

Genova, July 7, 2003

Molecular Beam Spectroscopy

Using Low T Detectors



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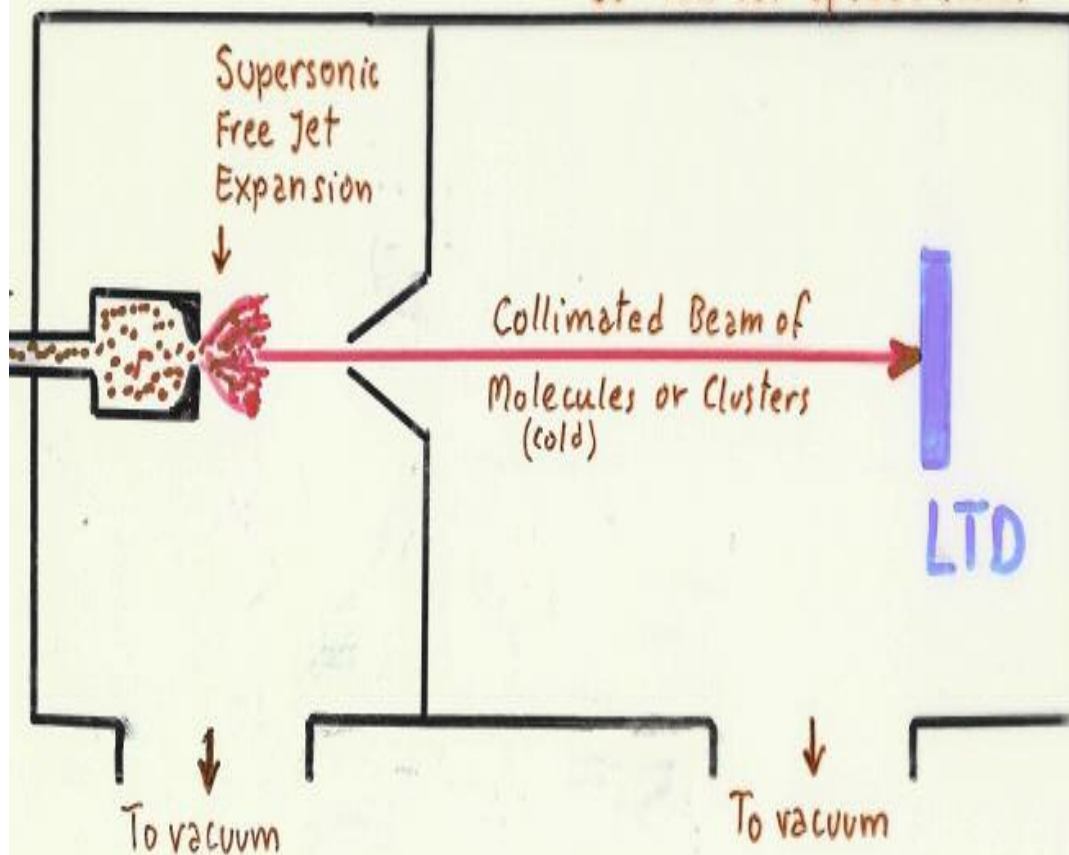
- What is a molecular Beam?
- Why Use a mol. Beam in Spectroscopy?
- Why Use a LTD in Mol. Beam Spectroscopy?
- Examples:
 - 1 High Resolution (sub-Doppler) Spectroscopy
(both single and double resonance)
 - 2 Spectroscopy of van der Waals molecules
 - 3 Spectroscopy in superfluid ^4He Nanodroplets.
- Conclusions

What is a molecular Beam?



①

- 1) High Intensity (10^{14} s^{-1} for 1 deg div.)
- 2) Hyperthermal velocity (only $\times 1.3$)
but low vel. spread (cold)



MOLECULAR BEAMS ARE VERY THIN TARGETS!

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Signal Detection in Molecular Beam CW Laser Spectroscopy



1) Fluorescence detection

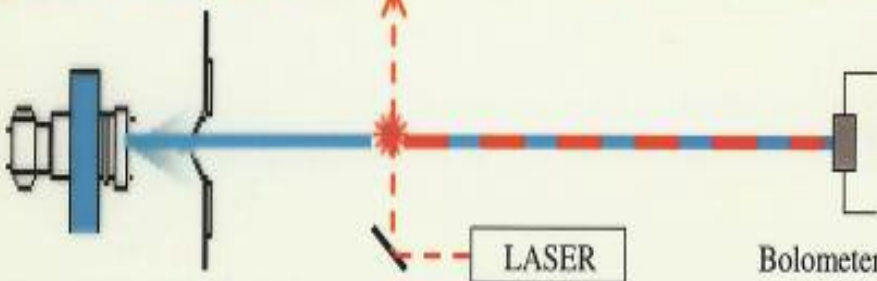
Levy, Smalley & Wharton (1974)



Needs
Fluorescence!

2) Beam pumping

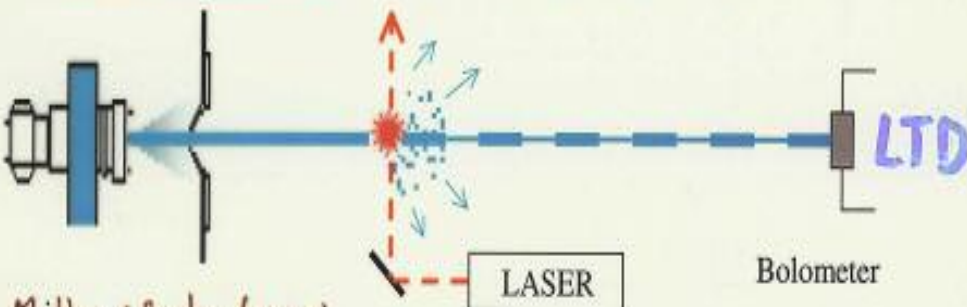
Gough, Miller & Scoles (1977)



(very often there is no fluorescence!)
(in the IR for instance)

3) Beam depletion

(requires fragmentation)



Gough, Miller & Scoles (1978)

How it all started:



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- A remark by the junior colleague **Gaetano Gallinaro**: "Giacinto did you know that the power sensitivity of modern (1966) bolometers corresponds to the flux of a few millions of thermal molecules?"
- An undergraduate student **Manfredo Cavallini** who did not like examinations but had absolutely no problems in making things work!
- (The story of the newspaper and of the "merely technical details")

ZEITSCHRIFT FÜR NATURFORSCHUNG
Verlag der Zeitschrift für Naturforschung, Tübingen

Band 22 a, Heft 3, 1967

1967

Genova

High Sensitivity Bolometer Detector for Molecular Beams

M. CAVALLINI, G. GALLINARO, and G. SCOLES

Istituto di Fisica dell'Università, Genova, Italy
Gruppo Nazionale di Struttura della Materia del C.N.R.

(Z. Naturforschg. 22 a, 413—414 [1967]; received 3 February 1967)

It is shown how a high sensitivity infra-red detector can be used as molecular beam detector.

The max sensitivity achieved is $2 \cdot 10^8$ molecules sec^{-1} .

Furthermore the advantages of using this kind of detector in scattering experiments are pointed out.

(This paper was rejected by the J. of Chem. Phys.)

What is the energy contents of a beam?

③



1) For an **atomic** beam:

Kinetic energy = $\frac{5}{2} kT_{\text{source}}$ (not $\frac{3}{2}$ because of expansion)

Condensation energy = 6ϵ (ϵ = well depth of potential)

for Argon $2.5 \times 300 + 6 \times 140 = \underline{1600 \text{ K}}$

2) For a **molecular** beam (e.g. CO)

Somewhat more than above because the internal degrees of freedom (rotation + vibration) have been cooled by the free jet expansion.

HOWEVER

if, using a laser, you pump 1 quantum of vibrational energy into the molecule you add from **3000** to **6000 K** of energy!

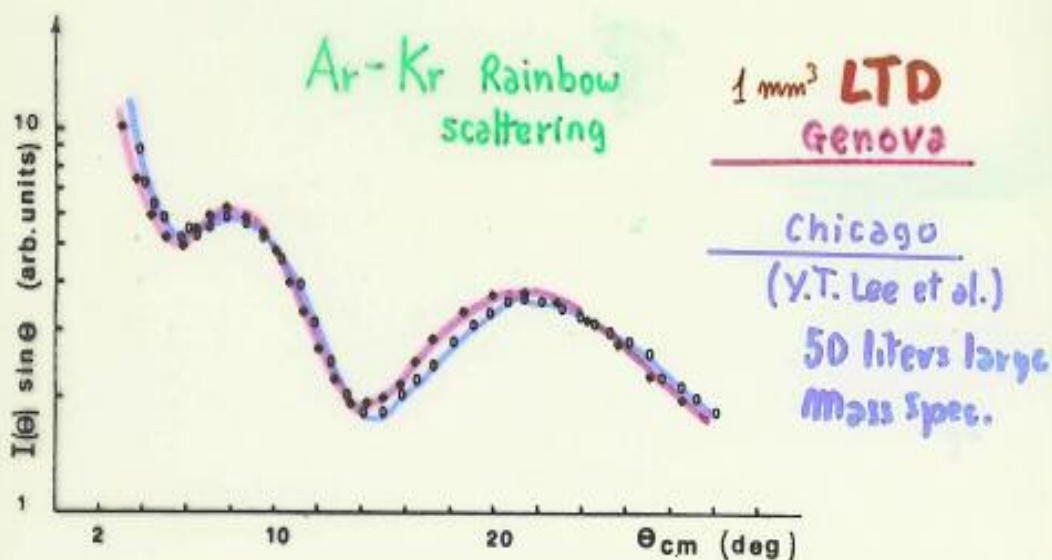


A Molecular Beam Scattering Apparatus with a Low Temperature Bolometer Detector*

M. CAVALLINI,† L. MENEGHETTI,‡ G. SCOLES,§ AND M. YEALLAND||

Istituto di Scienze Fisiche dell'Università, 16132 Genova, Italy

(Received 30 June 1971; and in final form, 10 August 1971)



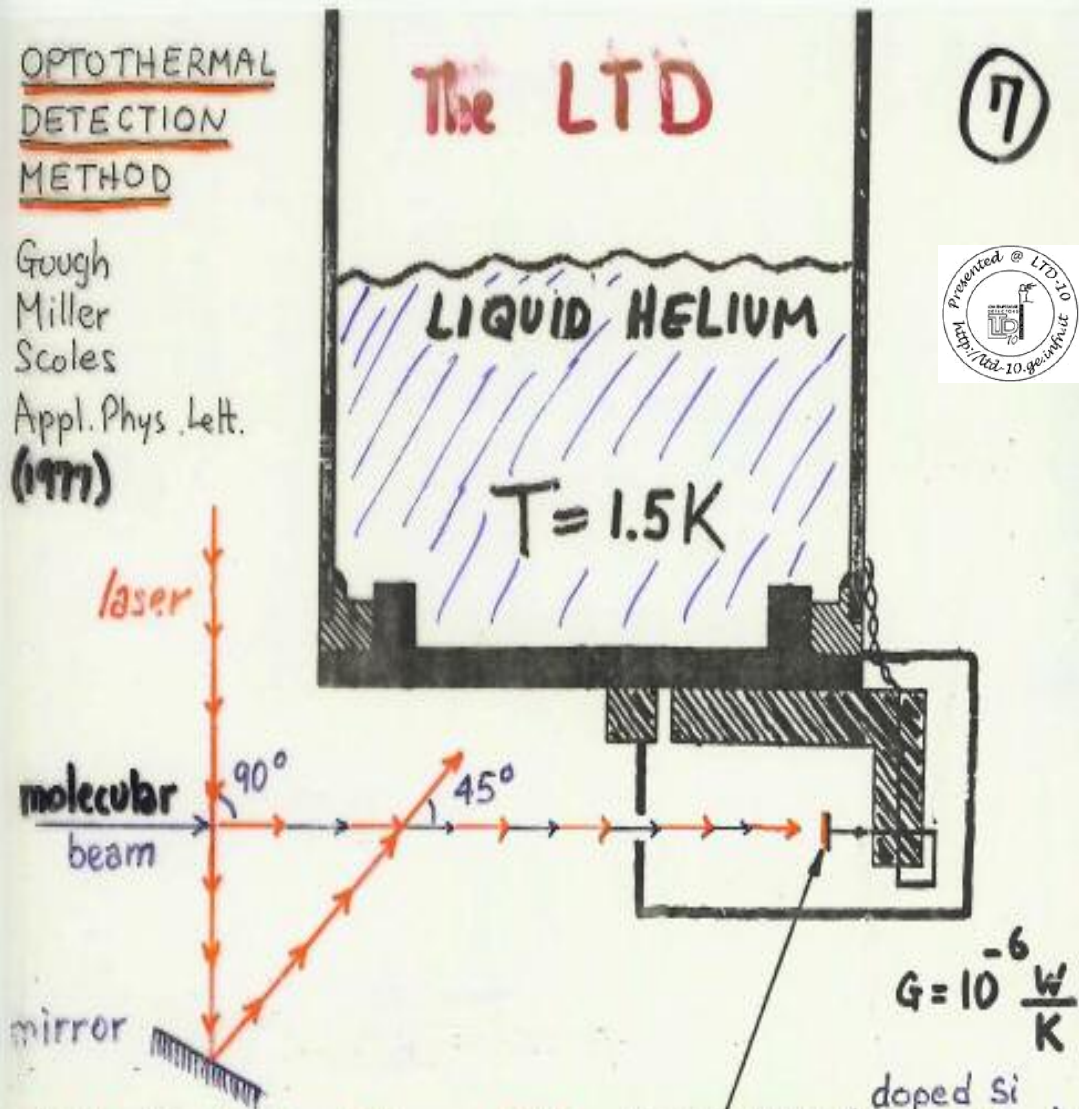
..... the incorporation of cooling and the bolometer detector allows its ready adaption to other experiments. Included are atomic H experiments (extremely difficult using mass spectrometry) and scattering experiments from crystal surfaces (made possible by a simple modification of the liquid N₂ shield, thus obtaining background conditions difficult to obtain with ion pumping techniques). The Genova group later on became well known for their surface scatt. experiments.

OPTOTHERMAL
DETECTION
METHOD

Gough
Miller
Scales
Appl. Phys. Lett.
(1977)

The LTD

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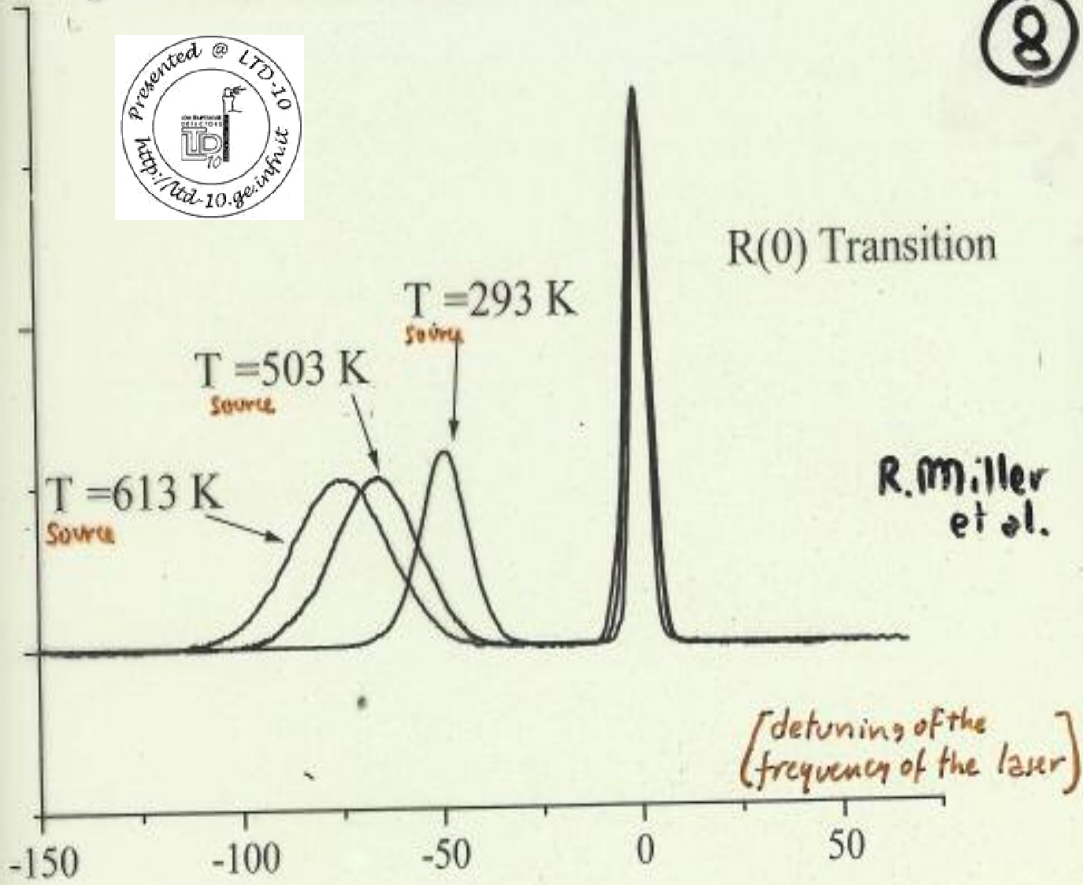
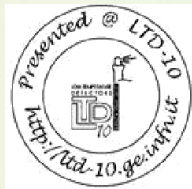


Noise Equivalent Power NEP BOLOMETER (thermistor)
 $= 3 \cdot 10^{-14} \text{ watt Hz}^{-\frac{1}{2}} \approx 10^6 \text{ photons} \cdot \text{s}^{-1} \quad \Delta T = 10^{-8} \text{ K}$

A TYPICAL MOLECULAR FLUX ON A 1 mm^2 BOLOMETER LOCATED AT 40 cm FROM THE SOURCE IS $2 \cdot 10^{12} / \text{sec}$. IF 20 J,K STATES ARE PRESENT IN THE BEAM THE USEFUL FLUX IS $10^{11} / \text{sec}$. IF AN INFRARED LASER IS AVAILABLE THAT CAN SATURATE THE TRANSITION THE $\frac{S}{N}$ RATIO IS $= \frac{10^{11}}{10^6} = 10^5 !!$

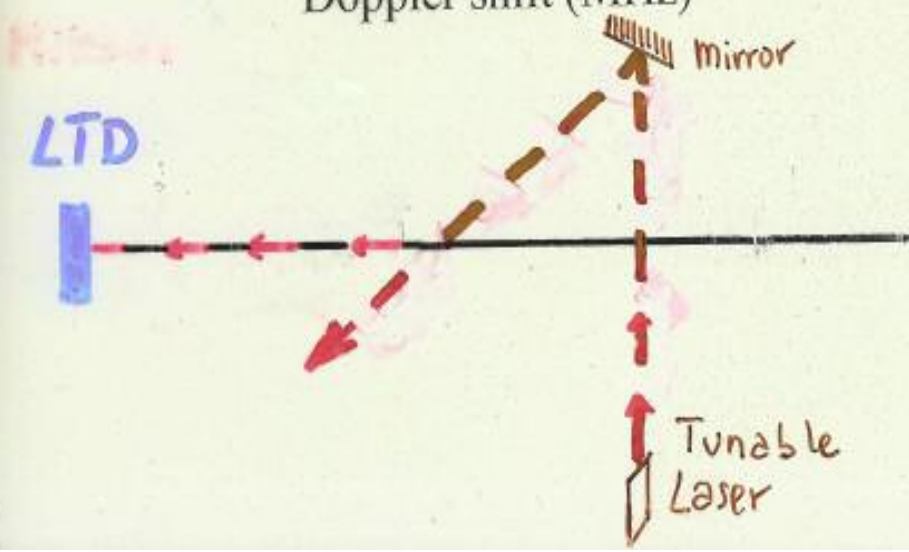
Optothermal Doppler Spectrum of Methane

8



R. Miller et al.

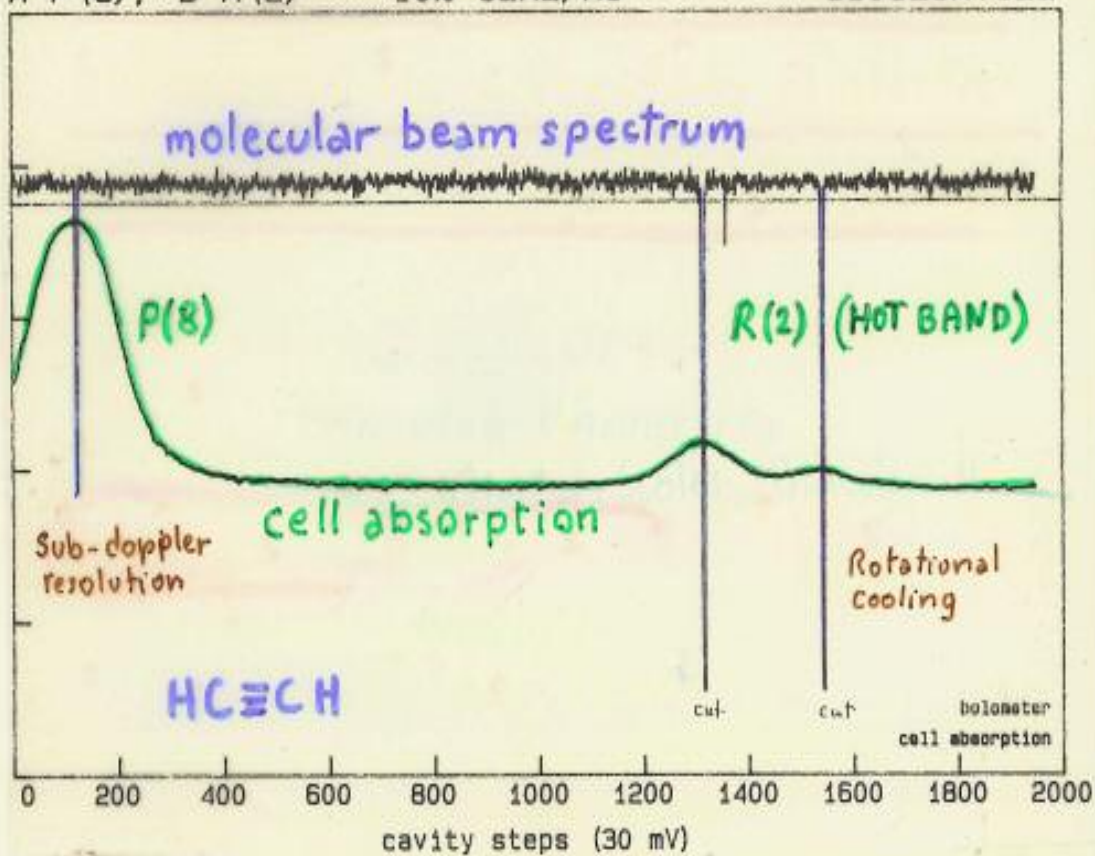
Doppler shift (MHz)



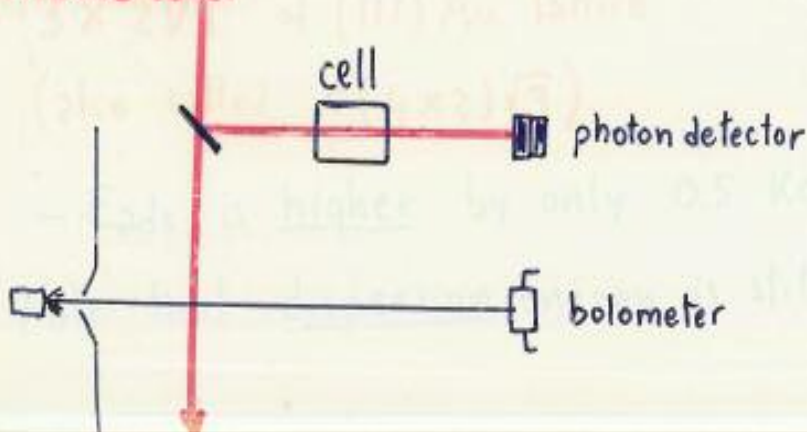
The power of this method is perhaps best demonstrated 9
 by showing the results of an experiment carried out by
 Henning Meyer and Eric Kerstel in Princeton soon after
 the setting up of my new lab there.

A-P (8), B-R (2) -- 10% C₂H₂/He

880929A.CL2

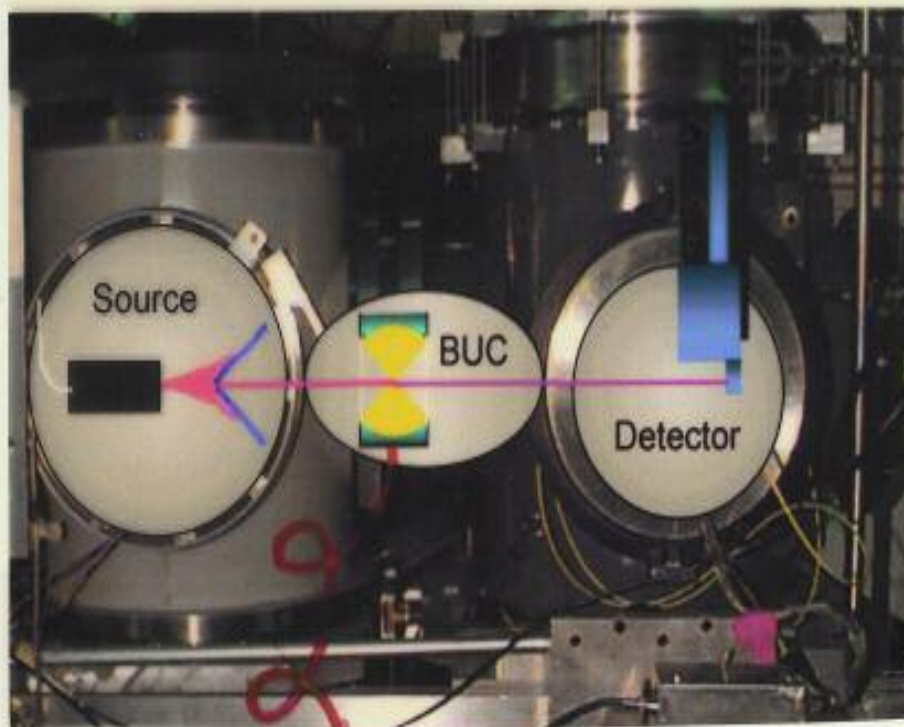


tunable laser



The Beam Machine.

10



COLOR
CENTER
LASER

100 mW 1.5 μ m 10 MHz wide

◆ problems with overtone spectroscopy

1: low transition dipole: **Solution:** use a Power Build-up cavity

The resonant power Build-Up Cavity (BUC) which is tuned at the same frequencies as the laser building up the power of the latter by a factor of 1000.

The fact that the BUC could be coupled to the laser via fiber optics, decoupling the beam machine vibrations from the laser table vibrations.

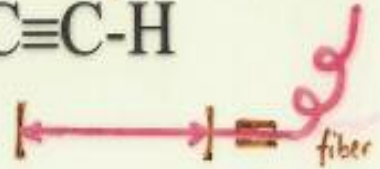
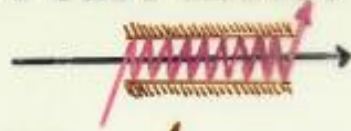
Sub-doppler resolution overtone spectroscopy becomes almost easy!





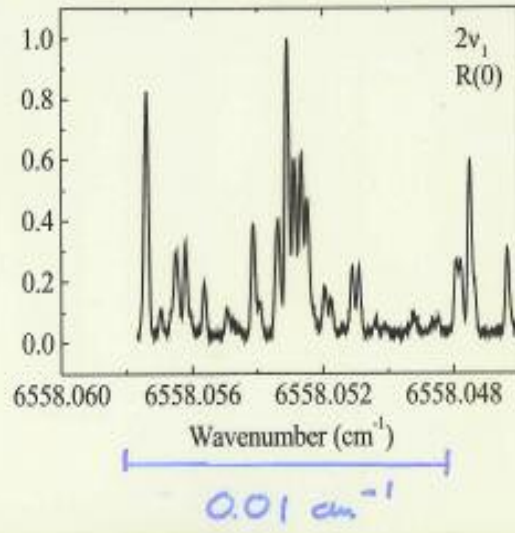
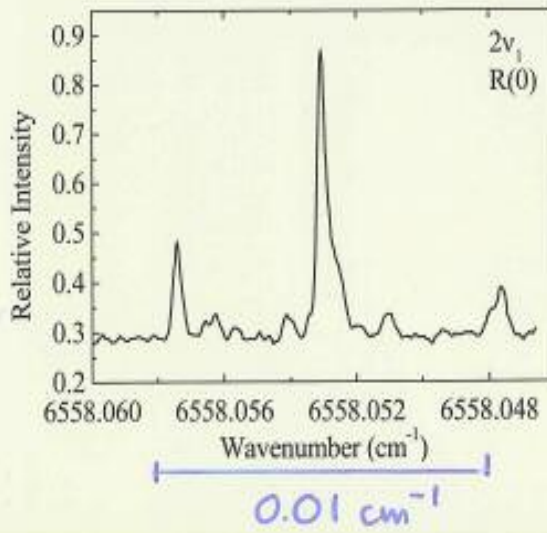
A case molecule, $F_3CC\equiv C-H$

OVERTONE
 $2\nu_1$



BEFORE:
multi-pass cell
without laser stabilization (3 MHz)

AFTER:
build-up cavity
with laser stabilization (100 kHz)

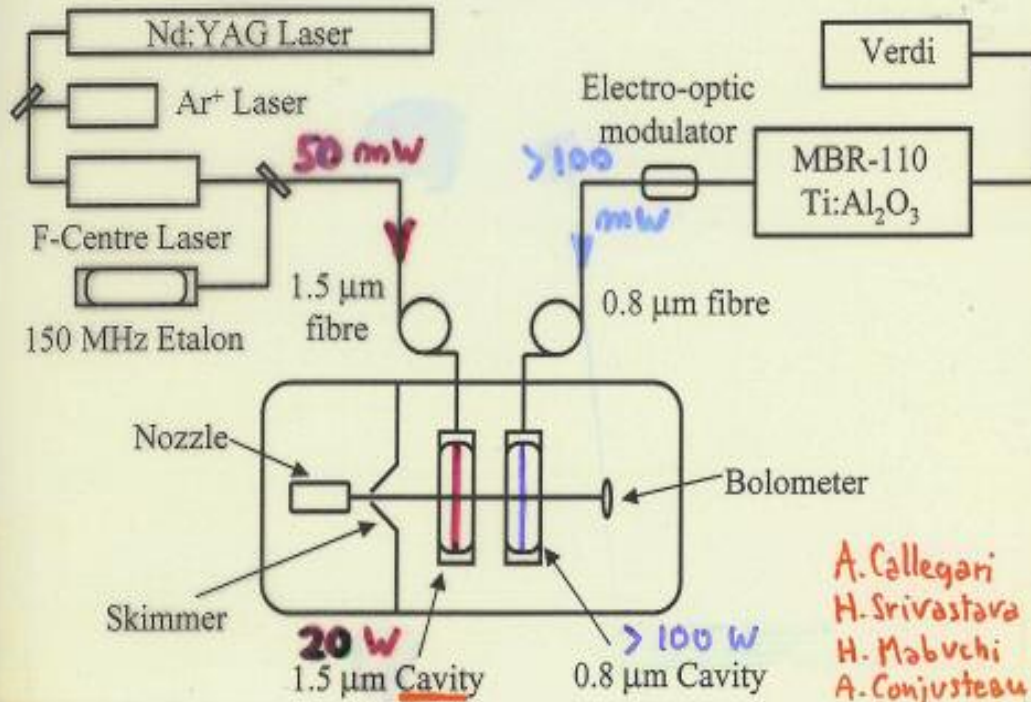


Double Resonance Experimental Setup

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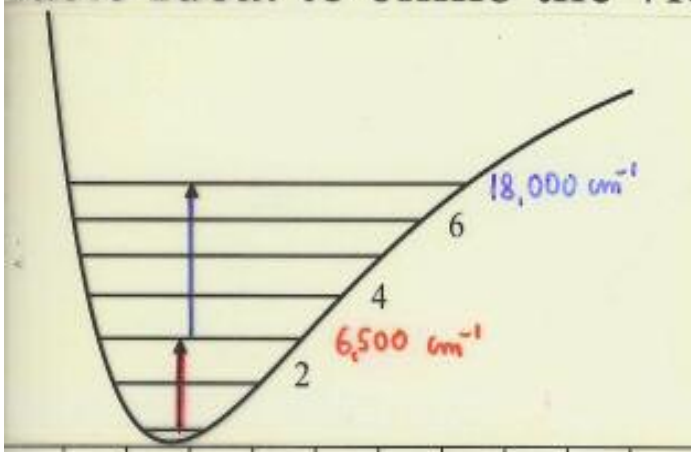


Extreme bolometry
(Do not try this at home)



A. Callegari
H. Srivastava
H. Mabuchi
A. Conjusteau

Basic Idea: to climb the vibrational ladder



| Transition | Saturation Power (W) |
|------------|----------------------|
| 0→2 | 1 |
| 0→4 | 600 |
| 0→6 | 48 000 |
| 2→6 | 50 |

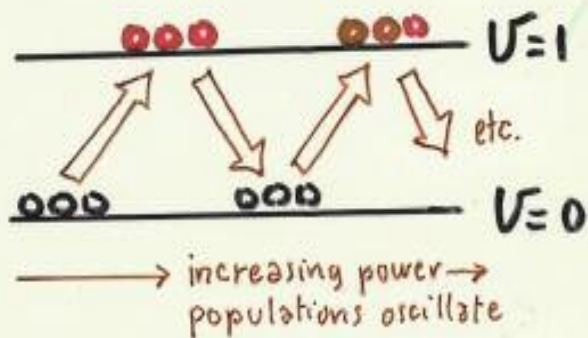
(13)

If you work hard at aligning the laser and placing the laser beam waist exactly on the mol. beam you can see COHERENCE EFFECTS.

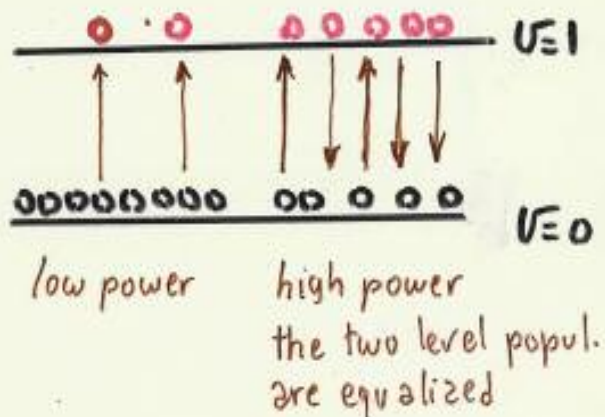


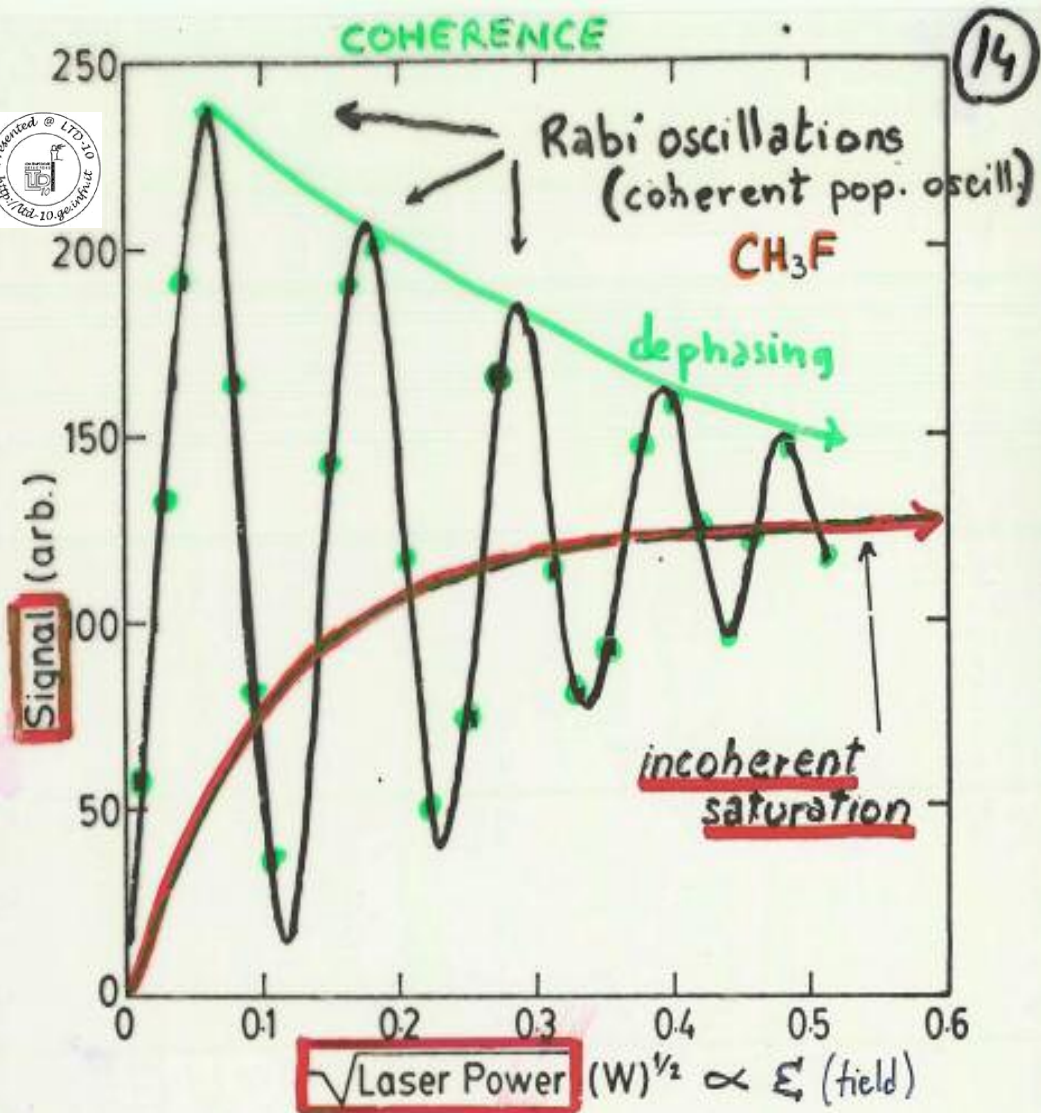
Let us consider a **Two level system:**

Coherent excitation



incoherent excitation





$Q(1,1) - 1 \leftarrow 0$ Transition ν_3 band

$$\text{SIGNAL} \propto 1 - \cos\left(\frac{\mu}{\hbar} E_{\text{eff}}\right)$$

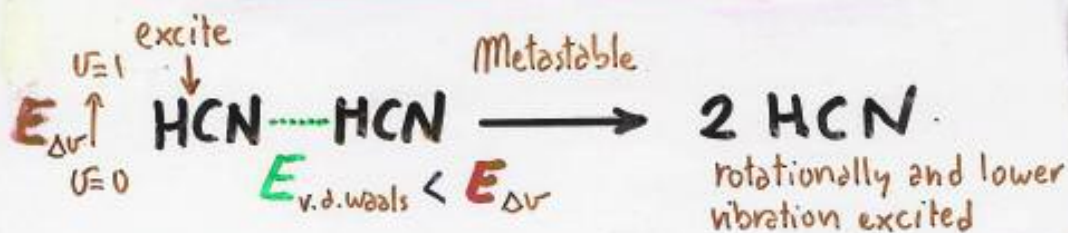
$$E_{\text{eff}} = \frac{2}{c} \left(\frac{P}{\epsilon_0}\right)^{1/2}$$

The transition dipole moment
can therefore be measured
with good precision

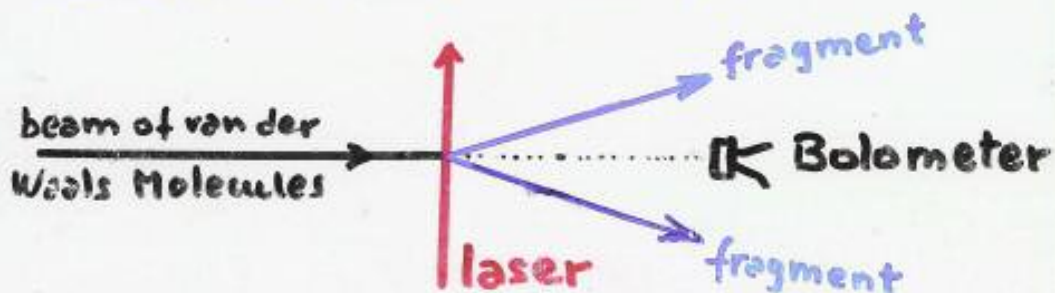
$$\mu = 0.210 \pm 0.01 \text{ D}$$

Photodissociation Spectroscopy of van der Waals Molecules

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Instead of measuring the energy deposited into the bolometer by the pumped molecules, what is measured is the energy missing at the bolometer due to the dissociation of the complexes.



The sensitivity is similar but the flux of van der Waals molecules is generally smaller than the flux of stable molecules.

R.E. Miller, et al., Univ. of North Carolina at Chapel Hill.



HCN-HCN

ν_1 band

EXPAND

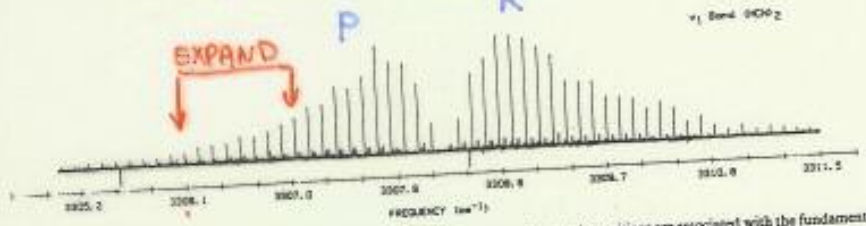


FIG. 1. The high resolution spectrum for the ν_1 band of $(HCN)_2$. The strong equally spaced transitions are associated with the fundamental band, whereas the weaker transitions are due to the $\nu_1 + \nu_4 - \nu_4$ and $\nu_1 + \nu_2 - \nu_2$ hot bands.

J. Chem. Phys., Vol. 88, No. 10, 15 May 1988

HCN-HCN

ν_2 band

5 times more intense

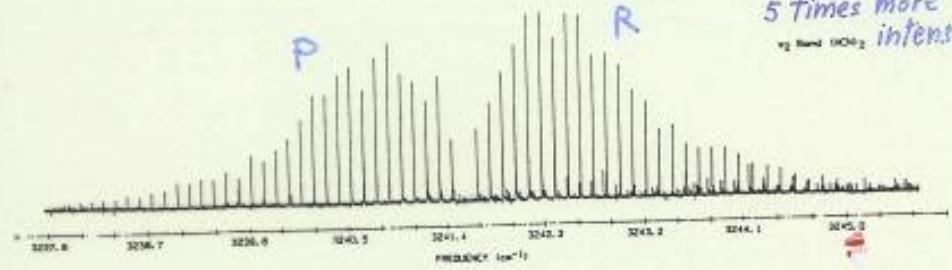


FIG. 5. The high resolution spectrum for the ν_2 band of $(HCN)_2$. A number of hot band transitions can be seen to the high frequency end of the spectrum.

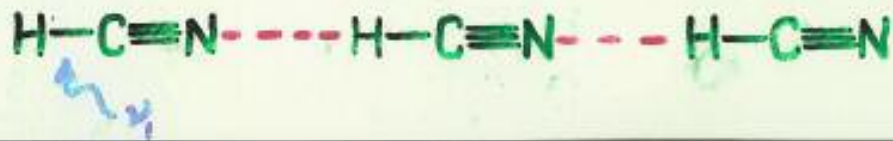
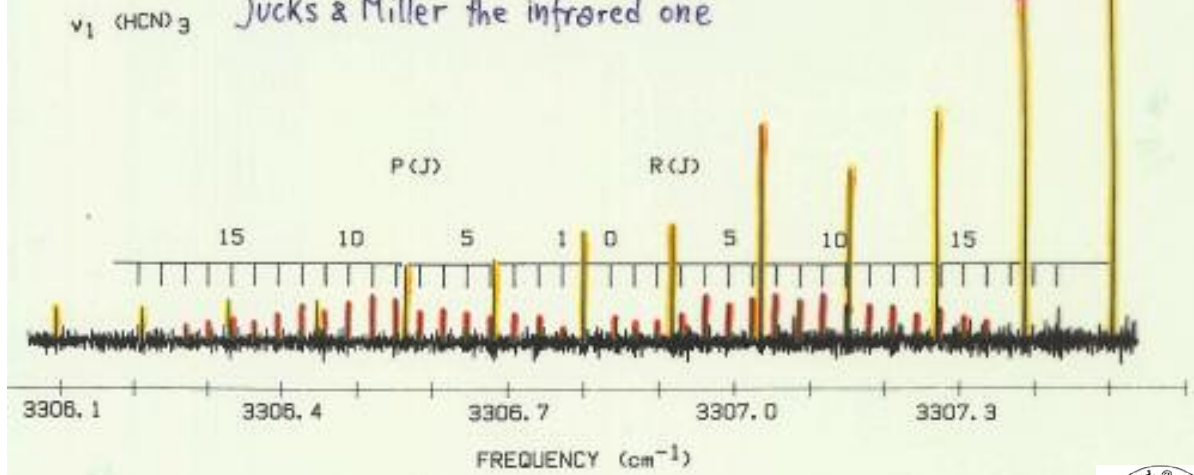
J. Chem. Phys., Vol. 88, No. 10, 15 May 1988

Linear Trimer

Jucks & Miller

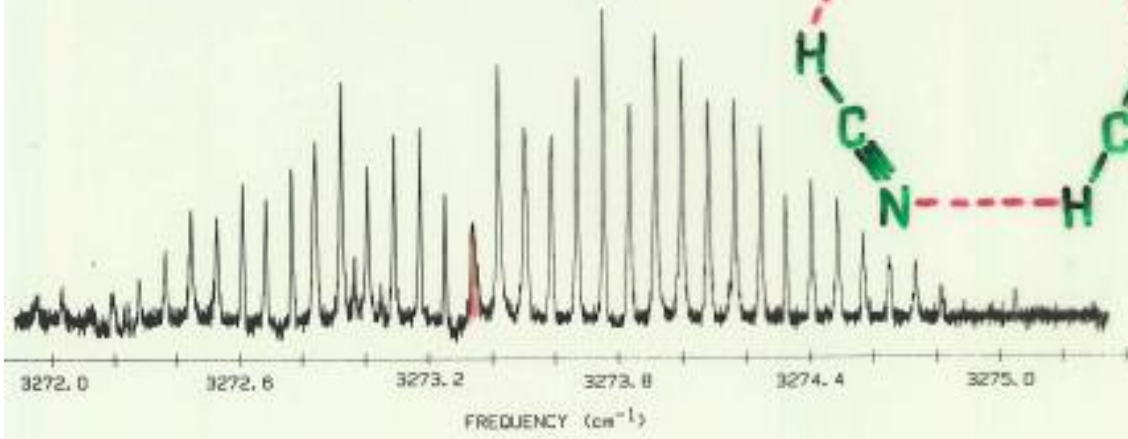
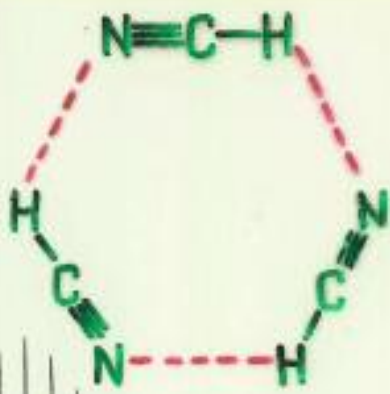
(17)

Gutowsky et al. have measured the microwave spectrum
Jucks & Miller the infrared one



(18)

NO ABSORPTION IN THE MWAVES
HAS BEEN FOUND. (NO DIPOLE MOM.)

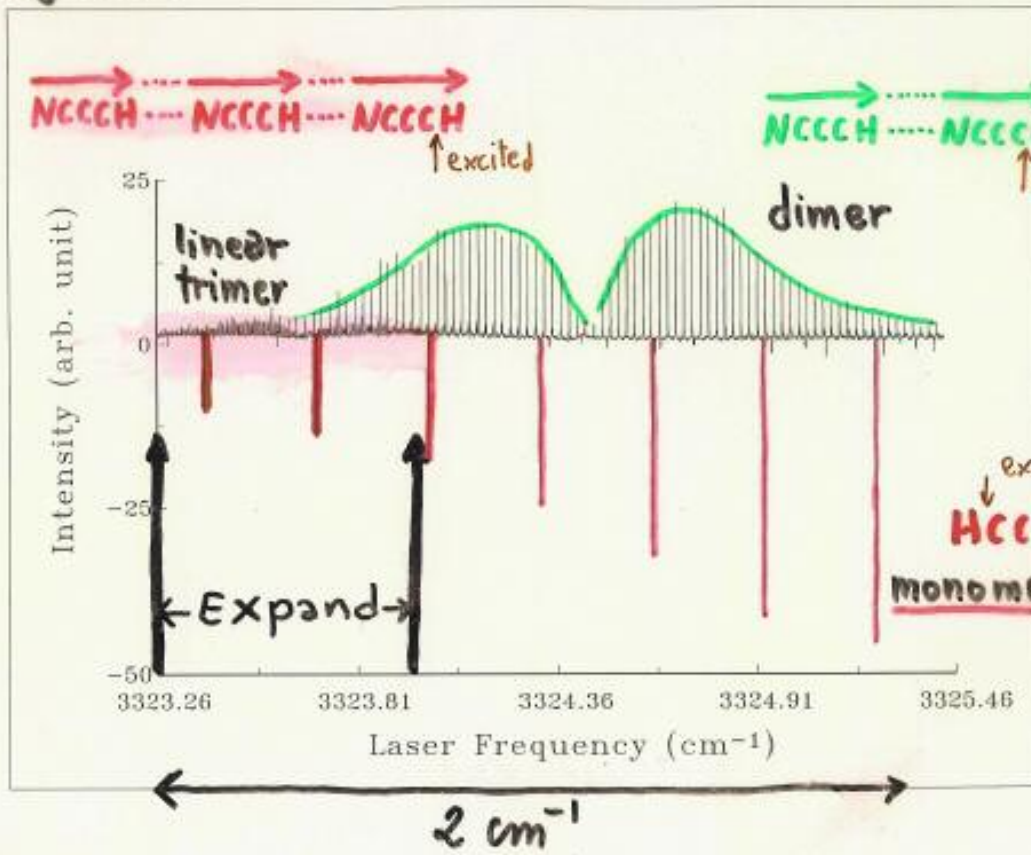


Planar Symmetric Top (Oblate)
 100 times more abundant!
 note broader linewidth.



Jacks + Miller

Yang 1992



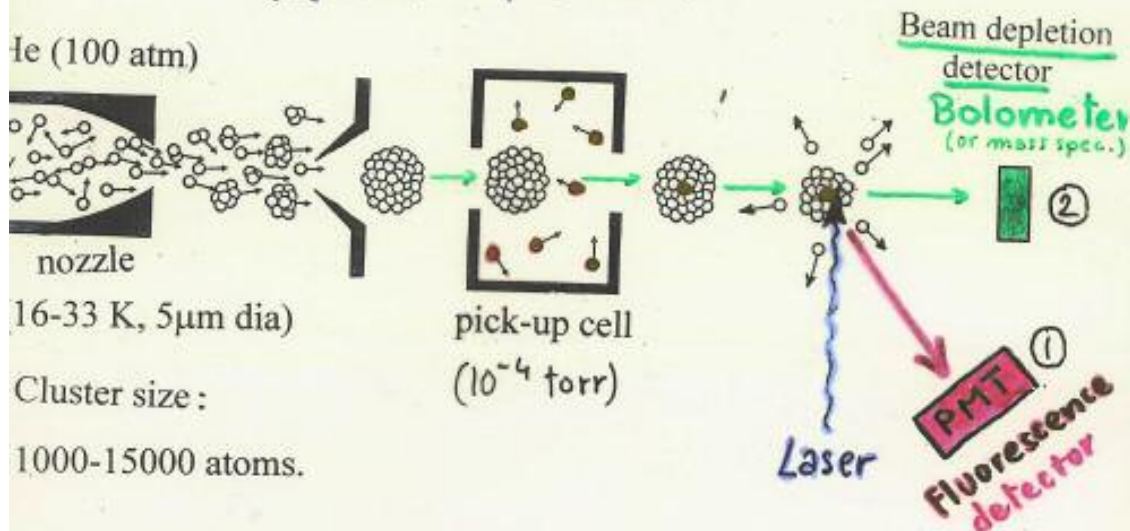
2-19

Helium Nanodroplet Isolation Spectroscopy

Experimental methodology:

(figure drawn by A. Vilesov)

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1) Detection: **Fluorescence** (with a PMT)

2) Detection: **Depletion**

2a) Detector: liquid He cooled (1.5 K) silicon bolometer.

2b) Detector: mass spectrometer.

• Detection scheme:

absorption of photon(s) + energy relaxation into the cluster causes evaporation of He atoms

⇒ beam depletion.



Main advantages:

a) Control of aggregation + no walls.

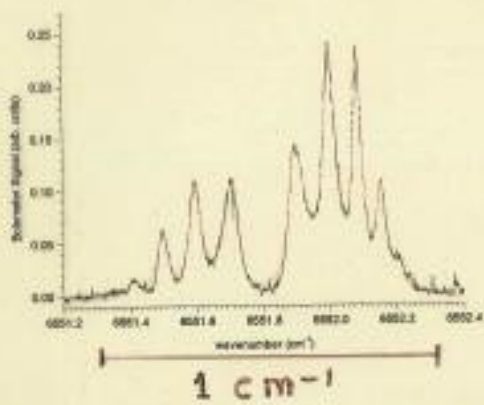
b) Superfluidity. I.e. rotational resolution

c) Low T: very unstable species can be prepared, including **high spin species**.

EXAMPLES OF SPECTRA

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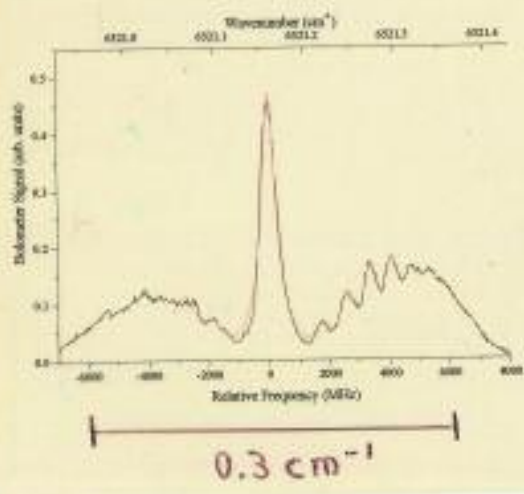
Cyanoacetylene
NCCCH (medium)



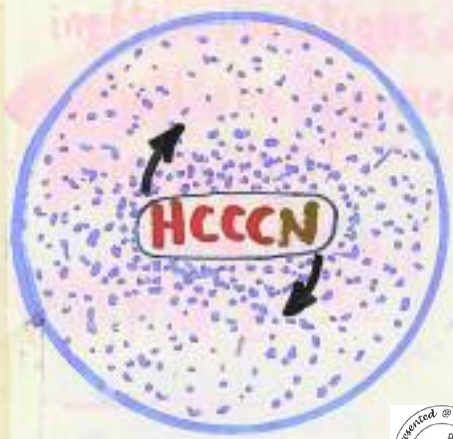
THE MESSAGE:

The moments of inertia are larger than for the free molecule in the gas phase as shown for SF₆ and OCS at the MPI.

Trimethylsilylacetylene
(CH₃)₃SiCCH (large)



WHY?



(22)

APPLICATION:

Molecular Spectroscopy

Nanomatrices are cool

G. Scoles and K. K. Lehmann
Science **287**, 2429 (2000)

When a third HCN molecule would land in the cluster the same phenomenon would occur again and the linear trimer would form instead of

In the helium droplet, instead, when the dimer forms it is already cold and the linear addition process can go on.



Conclusions & Outlook

(23)

- 1 - Bolometric LTDs have had a tremendous impact in the field of spectroscopy and more generally on chemical-physics.
- 2 - As the NEPs used so far are $\sim 10^{-13} \div 10^{-14}$ the field is far from saturated since improvements of a factor of 10^3 are "easily" available.
- 3 - Other than the use of lower T and greater sensitivity one can foresee developments in the following directions:
 - a) Use of bolometer arrays for miniaturized scattering (especially surface scattering) experiments.
 - b) Use of fast detectors for T. O. F. experiments and single molecules.

BUT REMEMBER: **CHEMISTRY is not PHYSICS!**

WE NEED APPARATA THAT CAN WORK RELIABLY AND ROUTINELY EVERY DAY IN THE HANDS OF NON-SPECIALISTS.