2D}{y} - D - \frac{Ar_e^2}{y^2r^2}\right)S = 0$$

For A = 0, i.e., J=0 it is possible to find an analitycal solution. In the general case the solution is given by

$$\frac{W_{Jv}}{h} = \omega_e(v + \frac{1}{2}) - x_e\omega_e(v + \frac{1}{2})^2 + J(J + 1)B_e - D_eJ^2(J + 1)^2 - \alpha_e(v + \frac{1}{2})J(J + 1)$$

where
$$\omega_e = \frac{a}{2\pi} \sqrt{\frac{2D}{\mu}} \qquad x_e = \frac{h\omega_e}{4D} \qquad B_e = \frac{h}{8\pi^2 I_e}$$
$$D_e = \frac{h^3}{128\pi^6 \mu^3 \omega_e^2 r_e^6} = \frac{4B_e^3}{\omega_e^2}$$
$$\alpha_e = \frac{3h^2 \omega_e}{16\pi^2 \mu r_e^2 D} \left(\frac{1}{ar_e} - \frac{1}{a^2 r_e^2}\right) = 6\sqrt{\frac{x_e B_e^3}{\omega_e}} - \frac{6B_e^2}{\omega_e}$$

The first term of the energy corresponds to the energy of an harmonic oscillator with quantified energy levels (v + 1/2).

The second term represents the anharmonicty

The term depending on $J^2(J+1)^2$ corresponds to the centrifugal distorsion introduced by the rotation.

Additional terms (no included in the expression) are often needed and represent corrections of higher order.

There is another potential proposed by Dunham. It is represented by a series in $(r-r_e)$, where r_e is the equilibrium distance

$$U = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \cdots) + B_eJ(J + 1)(1 - 2\xi + 3\xi^2 - 4\xi^3)$$

Where $\xi = (r-r_e)/r_e$ and Be=h/8 $\pi^2 \mu r_e^2$

The solution can be given as

$$F_{vJ} = \sum_{l,j} Y_{lj} (v + \frac{1}{2})^l J^j (J + 1)^j$$

Where the terms Y_{li} are the Dunham coefficients

$$\begin{split} &Y_{00} = B_e/8(3a_2 - 7a_1^2/4) \\ &Y_{10} = \omega_e[1 + (B_e^2/4\omega_e^2)(25a_4 - 95a_1a_3/2 - 67a_2^2/4 \\ &+ 459a_1^2a_2/8 - 1155a_1^4/64)] \\ &Y_{20} = (B_e/2)[3(a_2 - 5a_1^2/4) + (B_e^2/2\omega_e^2)(245a_6 - 1365a_1a_5/2 \\ &- 885a_2a_4/2 - 1085a_3^2/4 + 8535a_1^2a_4/8 + 1707a_2^2/8 \\ &+ 7335a_1a_2a_3/4 - 23,865a_1^3a_3/16 - 62,013a_1^3a_2^2/32 \\ &+ 239,985a_1^4a_2/128 - 209,055a_1^6/512)] \\ &Y_{30} = (B_e^2/2\omega_e)(10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 \\ &- 705a_1^4/32) \\ &Y_{40} = (5B_8^3/\omega_e^2)(7a_6/2 - 63a_1a_5/4 - 33a_2a_4/4 - 63a_3^2/8 \\ &+ 543a_1^2a_4/16 + 75a_2^3/16 + 483a_1a_2a_3/8 - 1953a_1^3a_3/32 \\ &- 4989a_1^2a_2^2/64 + 23,265a_1^4a_2/256 - 23,151a_1^6/1024) \\ &Y_{01} = B_e\{1 + (B_e^2/2\omega_e^2)[15 + 14a_1 - 9a_2 + 15a_3 - 23a_1a_2 \\ &+ 21(a_1^2 + a_1^3)/2]\} \\ &Y_{11} = (B_e^2/\omega_e)\{6(1 + a_1) + (B_e^2/\omega_e^2)[175 + 285a_1 - 335a_2/2 \\ &+ 190a_3 - 225a_4/2 + 175a_5 + 2295a_1^2/8 - 459a_1a_2 \\ &+ 1425a_1a_3/4 - 795a_1a_4/2 + 1005a_2^2/8 - 715a_2a_3/2 \\ &+ 1425a_1a_3/4 - 795a_1a_4/2 + 1005a_2^2/8 - 715a_2a_3/2 \\ &+ 1155a_1^3/4 - 9639a_1^2a_2/16 + 5145a_1^2a_3/8 \\ &+ 4677a_1a_2^2/8 - 14,259a_1^3a_2/16 \\ &+ 31,185(a_1^4 + a_1^5)/128]\} \\ &Y_{21} = (6B_e^3/\omega_e^2)[5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 \\ &+ 15(a_1^2 + a_1^3)/2] \\ &Y_{31} = (20B_e^4/\omega_e^3)[7 + 21a_1 - 17a_2/2 + 14a_3 - 9a_4/2 + 7a_5 \\ &+ 225a_1^2/8 - 45a_1a_2 + 105a_1a_3/4 - 51a_1a_4/2 + 51a_2^2/8 \\ &- 45a_2a_3/2 + 141a_1^3/4 - 945a_1^2a_2/16 + 435a_1^2a_3/8 \\ &+ 411a_1a_2^2/8 - 1509a_1^3a_2/16 + 3807(a_1^4 + a_1^5)/128] \\ &Y_{02} = -(4B_e^2/\omega_e^2)\{1 + (B_e^2/2\omega_e^2)[163 + 199a_1 - 119a_2 + 90a_3 \\ &- 45a_4 - 207a_1a_2 + 205a_1a_3/2 - 333a_1^2a_2/2 + 693a_1^2/4 \\ &+ 46a_2^2 + 126(a_1^3 + a_1^4/2)]\} \\ &Y_{12} = -(12B_e^4/\omega_e^3)(5 + 125a_1 - 61a_2 + 30a_3 - 15a_4 \\ &+ 495a_1^2/4 - 117a_1a_2 + 26a_2^2 + 95a_1a_3/2 - 207a_1^2a_2/2 \\ \end{aligned}$$

 $+ 90(a_1^3 + a_1^4/2)]$

Obviously, there is a relation between the de Dunham coefficients and those obtained with the Morse potential

The empirical expression used in spectroscopy to fit the rovibrational spectra of diatomic molecules is

$$F_{vJ} = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \omega_e y_e (v + \frac{1}{2})^3 + \omega_e z_e (v + \frac{1}{2})^4 + B_v J (J + 1) - D_e J^2 (J + 1)^2 + H_e J^3 (J + 1)^3 + \cdots$$

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 \dots$$

From the spectroscopic constants it is possible to derive important information, through the Morse or Dunham expression for the potential energy, on the dissociation energy, equilibrium distance, etc.

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 $B_e(^{13}CO) = \mu(^{12}CO)/\mu(^{13}CO) B_e(^{12}CO) =$ 0.95591388*57897.5 = 55345.02 MHz Experimental = 55344.9 MHz

m(¹³C)=13.00335483; m(¹²C)=12; m(O)=15.99491464

r_e(CO)=1.1283 Å

I(CO) = 6.856208642 u.a.

 $B_e(CO)=505379.05/I(CO)/r_e(CO)^2$

B_e(CO)=57897.5 MHz

EXAMPLE

EXAMPLES :

Mole- cule	Y ₀₁ (approx. B _c), Mc	$\begin{array}{c} Y_{01} \\ (\text{approx. } B_{e}), \\ \text{cm}^{-1} \end{array}$	αe, Mc	$I_{s},$ A ² × atomic mass units	<i>r</i> _e , A	$\omega_{e}, \mathrm{cm}^{-1}$	$D_e = \frac{4B_e^3}{\omega_e^2},$ Mc	μ, debyes	Reference
$\begin{array}{c} H^1Cl^{35} \\ DI^{127} \\ C^{12}O^{16} \\ Cl^{35}F^{19} \\ Cl^{37}F^{19} \\ Br^{79}F^{19} \\ Br^{81}F^{19} \\ K^{41}Cl^{35} \\ K^{39}Cl^{35} \\ K^{39}Cl^{37} \\ I^{127}Cl^{35} \end{array}$	$317,510$ $(B_0 = 97,537.2)$ $57,897.5$ $55,344.9$ $15,483.69$ $15,189.22$ $10,706.9$ $10,655.7$ $3,767.394$ $3,856.370$ $3,746.583$ $3,422.300$ $2,275,235$	$\begin{array}{c} 10.591 \\ (B_0 = 3.25348) \\ 1.93124 \\ 1.84610 \\ 0.516479 \\ 0.506657 \\ 0.357143 \\ 0.355435 \\ 0.125667 \\ 0.128634 \\ 0.124972 \\ 0.114155 \\ 0.10002020 \end{array}$	$\begin{array}{c} 9050\\ 1840\\ 524.0\\ 488.3\\ 130.67\\ 126.96\\ 156.3\\ 155.8\\ 22.865\\ 23.680\\ 22.676\\ 16.06\\ 15.05\end{array}$	$1.592 \\ (I_0 = 5.183) \\ 8.731 \\ 9.134 \\ 32.65 \\ 33.28 \\ 47.21 \\ 47.44 \\ 134.2 \\ 131.1 \\ 134.9 \\ 147.7 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 \\ 154.2 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154.$	$\begin{array}{c} 1.275\\ 1.604\\ 1.128\\ 1.128\\ 1.628\\ 1.628\\ 1.759\\ 1.759\\ 2.667\\ 2.667\\ 2.667\\ 2.321\\ 2.221\end{array}$	$\begin{array}{c} 2989.74\\ 1630\\ 2170.21\\ 2074.81\\ 793.2\\ 778.6\\ 671\\ 670\\ 300\\ 300\\ 300\\ 300\\ 384.2\\ 276\end{array}$	$15.94 \\ 1.56 \\ 0.1834 \\ 0.1753 \\ 0.02626 \\ 0.02527 \\ 0.0121 \\ 0.0121 \\ 0.003 \\ 0.003 \\ 0.003 \\ 0.003 \\ 0.00121 \\ 0.00121 \\ 0.00121 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 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0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.0011 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.00111 \\ 0.$	$\begin{array}{c} 1.18\\ 0.38\\ 0.10\\ 0.10\\ 0.88\\ 0.88\\ 1.29\\ 1.29\\ 10.48\\ 10.48\\ 10.48\\ 10.48\\ 0.65\\ 0.65\end{array}$	[336 <i>a</i>] [471] [755 <i>a</i>] [827 <i>a</i>] [782 <i>b</i>] [336 <i>a</i>] [457] [457] [366] [534] [534] [835] [938] [835] [938] [835] [938] [330]

TABLE 1-1a. MOLECULAR CONSTANTS OF SOME REPRESENTATIVE DIATOMIC MOLECULES

m(¹³C)=13.00335483; m(¹²C)=12; m(O)=15.99491464

$B_{e}^{(13}CO) = \mu(^{12}CO)/\mu(^{13}CO) B_{e}^{(12}CO) = 0.95591388*57897.5=55345.02$



ROTATIONAL SPECTRUM OF CARBON MONOXIDE



Selection rules $\Delta J=\pm 1$



By selecting the appropriate molecule we can trace different physical conditions.

Molecules with low dipole moment, as CO, are easily excited through collisions with H₂, even for low volume densities. Under some assumptions these molecules could trace the kinetic temperature of the gas.

High dipole moment molecules could be -used as tracer of the gas volume density -(n(H₂)).



A few facts...

Continuous term spectra and dissociation

If oscillator has more energy E' than, hcD_e , then $r \to \infty$ and molecule dissociates. For $E' > hcD_e$, system has excess energy (kinetic energy) after dissociation. $\therefore (K.E)_{\text{atoms}} > 0$ and not quantized.





Fig. 4.9 Rotational fine structure of a vibration-rotation band of a diatomic molecule. Note the decreasing spacing with increasing J in the R branch, and the increasing spacing with increasing J in the R branch, and the increasing spacing with increasing J in the P branch.



Fig. 4.10 Appearance of a vibration-rotation band of a diatomic molecule under low resolution.

Perhaps in dark clouds infrared effects are much less important. The kinetic temperature is too low to pump vibrational levels. But !!!!



History of Radioastronomy



William Herschel noticed that the highest temperature was measured in a portion of the spectrum beyond the red where no sunlight was visible

INFRARED RADIATION



11:00 A.M.

12:00 noon

10:00 A.M.

Bell Labs asks K. Jansky to investigate perturbations of radio voice transmission between USA and Europe. He builts an antenna of 30x4 m that rotates every 20 minutes. He discovers a "steady hiss static of unknown origin".

1933-35 Jansky resolves mystery

The source of the radiation is established to be in a fixed direction of the sky with the following approximatecoordinates:

RA: 18h dec: -10 deg

(The Galactic Center)



G. Reber was interested in investigating the nature of the signals revealed by Janky's experiment. He could not get a job to do this due to great depression so he built this radiotelescope in his back yard.

Aprox. 10 m diameter, amplification of several million on the receiver placed within the cylinder at the focus. Signals recorded on a chart.

The parabolic design concentrates waves of all wavelengths to the same focus.

The first radio map of the Galaxy



First two receivers (3300 and 900 MHz failed to detect signals from outer space.

Finally, a third receiver at 160 MHz (1.9 meter wavelength made detection of the radio emission from the Milky Way and the Sun (broad features on the chart readings). Narrow peaks are due to interference with automobile engine sparks.

The first radio map of the Galaxy



Reber presented his results in the form of contour diagrams showing that the brightest areas correspond to the Milky Way, specially towards its center. Other bright radio sources such as Cygnus and Cassiopeia were also discovered for the first time.

...essentially centimeter wavelengths



Nancay

Effelsberg

Present day facilities:

millimeter and submillimeter single antenna









Present day falicilities:

millimeter interferometry





What is a Radiotelescope?

...a watt meter (amplification to be achieved ~ 10^{10} (signals are extremely week)

Parts of a Radiotelescope



Transition region between the free-space propagating wave and the guided wave

What do we detect with a Radiotelescope?

Continuum

- Free-free
- Synchrotron
- Dust

Line Radiation

- "Normal" molecular lines
 - Masers
 - atomic (HI fine structure or recombination)

What do we detect with a Radiotelescope? (II)

IMAGE: CFHT BAND K

CONTINUUM EMISSION (from dust, thermal, synchrotron,...)



Dust radiation

Mass absorption coefficient

$$\kappa = \kappa_0 \left(\frac{\nu}{230 \,\mathrm{GHz}} \right)^{\nu} \mathrm{cm}^2 \mathrm{g}^{-1}$$

- κ_o is typically 0.4 cm² g⁻¹ in the ISM, but can vary with
 - Grain size
 - Grain properties (fluffy, ice mantle)
- β is around 2 in the ISM, and lower (1 or so) in disks (grain growth)
Synchrotron radiation

- Radiation by relativistic electrons through gyration around magnetic fields
- $I_{\nu} \propto \nu^{-\alpha}$ with $\alpha \approx 0.6$

Visible in low radio range

 Information about magnetic fields and relativistic electrons



Free-Free radiation

- Free-Free or Bremsstrahlung
 - Acceleration of electrons by protons in plasma

 $\tau_{v} = 8.24 \times 10^{-2} T_{e}^{-1.35} v^{-2.1} EM$ $EM = \int n_{e}^{2} dr \text{ Emission measure}$ $n_{e} \text{ electron density}$ $I_{v} \propto \begin{vmatrix} v^{2} T_{e} \text{ for } \tau_{v} \gg 1 \\ v^{-0.1} T_{e}^{-0.35} EM \text{ for } \tau_{v} \ll 1 \end{vmatrix} \text{ Rayleigh-Jeans}$



Synchrotron/Free-Free radiation



Peter Schilke

Free-Free radiation

- Determines Parameters of HII regions
 - Electron density
 - Electron temperature (with recombination lines)
 - Number of Lyman continuum photons
 - Gives hint to nature of exciting star



Why looking for low abundance species ?

- Some times these species play a crucial role in the chemistry and in the dynamical evolution of the clouds.
- Each molecule brings information from different regions of molecular clouds.
- From a spectral point of view (molecular physics) many of these molecules have been never observed in the Earth (complex radicals) : Lab. Chemistry.
- Gas phase and dust grain chemistry need of clear discrimators
- Except for hot cores and corinos all complex molecules have low abundances
- Note that a low dipole moment molecule will produce weak lines even if its abundance is similar to that of HCO⁺
- Key Molecules such as C₂H₂, CH₄, C₂H₄,..., do not have pure rotational spectrum and very little information is available on their abundances

- How to interpret spectra with thousands of lines ? We need laboratory spectroscopy
- What methods have to be implemented to deal with these expected line forests ?
 We need collaboration with software developers under the supervision of specialists
- What we get from line surveys ?
 We need modeling : chemical, physical, dynamical evolution of the gas,...
- To look for new molecules we need more sensitive instruments.
- To look for new physical and chemical processes we need more sensitive instruments
- To understand the evolution of gas from protoplanetary disks to high redshift objects we need more sensitive instruments :

HERSCHEL & ALMA & eVLA & ELT & ...

A Confusion Limited Spectral Survey of Orion KL (80-280 GHz) And a 2D Spectral Line Survey at 1mm

CO (2-1)

Belén Tercero, Gisela B. Esplugués, Tom Bell (CAB, Spain), Nuria Marcelino (NRAO), Aina Palau (ICE, Spain)

Line Surveys in Orion-KL

The closest (brightest) massive star forming region, contains several compact objects

 Prototypical source: observed extensively at mm and submm wavelengths

Exhibits an intense and prolific spectrum

Many spectral line surveys performed in the last 20 years (ground and space) covering most of the 70 to 2000 GHz domain.

 Very rich and complex chemistry (warm gas-phase, shocks, grain mantle evaporation/desorption, etc.)

Cloud components of Orion-KL

Extended Ridge: gas-phase ion-molecule chemistry;
 C-rich molecules (CS, CN, CCH), lack of O-rich species

• <u>Compact Ridge</u>: shocked gas, release of oxygen from grains; abundant in complex organic molecules (CH_3OH_3 , $HCOOCH_3$, CH_3OCH_3 , etc.)

 Hot Core: warm gas-phase with N-rich and Hsaturated species from grains; NH₃, HDO, CH₃CN, CH₃CH₂CN, etc.

 <u>Plateau</u>: outflows; high velocity wings of CO and HCO⁺; SiO, SO, SO₂, etc.; and maser emission (H₂O, OH, SiO)



IRAM 30m Line Surveys:

- Freq. range: $80 280 \text{ GHz} \rightarrow \text{multiple transitions}$ from the same species
- □ Spectral resolution: ~1 MHz (3–1 km/s)
- HPBW = 29 9"

Line confusion limited survey ->
 deep insight into the chemistry, and
 detection of new molecules (isotopologs
 and vibrationally excited states)



Ground Based observations of high Mass star forming regions

A&A 517, A96 (2010) DOI: 10.1051/0004-6361/200913501 9 ESO 2010

Astronomy Astrophysic



A&A 517, A96 (2010)





ALMA WILL BE 8 times more sensitive than the 30-m radio telescope

BARRIDO ESPECTRAL Reducción de las observaciones

Eliminación de la banda imagen: tomamos el mismo espectro desplazado en 20 MHz



IRAM 30m Line Surveys:

15000 lines detected (above confusion limit), of which 10000 have been assigned to 44 molecules and their isotopologues

New detections of multiple isotopic substitutions (¹⁸O, D) of HCOOCH₃ and CH₃CH₂CN, for which new laboratory measurements were needed (Collaboration with Lille Spectroscopy Group).

5000 lines remain unidentified above the confusion limit (0.05 K at 3mm, 0.1 K at 2mm and 1mm) A&A 528, A26 (2011)



Species	Extended ridge	Compact ridge	Plateau	Hot core
	$N \times 10^{15} (\text{cm}^{-2})$	$N \times 10^{15} (\text{cm}^{-2})$	$N \times 10^{15} (\text{cm}^{-2})$	$N \times 10^{13} (\text{cm}^{-2})$
OCS	2.0 ± 0.5	3.0 ± 0.8	7.5 ± 1.9	15 ± 4
OCS assuming ${}^{32}S/{}^{34}S = 20$	2.0 ± 0.5	14 ± 4	10 ± 3	60 ± 15
OCS assuming ${}^{12}C/{}^{13}C = 45$	2.7 ± 0.5	18 ± 4	13.5 ± 3	45 ± 9
OCS (average)	2.4 ± 0.5	16 ± 4	11.8 ± 3	53 ± 10
$OC^{34}S$	0.15 ± 0.03	0.70 ± 0.18	0.50 ± 0.13	3.0 ± 0.8
$OC^{33}S$	0.050 ± 0.025	0.090 ± 0.045	0.10 ± 0.05	0.30 ± 0.15
O ¹³ CS	0.060 ± 0.015	0.40 ± 0.10	0.30 ± 0.08	1.0 ± 0.3
¹⁸ OCS	0.010 ± 0.005	0.070 ± 0.035	0.030 ± 0.015	0.10 ± 0.05
$O^{13}C^{34}S$	≲0.010	≲0.050	≲0.050	≲0.070
¹⁷ OCS	≲0.005	≲0.020	≲0.010	≲0.020
$OC^{36}S$	≲0.005	≲0.030	≲0.020	≲0.030
OCS $v_2 = 1$				1.5 ± 0.4
OCS $v_3 = 1$		•••		0.15 ± 0.07

Species	Extended ridge $N \times 10^{14} \text{ (cm}^{-2})$	Compact ridge $N \times 10^{14} (\text{cm}^{-2})$	Plateau $N \times 10^{14} (\text{cm}^{-2})$	Hot core $N \times 10^{14} \text{ (cm}^{-2})$
o-H ₂ CS	4 ± 1	10 ± 3	7 ± 2	10 ± 3
p-H ₂ CS	1.5 ± 0.4	5 ± 1	3.0 ± 0.8	6 ± 2
o-H ₂ C ³⁴ S	0.20 ± 0.05	0.40 ± 0.10	0.20 ± 0.05	0.7 ± 0.2
p-H ₂ C ³⁴ S	0.07 ± 0.02	0.20 ± 0.05	0.08 ± 0.02	0.35 ± 0.09
o-H ₂ ¹³ CS	0.10 ± 0.03	0.20 ± 0.05	0.15 ± 0.04	0.50 ± 0.13
p-H ₂ ¹³ CS	0.035 ± 0.009	0.10 ± 0.03	0.065 ± 0.016	0.30 ± 0.08
HDCS	0.40 ± 0.10	0.60 ± 0.15	0.40 ± 0.10	0.8 ± 0.2
o-D ₂ CS	≲0.10	≲0.20	≲0.10	≲0.40
p-D ₂ CS	≲0.050	≲0.10	≲0.050	≲0.20

From Tercero et al., 2010, A&A, 517, A96 & 2011, A&A, 528, A26

Molecule	Column density $\leq N \times 10^{14} \text{ (cm}^{-2}\text{)}$	Dipole moment (D)	References spectroscopic constants
SiC	1.3	1.600^{1}	(2)
SiC_2	0.35	2.393 ³	(4)
c-SiC ₃	0.13	4.200^{5}	(6)
SiC ₄	0.04	6.420^{7}	(8)
SiN	0.61	2.560^{9}	(10)
SiCN	0.31	2.900^{11}	(12)
SiNC	0.31	2.000^{11}	(12)
ob-SiC ₃	0.16	2.200^{5}	(13)
l-SiC3	0.04	4.800^{14}	(14)
Si ₃	4	0.350^{15}	(16)
SiCCO	0.40	1.937 ¹⁷	(18)
SiCCS	0.65	1.488^{19}	(19)
o-SiH ₂	13	0.075^{20}	(21)
o-H ₂ CSi	1.7	0.300^{22}	(22)
p-H ₂ CSi	1.4	0.300^{22}	(22)
$mb-Si_2H_2$	0.34	$\mu_{\rm a} = 0.962/\mu_{\rm b} = 0.039^{23}$	(24)
$o\text{-}db\text{-}Si_2H_2$	2.5	$\mu_{\rm c} = 0.480^{25}$	(25)

Using MADEX: upper limits to the column density of hundreds of potentially interesting species

From Tercero et al., 2011, A&A, 528, A26

Ethyl Cyanide (The Contaminator), CH₃CH₂CN



Ethyl Cyanide, CH₃CH₂CN (ground state)





Ethyl Cyanide, CH₃CH₂CN (ground state)







Collaboration with L. Margules, I. Kleiner et al. →

More than 800 lines from the isotopes of CH_3CH_2CN

Around 600 lines from the vibrational excited states of ethyl cyanide

More than 400 lines from those of CH_3OCOH

Around 800-1000 lines identified every 2 years in Orion. All lines above confusion limit could be identified around 2020 !!!

Belen started her PhD based on this line survey in 2006.

When combined with HEXOS data=> Work for a long period

ALMA ?

Sym.	No	Approximate	Freq.	Infrared
Species		type of mode	Value	Value
a'	1	CH3 d-str	3001	3001 <u>VS</u>
a'	2	CH2 s-str	2955	2955 <u>VS</u>
a'	3	CH3 s-str	2900	2900 <u>S</u>
a'	4	CN str	2254	2254 <u>VS</u>
a'	5	CH3 d-deform	1465	1465 <u>S</u>
a'	6	CH2 scis	1433	1433 <u>S</u>
a'	7	CH3 s-deform	1387	1387 <u>M</u>
a'	8	CH2 wag	1319	1319 <u>M</u>
a'	9	C-CN str	1077	1077 <u>S</u>
a'	10	CC str	1005	1005 <u>M</u>
a'	11	CH3 rock	836	836 <u>W</u>
a'	12	CCC deform	545	545 <u>M</u>
a'	13	CCN bend	226	226 <u>M</u>
а	14	CH3 d-str	3001	3001 <u>VS</u>
а	15	CH2 a-str	2849	2849 <u>S</u>
а	16	CH3 d-deform	1465	1465 <u>S</u>
а	17	CH2 twist	1256	1256 <u>VW</u>
а	18	CH3 rock	1022	
а	19	CH2 rock	786	786 <u>M</u>
а	20	CCN bend	378	378 <u>M</u>
а	21	Torsion	222	

Possible vibrational levels of CH₃CH₂CN in Orion:

V₂₁, V₂₀, V₁₉, V₁₁, V₁₂, V₁₃

 $v_{21}+v_{20}, v_{21}+v_{19}, v_{21},$

ν₁₂+ν₁₃,

For a vibrational temperature of 300 K all these levels will have a contribution 10 times larger than that of the isotopes ¹³C !!!

Collaboration with J.L. Alonso (Valladolid, Spain) and J. Pearson et al. (JPL)

many of these levels have been detected (in progress for all levels below 1000 cm⁻¹)

Strong perturbations, complex Hamiltonians.



	Hot core HOT	Hot core COLD	Plateau HOT	Plateau COLD
d_{sou}	4	7	15	25
offset	5	5	5	5
V_{exp}	5	5	13	22
V_{LSR}	5	5	3	3
T_{ETL}	240	150	130	60
CH_3CH_2CN (G.S.)	2.50×10^{16}	1.50×10^{16}	4.00×10^{15}	2.00×10^{15}
CH_3CH_2CN (inp-tor)	3.12×10^{15}	1.88×10^{15}	5.00×10^{14}	2.50×10^{14}
CH_3CH_2CN (outp)	1.25×10^{15}	7.50×10^{14}	2.00×10^{14}	1.00×10^{14}
13 CH $_3$ CH $_2$ CN	5.21×10^{14}	3.12×10^{14}	8.33x10 ¹³	4.17×10 ¹³
$CH_3^{13}CH_2CN$	5.21×10^{14}	3.12×10^{14}	8.33×10^{13}	4.17×10^{13}
$CH_3CH_2^{13}CN$	5.21×10^{14}	3.12×10^{14}	8.33×10^{13}	4.17×10^{13}
$A-CH_2DCH_2CN$	\leq 4.54x10 ¹⁴	\leq 2.73x10 ¹⁴	\leq 7.27x10 ¹³	\leq 3.64x10 ¹³
S-CH ₂ DCH ₂ CN	\leq 4.54x10 ¹⁴	$\leq 2.73 \times 10^{14}$	\leq 7.27x10 ¹³	\leq 3.64×10 ¹³
CH_3CH_2CN (v ₁₂)	4.17×10^{14}	2.50×10^{14}	6.67x10 ¹³	3.33x10 ¹³
CH ₃ CHDCN	$\leq 2.72 \mathrm{x} 10^{14}$	$\leq 1.63 ext{x} 10^{14}$	\leq 4.35x10 ¹³	$\leq 2.17 \times 10^{13}$
$CH_3CH_2C^{15}N$	1.47×10^{14}	8.82×10^{13}	2.35×10^{13}	1.18×10^{13}

What is the role of vibrationally excited molecules in chemistry ?

E_{vib}=800 K

Slow reactions involving ground state species could become very fast using the vibrational energy reservoir to overpass possible activation barriers.

See Agúndez et al (2010, ApJ, 713, 662) for C⁺ and H₂(v=1)

In high mass star forming regions such as Orion KL the contribution to the spectral density from diatomic and triatomic molecules is through their isotopologues: SiO, ²⁹SiO, ³⁰SiO, Si¹⁸O, Si¹⁷O CS, ¹³CS, C³⁴S, C³³S HCO⁺, DCO⁺, H¹³CO⁺, HC¹⁸O⁺, HC¹⁷O⁺ HCN, DCN, H¹³CN, HC¹⁵N,....

Lines from the vibrationally excited states of some of them are detected but are weak (lowest vibrational energies \approx 700-1000 cm⁻¹).

However, for heavy species the main contribution to the confusion is through their vibrationally excited states.

For T_{vib}=300 K all molecules having vibrationally excited states around 200 cm-1 will have N_{ground} / N_{vib} \approx 3 while ¹²C/¹³C \approx 45

Orion, the nightmare

- Chemical abundances show a stratification over scales of a few arcseconds.
- Observations with telescopes such as the 30-m reach the spectral confusion limit in a few minutes of observing time (ALMA could be a nightmare).
- Vibrationally excited species more important than isotopologues !!!

¹²C/¹³C≈45, ³²S/³⁴S ≈ 20, ¹⁴N/¹⁵N ≈250 CH₃CH₂CN(v=0)/CH₃CH₂CN(bending) ≈4-5 for T_{vib} =250 K

IRAM 30m Line Surveys:

- □ 2x2' maps (fully sampled) centred on IRc2
- □ Freq. range: 200 282 GHz
- □ HERA (3x3 pixels, 1 GHz) + EMIR (4 GHz)
- Spectral resolution: 2 MHz (~2.6 km/s)
- HPBW = 12 9'' Orion-KL source

components can be resolved

- Spatial Sampling 4"
- Confusion limited in 30"x30"

Observations completed, now in the reduction process...










2-D Line Survey



THE SPECTROSCOPY PROBLEM

- Weeds
- How to deal with future ALMA data ?
- What we need from laboratory groups ? -isotopologues, vibrationally excited states
- Which direction have we to follow ?
 - => high frequency (ALMA) => Physical processes => Low frequency (GBT, VLA, SKA) => Heavy species ?



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Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Note

LA-MB-FTMW spectroscopy of AlCCH and AgCCH with a discharge source

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MOLECULAR

Fig. 3. Time diagram to the LA-MB-FTMW spectrometer for a single experimental cycle in the ablation-discharge configuration. When the system works without dc discharge the time sequence is the same excepting the discharge pulse.

Fig. 1. $F = 2.5 \rightarrow 1.5$ hyperfine component of the $J = 1 \rightarrow 0$ rotational transition of CuCCH main isotopologue measured in this work in the 8.2 GHz frequency region. The line has been registered with 50 shots in the resonance frequency.

Masers & Lasers : Where Astrophysics becomes pure physics

HCN LASERS

ON THE EXPLANATION OF THE SO-CALLED CN LASER*



Fig. 1. Pattern of levels in HCN. The 11'0 level is split by *l*-type doubling.

David R. Lide, Jr. and Arthur G. Maki National Bureau of Standards Washington, D. C. (Received 19 May 1967)



l-type doubling.

Anions: Where Astrophysics becomes chemical physics



e.g. C_4H , C_6H , C_8H , C_3N , C_5N , ...

History:

2006 C_6H^- in IRC +10216 and TMC-1 (McCarthy et al.)

History:

2006 C_6H^- in IRC +10216 & TMC-1 (McCarthy et al.)

2007 C_4H^- in IRC +10216 (Cernicharo et al.)

2007 C_8H^- in IRC +10216 & TMC-1 (Remijan et al.; Brünken et al.)

2008 C_3N^- in IRC +10216 (Thaddeus et al.)

2008 C_5N^- in IRC +10216 (Cernicharo et al.)

History:

2006 C_6H^- in IRC +10216 & TMC-1 (McCarthy et al.)

2007 C_4H^- in IRC +10216 (Cernicharo et al.)

2007 C_8H^- in IRC +10216 & TMC-1 (Remijan et al.; Brünken et al.)

2008 C_3N^- in IRC +10216 (Thaddeus et al.)

2008 C_5N^- in IRC +10216 (Cernicharo et al.)

2010 CN- in IRC+10216 (Agúndez et al.)

Additional detections:

 $C_{6}H^{-}$ in L1527 (Sakai et al. 2007)

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C_{A}H^{-} in L1527 (Agúndez et al. 2008)
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 C_6H^- in L1544 y L1521F (Gupta et al. 2009)

2006 C_6H^- in IRC +10216 & TMC-1 (McCarthy et al.)

2007 $C_{4}H^{-}$ in IRC +10216 (Cernicharo et al.)

IRC +IU216 IRC the only source where all anions have been observed Is the only source where all anions have been observed **2007** C₈H⁻ in IRC +10216 & TMC-1 (Remijan

2008 C₃N⁻ in IRC +10216 (<u></u>]

2008 C₅N⁻ in

 CN^{-1} C_4H^{-1} C_6H^{-1} C_8H^{-1} C_3N^{-1} C_5N^{-1} (Sakai et al. 2007)

 $C_{4}H^{-}$ in L1527 (Agúndez et al. 2008)

 $C_{c}H^{-}$ in L1544 & L1521F (Gupta et al. 2009)

RESULTS: SPECIFIC RESULTS : ANIONS



Neutral species	Activation Energy (eV)	Anion / Neutral (%)	rate * k _{ra} (astro) cm ³ s ⁻¹	rate ** k_{ra} (theor) cm^3s^{-1}
C ₂ H	3.0	< 0.0014	< 10-11	2.0 10-15
C_4H	3.6	0.0074	4 10-11	1.1 10-8
C ₆ H	3.8	6.8	3 10-8	6.2 10-8
C ₈ H	4.0	26.	1.5 10-7	6.2 10-8
CN	3.8	0.25	2 10-9	1.4 10-17&
C ₃ N	4.6	0.42	3 10-9	2 10-10 @
C ₅ N	4.5	58. (?)	5 10-7 (?)	

* M. Agundez (PhD thesis 2009); rates scaled to 300 K
** Herbst & Osumara 2008, @Petrie & Herbst 1997
@ Petrie 1996

DETECTION OF C₅N⁻ AND VIBRATIONALLY EXCITED C₆H IN IRC +10216¹

J. CERNICHARO,² M. GUÉLIN,³ M. AGÚNDEZ,² M. C. MCCARTHY,⁴ AND P. THADDEUS⁴ Received 2008 July 2; accepted 2008 October 8; published 2008 October 29

ABSTRACT

We report the detection in the envelope of the C-rich star IRC +10216 of four series of lines with harmonically related frequencies: B1389, B1390, B1394, and B1401. The four series must arise from linear molecules with mass and size close to those of C₆H and C₅N. Three of the series have half-integer rotational quantum numbers; we assign them to the ${}^{2}\Delta$ and ${}^{2}\Sigma^{-}$ vibronic states of C₆H in its lowest (ν_{11}) bending mode. The fourth series, B1389, has integer J with no evidence of fine or hyperfine structure; it has a rotational constant of 1388.860(2) MHz and a centrifugal distortion constant of 33(1) Hz; it is almost certainly the C₅N⁻ anion.

TABLE 2

	В	D		
Series	(MHz)	(Hz)	$N_{\rm lines}$	J-Range
B1389	1388.860(2)	33(1)	13	8, 29-40
B1390	1389.878(7)	-35(3)	9	59/2-79/2
B1394	1394.609(10)	32(4)	22	29–41ª
B1401	1401.559(26)	139(7)	7	59/2-75/2

C₆H vib

Identification of C₅N⁻ based on comparison with ab initio calculations by Botschwina & Oswald (2008)



FIG. 1.—Spectra of IRC +10216 observed with the IRAM 30 m telescope, showing lines from the B1389 series assigned here to C_5N^- . The marginal weak line U83278 is worth noting, because it is within 0.1 MHz of the J = 1-0 line of CCH⁻ (see text). [See the electronic edition of the Journal for a color version of this figure.]



FIG. 2.—Spectra of IRC +10216 observed with the IRAM 30 m telescope showing selected lines pertaining to the series B1390, B1394, and B1401. These three series of lines are assigned to vibronic states of the ν_{11} bending mode of C₆H.



Letter to the Editor

Astronomical identification of CN⁻, the smallest observed molecular anion^{*,**}

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Table 1. Observed line parameters of CN⁻.

Transition	$\frac{v_0^a}{(MHz)}$	$\frac{\nu_{obs}}{(MHz)}$	$\frac{v_{\exp}^{b}}{(\mathrm{km}\ \mathrm{s}^{-1})}$	$\int_{(K \text{ km s}^{-1})}^{\int T_A^* \text{dv}}$
J = 1 - 0	112 264.8	112 264.8 ^c	14.5^{c}	$\sim 0.07(3)^d$
J = 2 - 1 J = 3 - 2	224 525.1 336 776.4	224 525.4(5) 336 777.0(12)	14.5^{c} 15.0(10)	$0.23(7)^e$ 0.13(2)

Notes. Number in parentheses are 1σ uncertainties in units of the last digits. ^(a) Frequencies derived from the rotational constants reported by Amano (2008). ^(b) v_{exp} is the half width at zero level. ^(c) Fixed value. ^(d) Highly uncertain estimate. Line severely blended with a strong C₆H line. ^(e) Line blended with a SiC₂ $v_3 = 2$ line.





New high angular&spectral resolution map of anions (PdBI, Guélin et al.)





 C_6H

M. Guélin et al., IAU Symp 280



Average intensity in concentric rings of radius R, for each velocity channel



First Conclusion: C_6H^- and C_5N^- appear at smaller radii than predicted

C₄H⁻ appears further out than predicted

Second Conclusion:

The observed abundances of C_4H^- and CN^- disagree with predictions based on direct electron attachment on C_4H and CN

Other production mechanism for CN⁻ and other anions ?

 $CN + e \Rightarrow CN^{-}$ $MgNC + e \Rightarrow CN^{-}$ $C_{n}^{-} + N \Rightarrow CN^{-} + C_{n-1}$ Dust grains

THE FINAL PRODUCT OF A DETAILED STUDY + GOOD INPUT FROM LABORATORY

- New Molecules
- Abundances for all species
- Isotopic abundances (nuclear evolution)
- Clear differentation of the different layers of the CSE
- Chemistry of exotic species (anions)
- A fine study of the missing reactions of the actual chemical networks

ALMA will surprise us in all fields. New experiments will be needed, new physical and chemical processes will be unveiled !!! This work is the result of a long collaboration with :

Astrophysics: M. Guélin M. Agúndez J.R. Goicoechea J.R. Pardo B. Tercero P. Fonfría

Spectroscopy: L. Margules I. Kleiner M. Carvajal J. Demaison K. Demyck G. Wlodarczak J.L. Alonso C. López J. Pearson