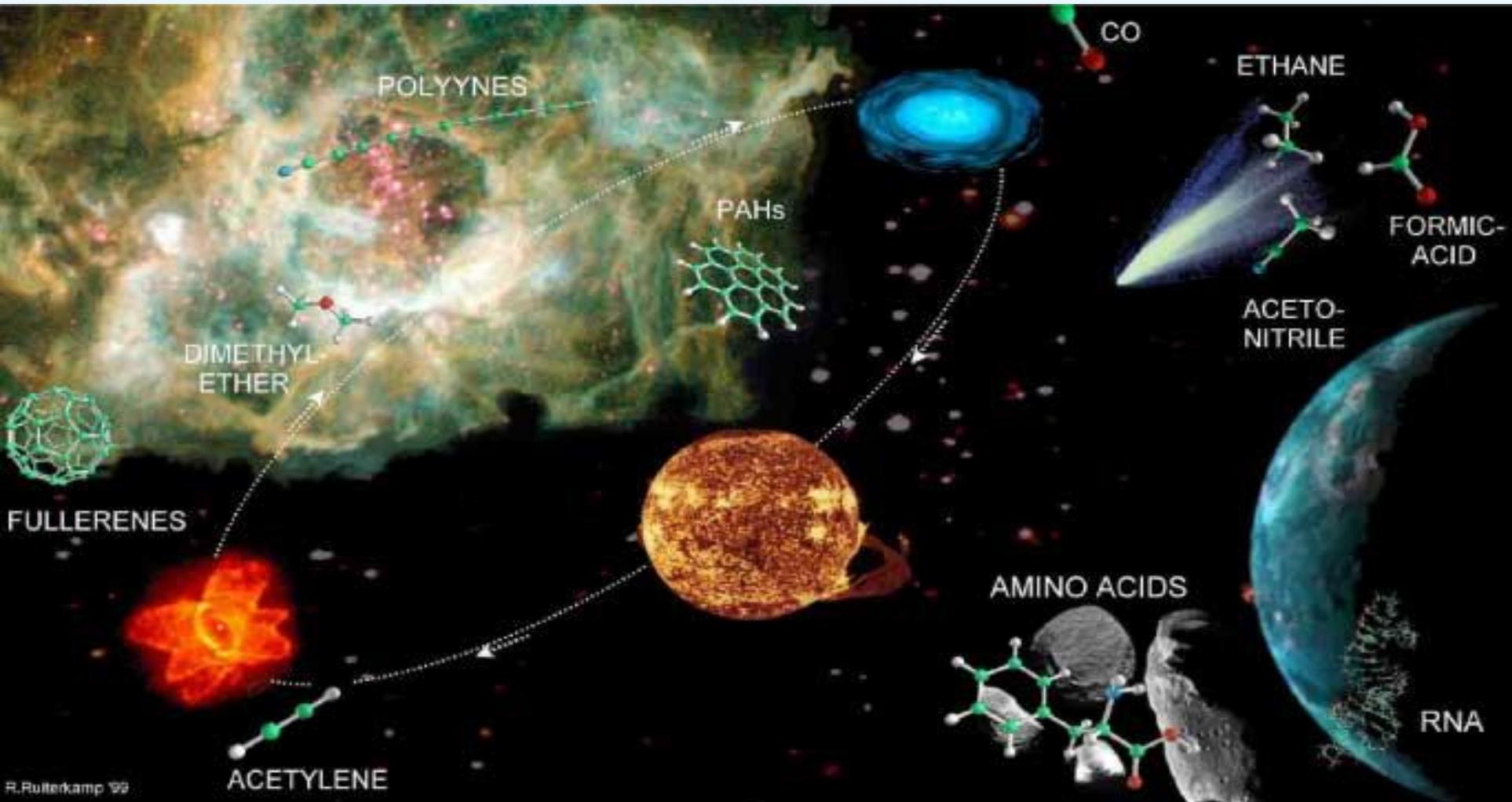


Svatopluk Civiš



Záporné ionty, jejich identifikace v laboratoři a v mezihvězdném prostoru

Úvod

- V mezihvězdném prostoru bylo doposud identifikováno přes 150 molekul a iontů
- Ionty mají dominantní úlohu v chemických reakcích
- Celkem identifikováno v mezihvězdném prostoru 17 kationtů:

(CH^+ , CO^+ , SO^+ , CF^+ , HCO^+ , HCS^+ , HOC^+ , N_2H^+ , H_3^+ , H_2D^+ , HD_2^+ , CH_2D^+ , HCNH^+ , HOCO^+ , H_3O^+ , H_2COH^+ , HC_3NH^+)

- Do roku 2006 nebyly identifikovány záporně nabitě ionty
- reakce v interstelární chemii jsou spjaty s reakcemi kationtů
⇒ pravděpodobný je i výskyt aniontů

Anionty

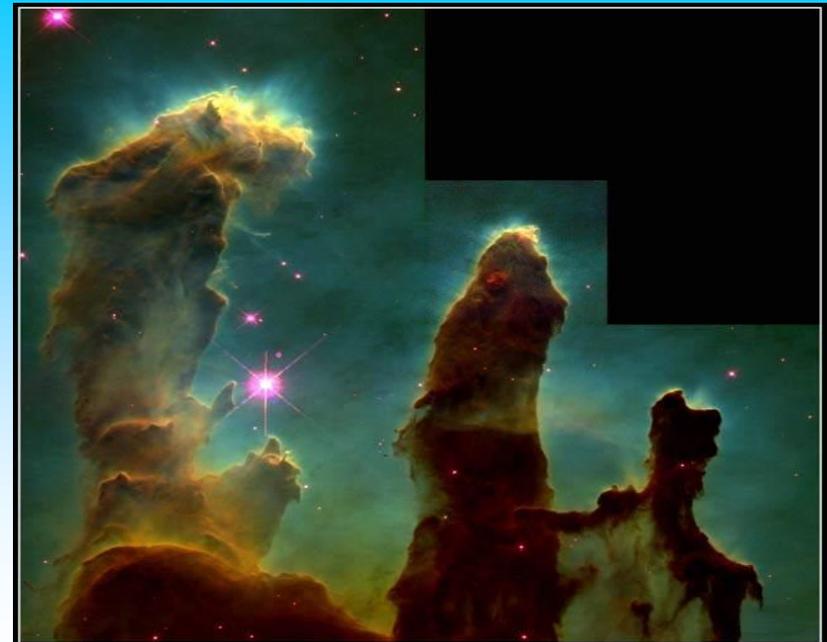
- V laboratoři bylo spektroskopicky detegováno do roku 2006 pouze 11 aniontů:

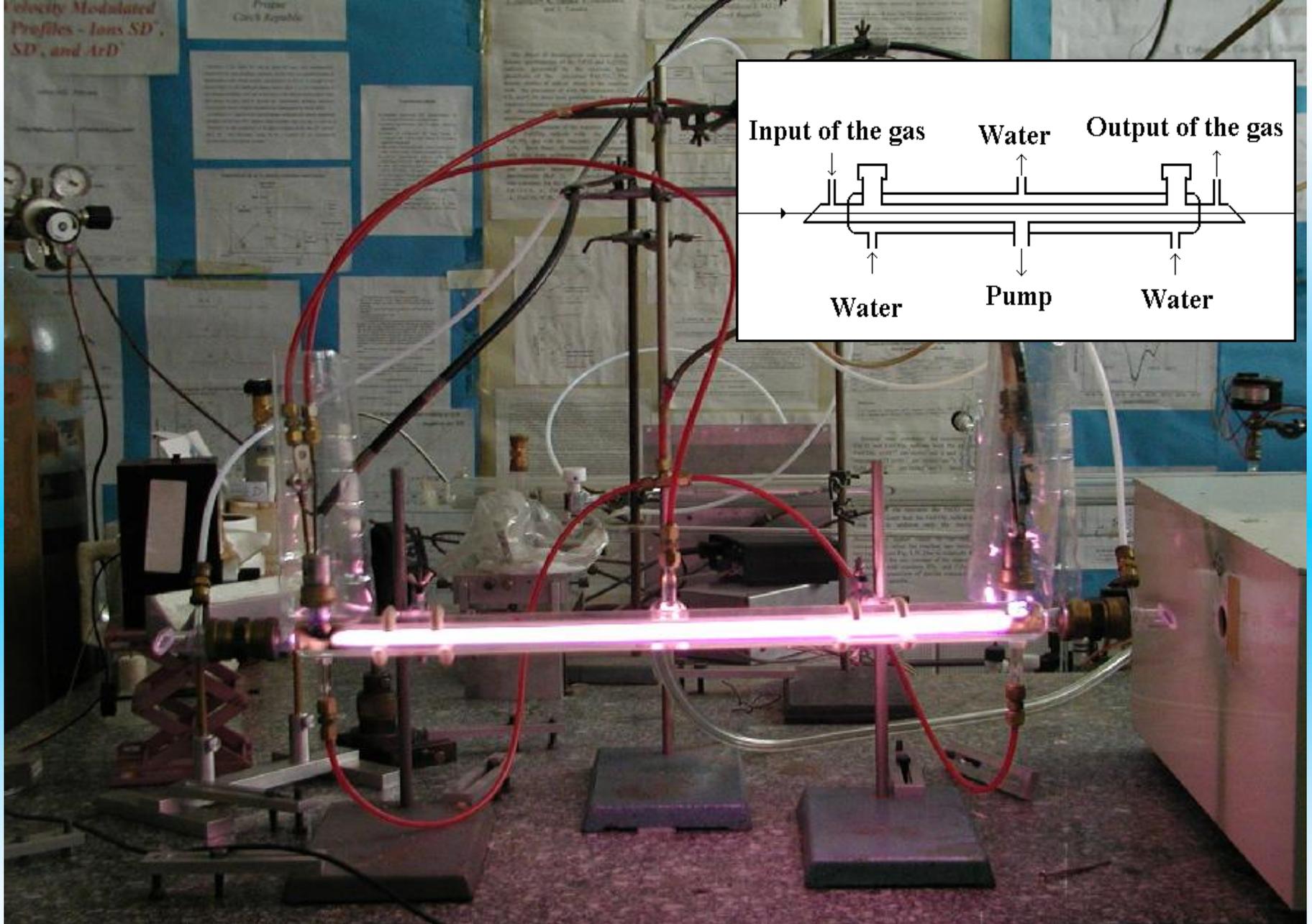
OH^- , SH^- , N_2H^- , N_3^- , NCO^- , NCS^- , NH^- , HNO^- , FHF^- , ClHCl^- , C_2^- ,

Úvod

Infračervená laser-diodová spektroskopie molekulárních iontů

Záporné ionty a jejich identifikace
v laboratoři a v mezihvězdném
prostoru

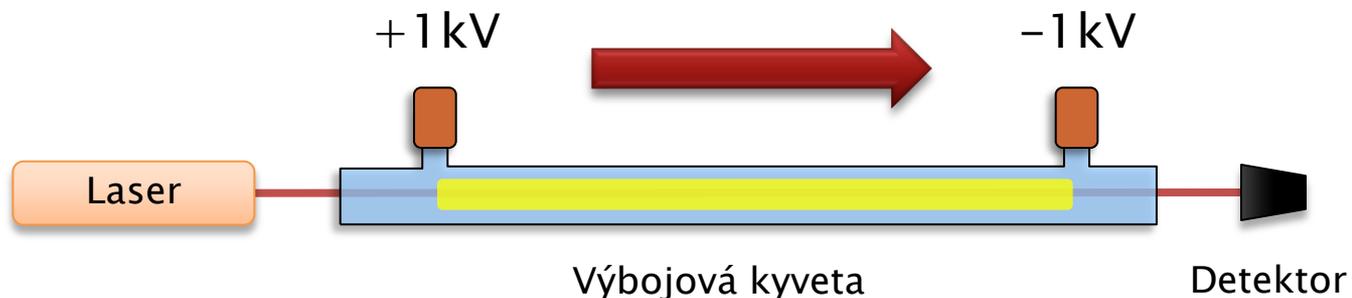




Zelinger, Z., Civiš, S., Kubát, P., and Engst, P.: „Diode laser application for research of molecular ions“, *Infrared Phys. Technol.*, 1995, **36**, 537-543

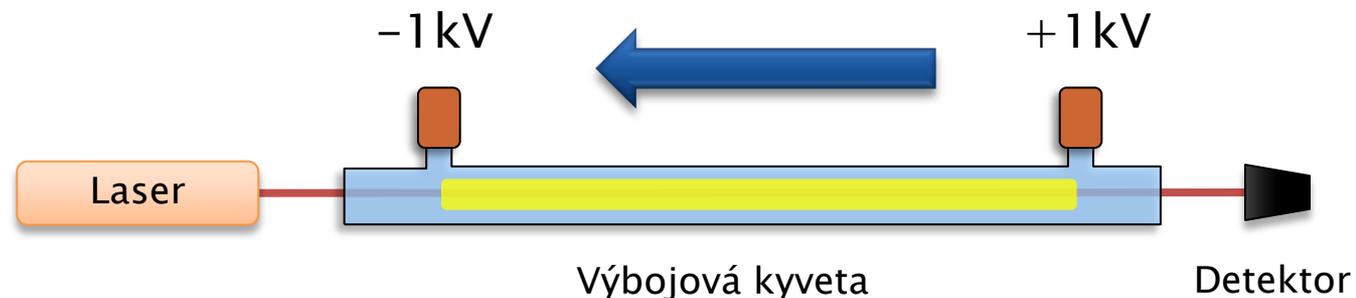
Rychlostně modulační spektroskopie (Dopplerovská modulace)

- ▶ Výboj v pozitivním sloupci
 - Vysoká koncentrace iontů, bohatá chemie
 - Kationty driftují ke katodě
 - Anionty opačným směrem
 - Absorpční profily iontů jsou dopplerovsky posunuty



Rychlostně modulační spektroskopie (Dopplerovská modulace)

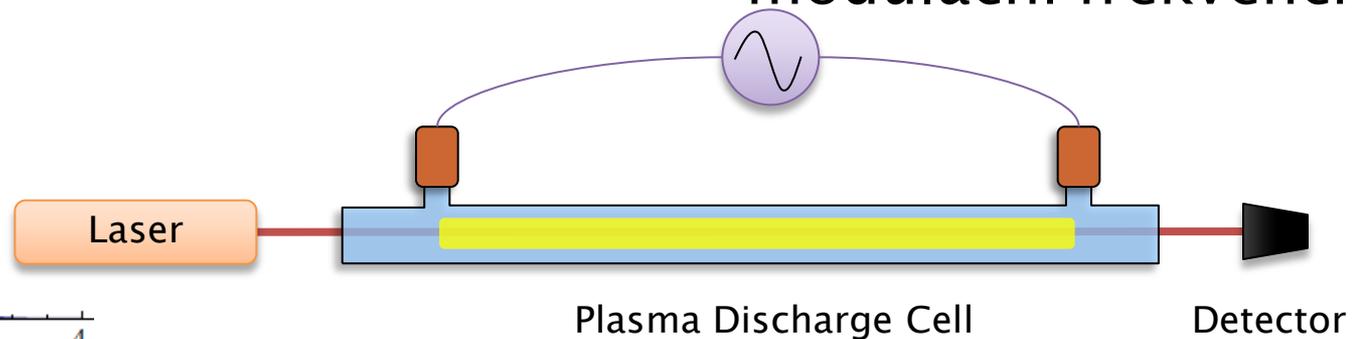
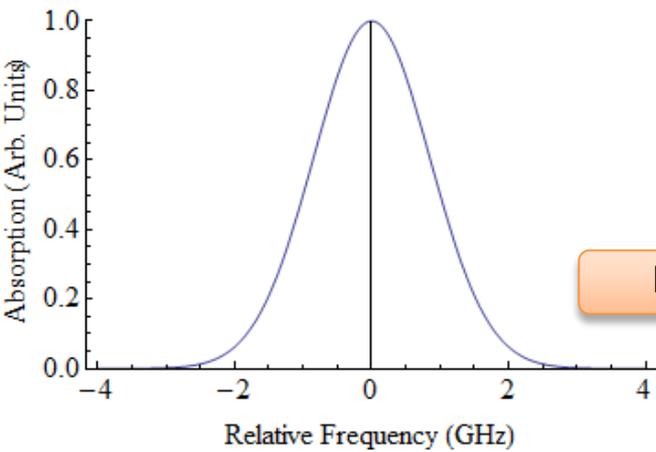
- ▶ Výboj v pozitivním sloupci
 - Vysoká koncentrace iontů, bohatá chemie
 - Kationty driftují ke katodě
 - Anionty opačným směrem
 - Absorpční profily iontů jsou dopplerovsky posunuty



Rychlostně modulační spektroskopie

- ▶ Výboj v pozitivním sloupci
 - Vysoká koncentrace iontů, bohatá chemie
 - Kationty driftují ke katodě
 - Anionty opačným směrem
 - Absorpční profily iontů jsou dopplerovsky posunuty
- ▶ Střídavé napětí:

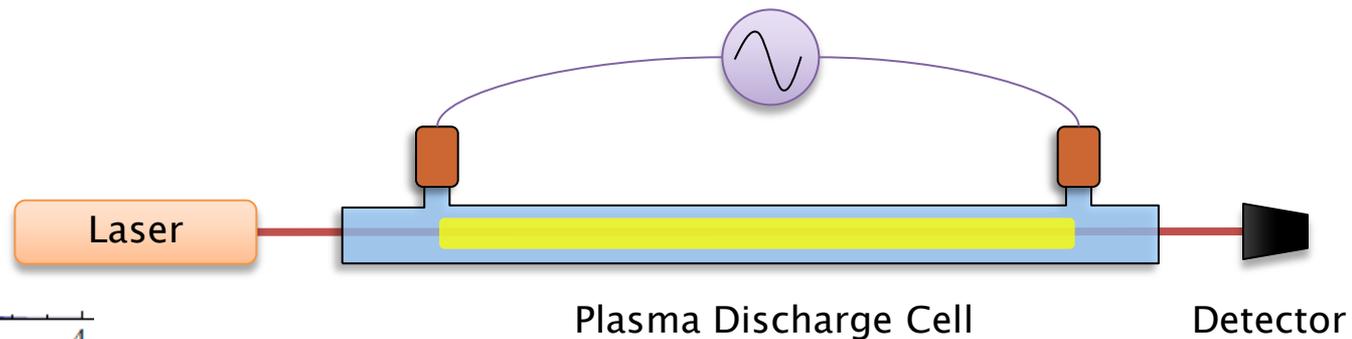
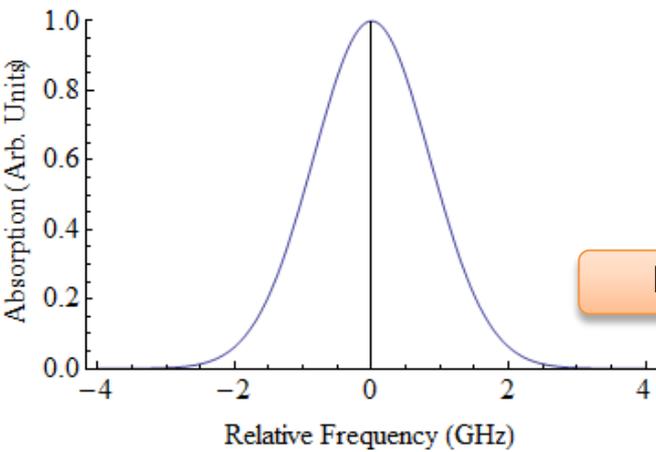
Dopplerovský profil iontu: červený/modrý posun vlnočtu, Demodulace signálu detektoru při modulační frekvenci



Rychlostní modulace

- Dopplerovský posun je dán vztahem:

$$\Delta\nu = \frac{v(\text{ion})}{c} \times f$$



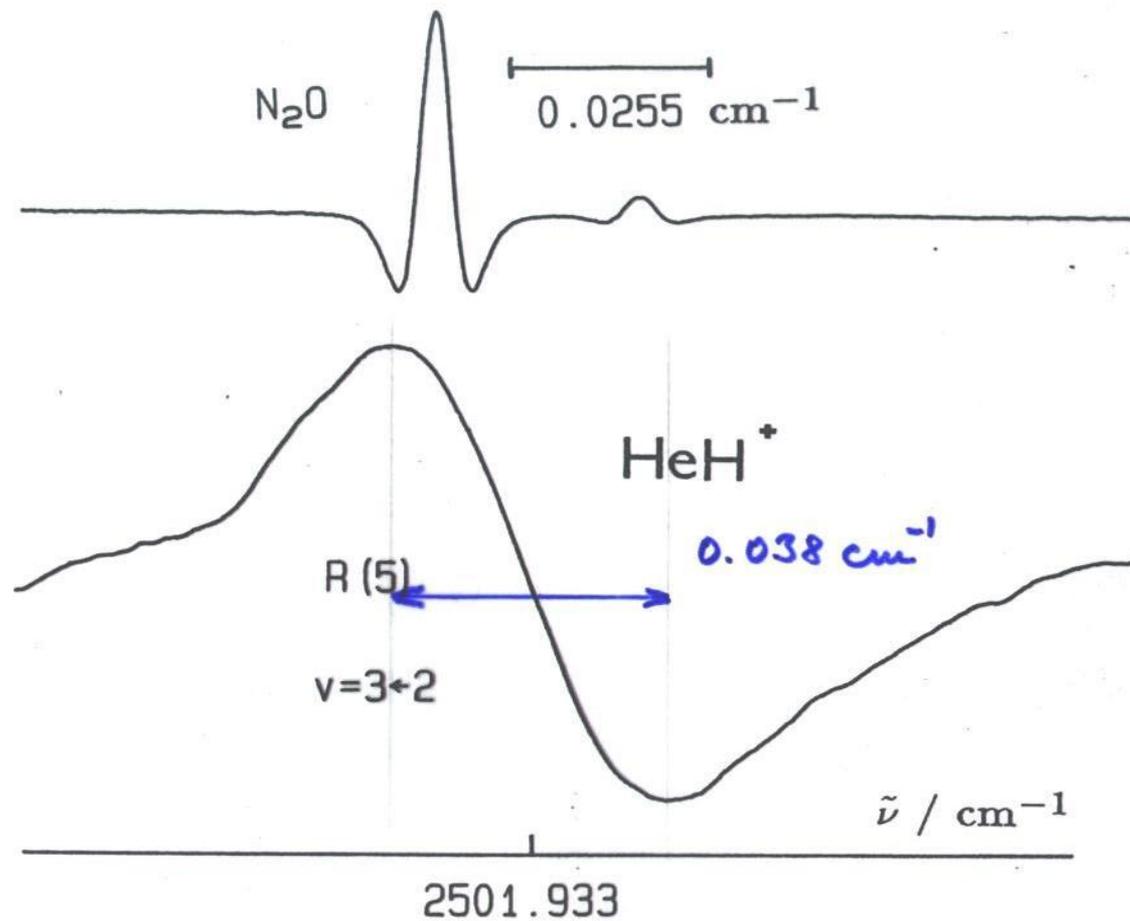
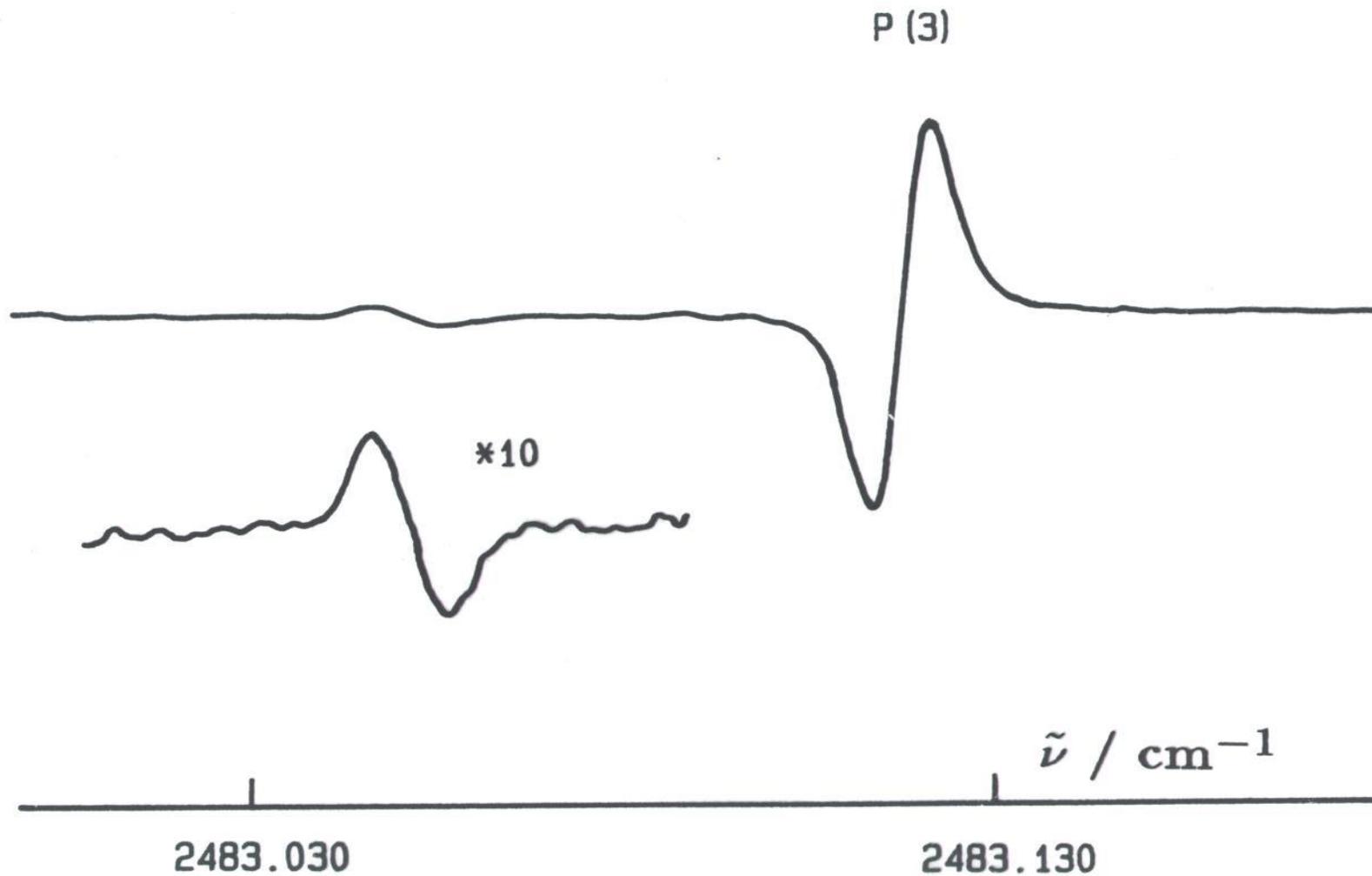


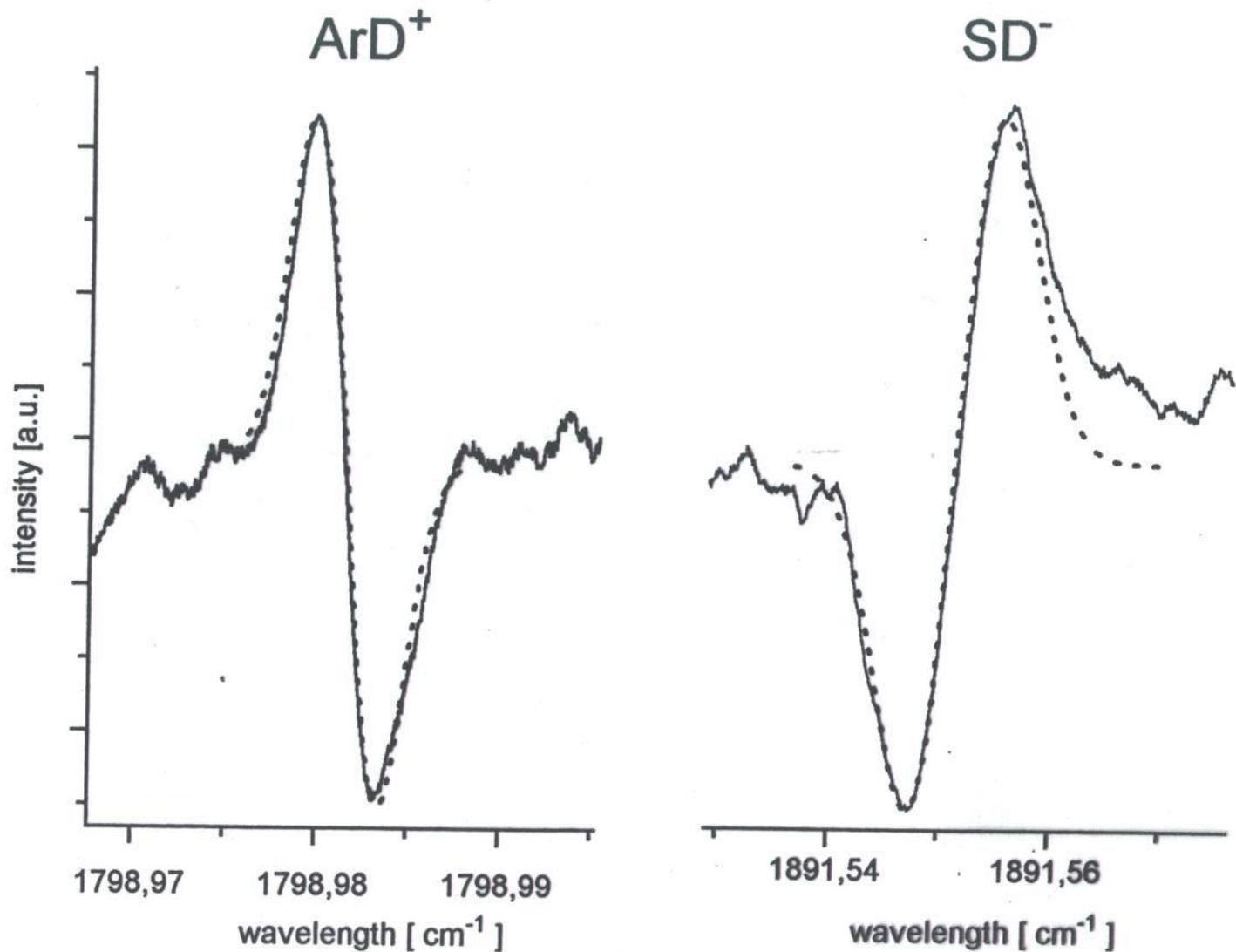
Figure 9. The $v = 3 \leftarrow 2$ R(5) transition of HeH^+

Německo, Universita v Giessenu, 1989

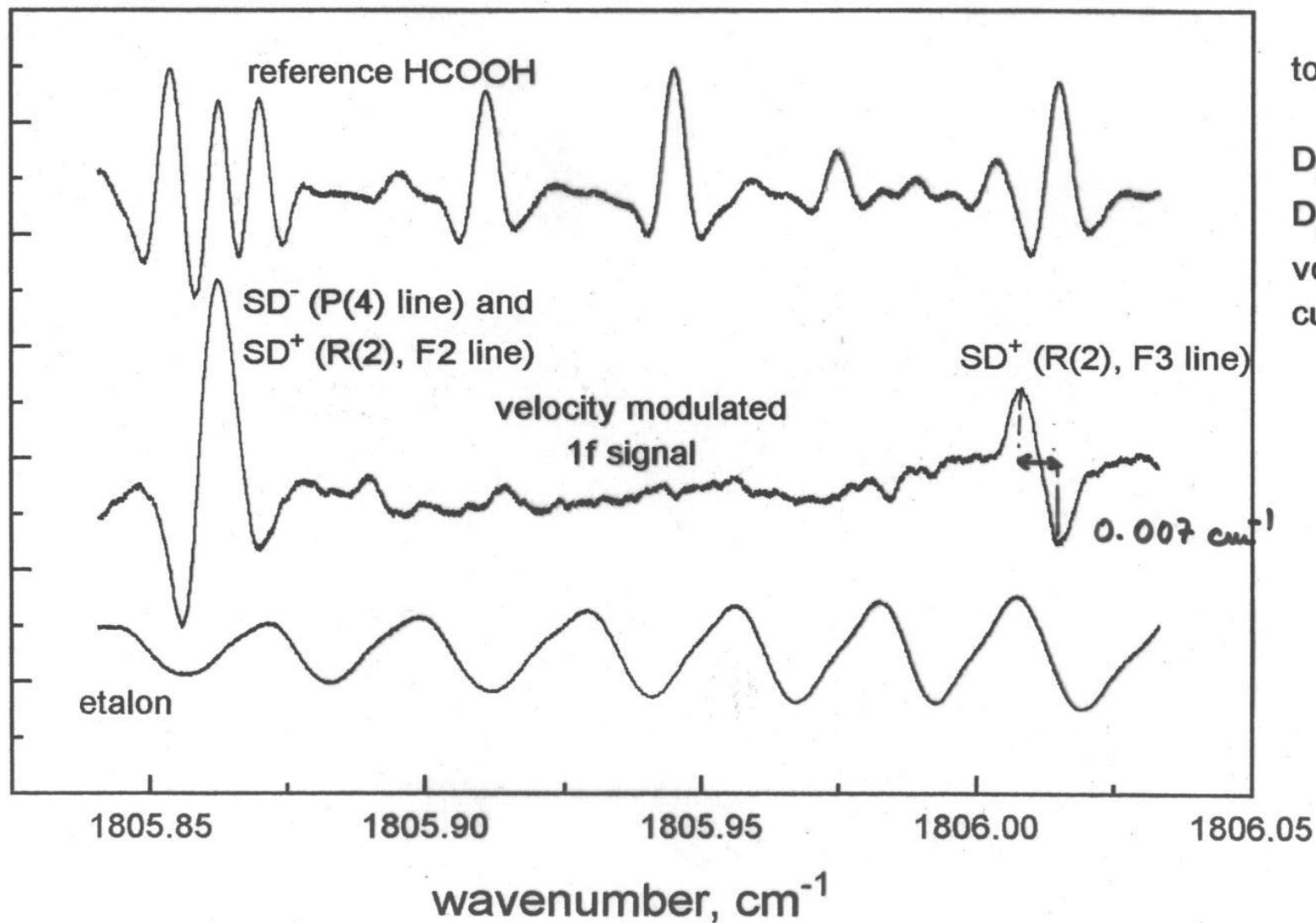


Civiš, Š., Blom, C. E., and Jensen, P.: „Diode Laser Infrared Spectra and Potential Energy Curve for SH^+ ”
J. Mol. Spectrosc., 1989, **138**, 69-78

Praha, 1994



Civiš, S.: „Infrared Diode Laser Study of ArH^+ and ArD^+ Ions in the Positive Column of an ac Glow Discharge“ *Chem. Phys.*, 1994, **186**, 63-76

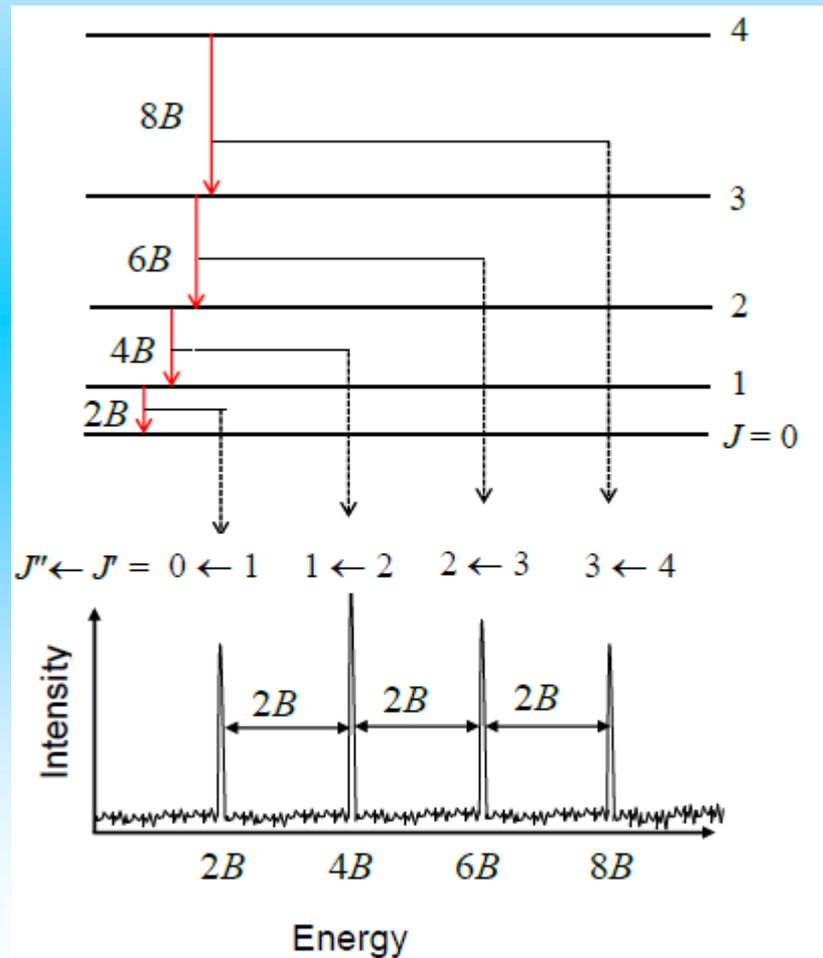


total pressure:
 1.45 Torr
 D₂: 0.008 Torr
 D₂S : 0.002 Torr
 voltage: 1370 V
 current: 0.18 A

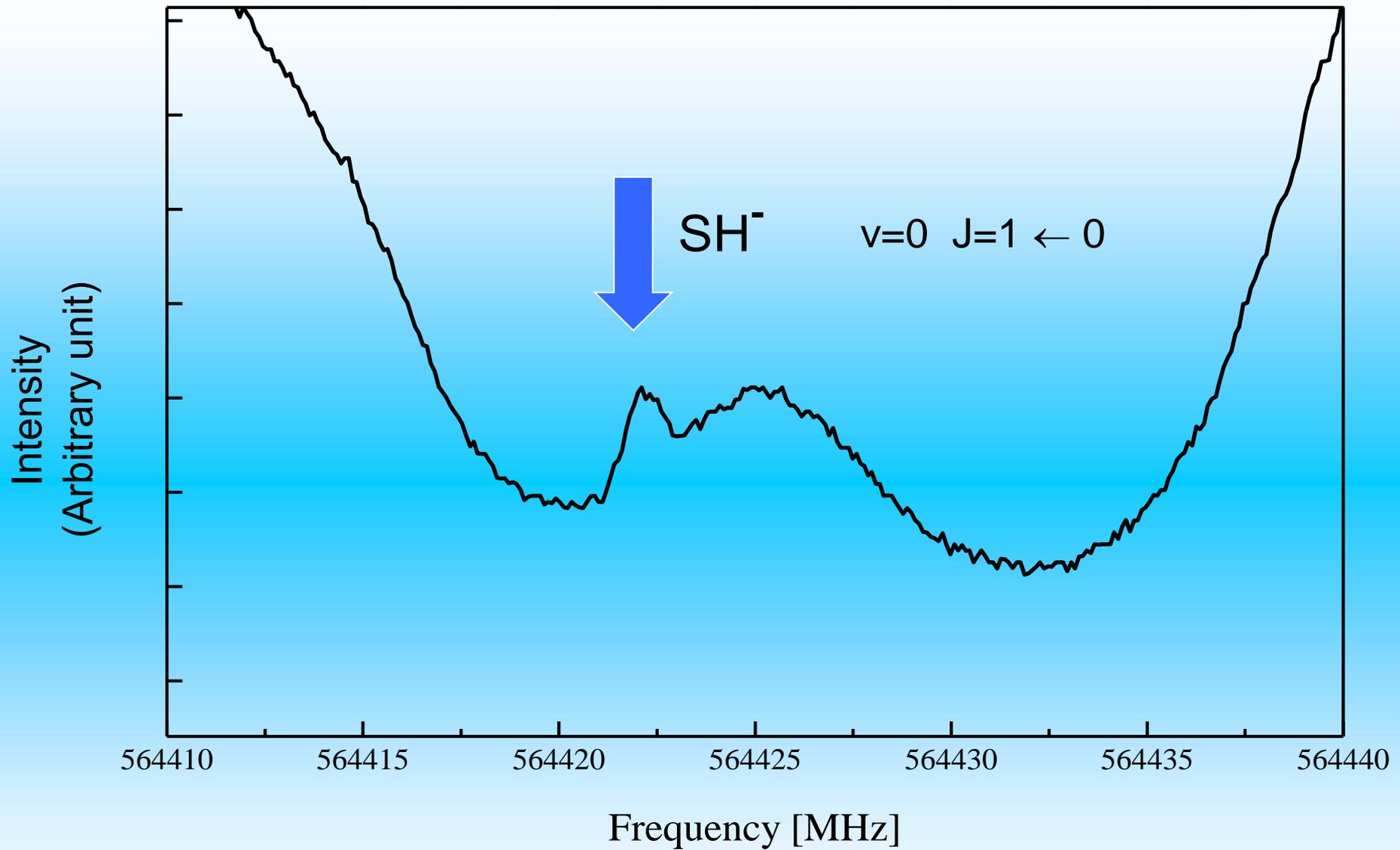
Mihovina M16



SH- Rotační spektrum-přechody

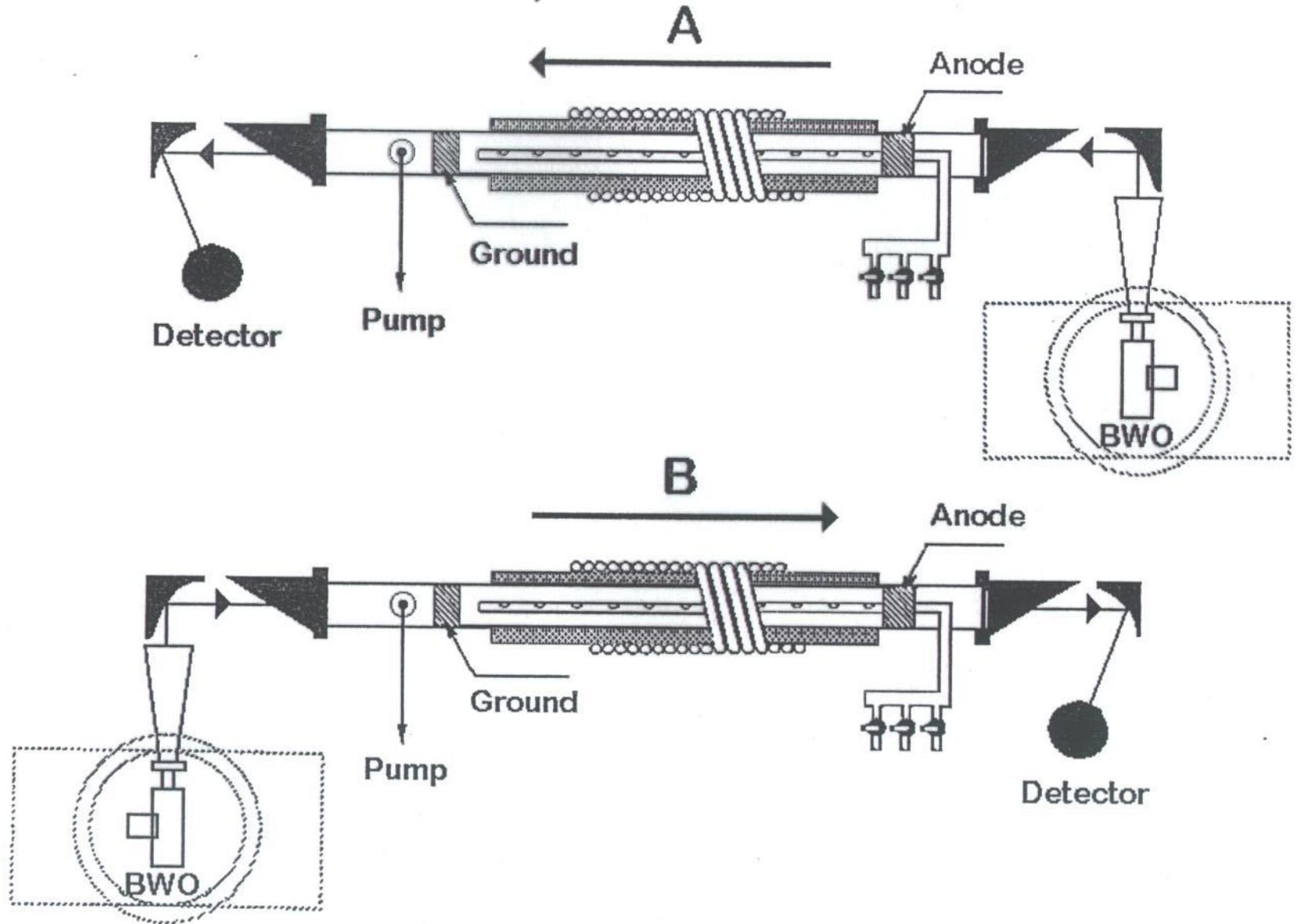


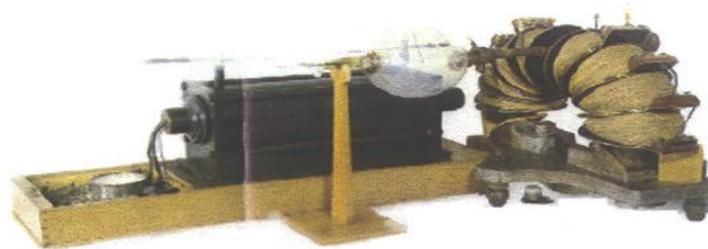
Francie, univerzita v Lille, 1995-1998



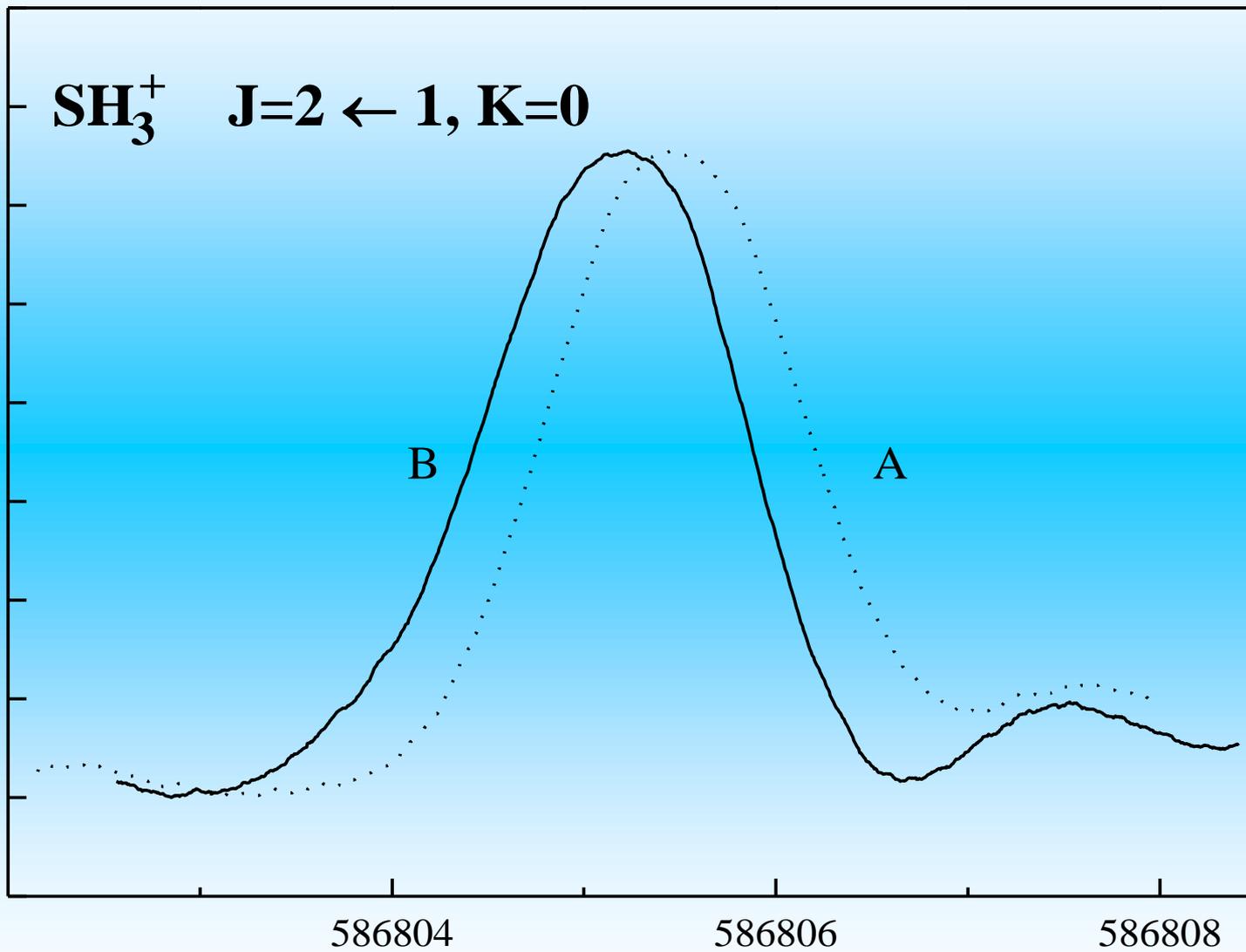
Civiš S., Tretyakov M.Yu., Bailleux S., Bogey M., and Walters A.: „First Identified Submillimeter-wave Spectral Lines of Negative Ions SH^- and SD^- “, *J. Chem. Phys.*, 1998, **108**, 8369-8373

Francie, Universita v Lille





SH₃⁺ J=2 ← 1, K=0



SD⁻ J=1 ← 0

A

B

292357

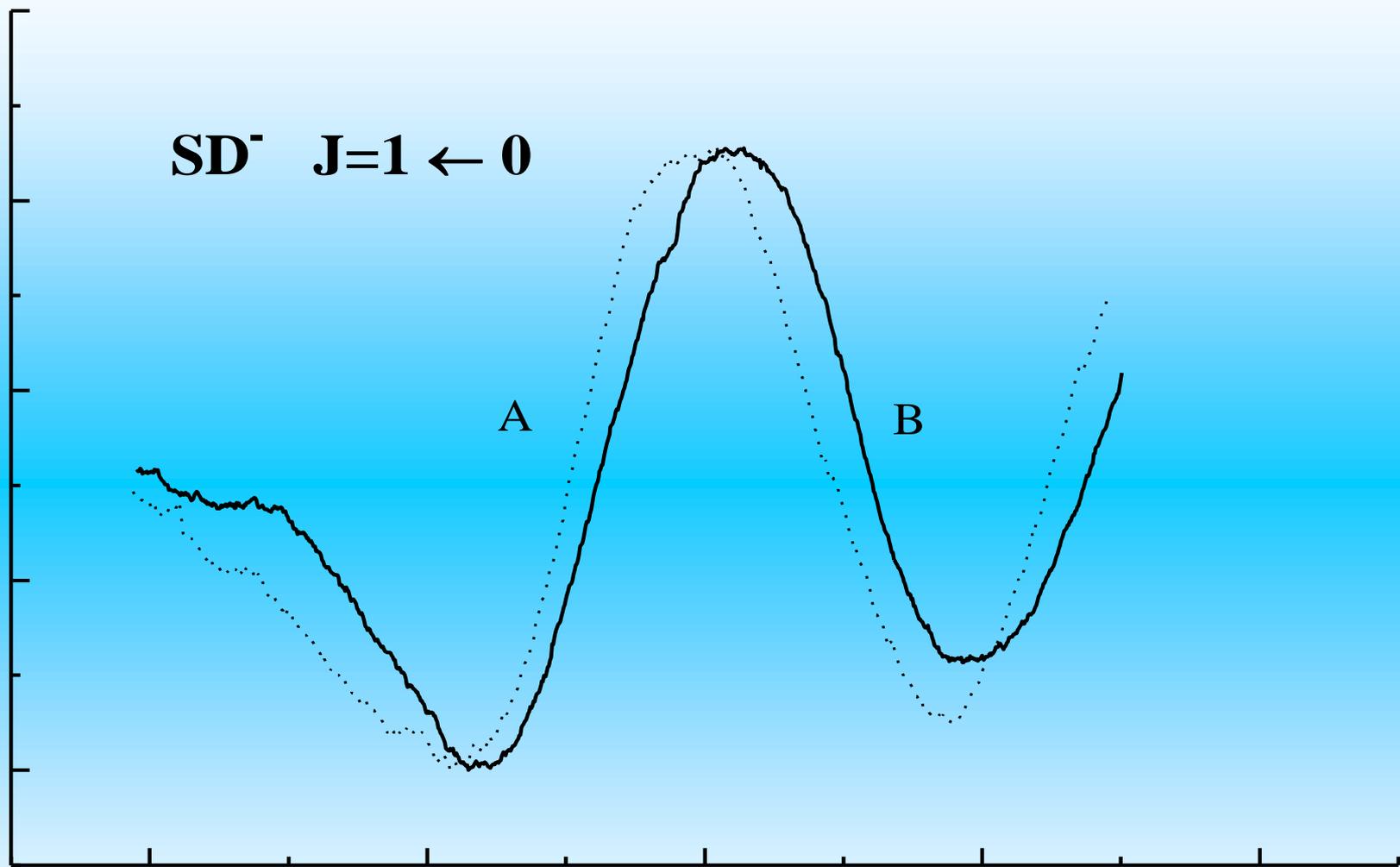
292358

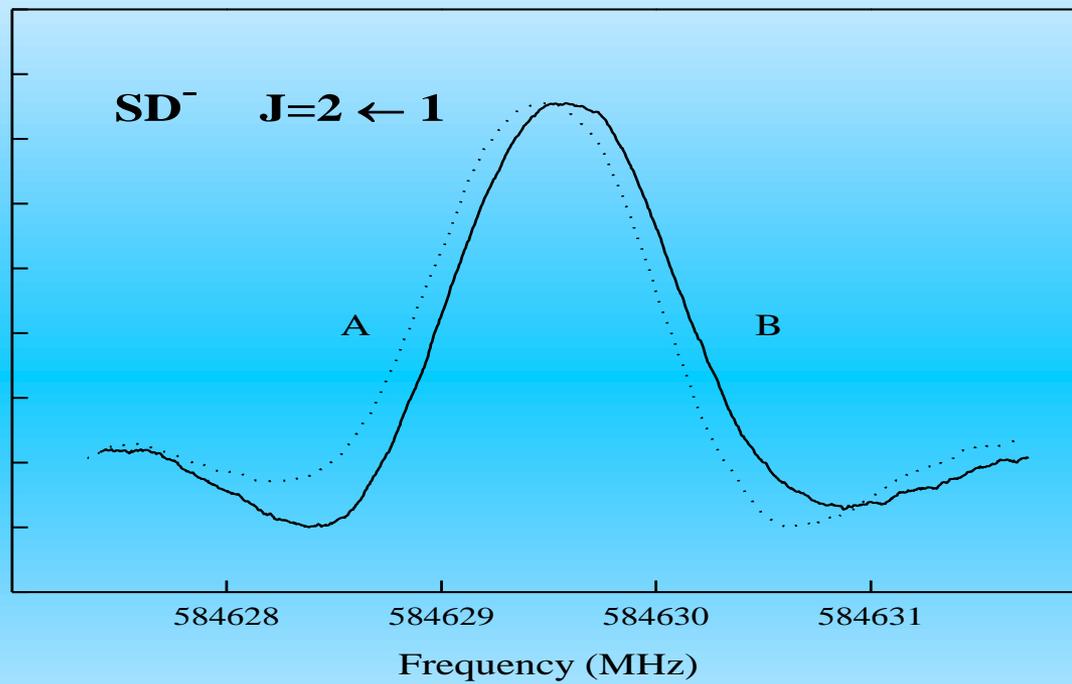
292359

292360

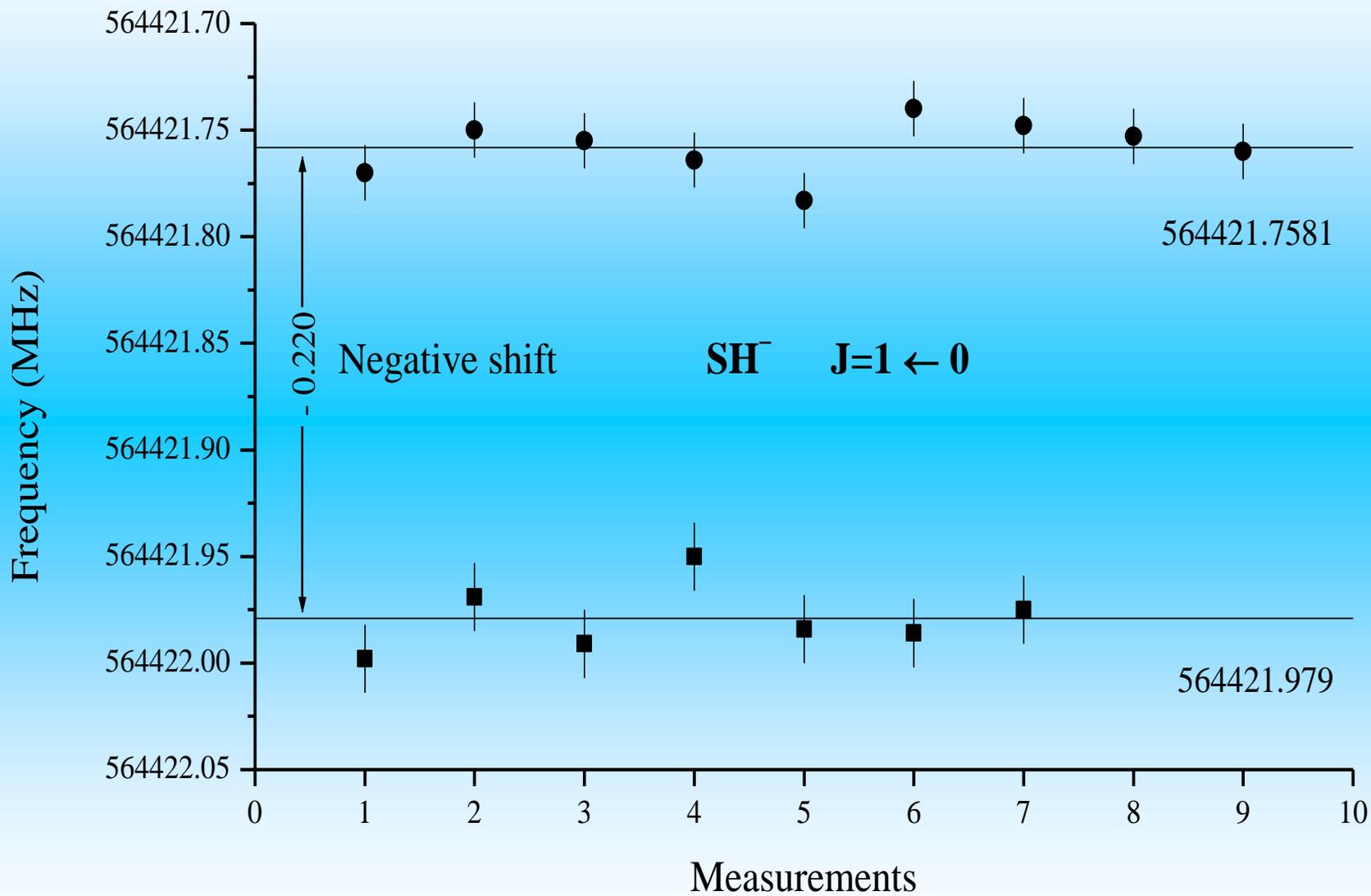
292361

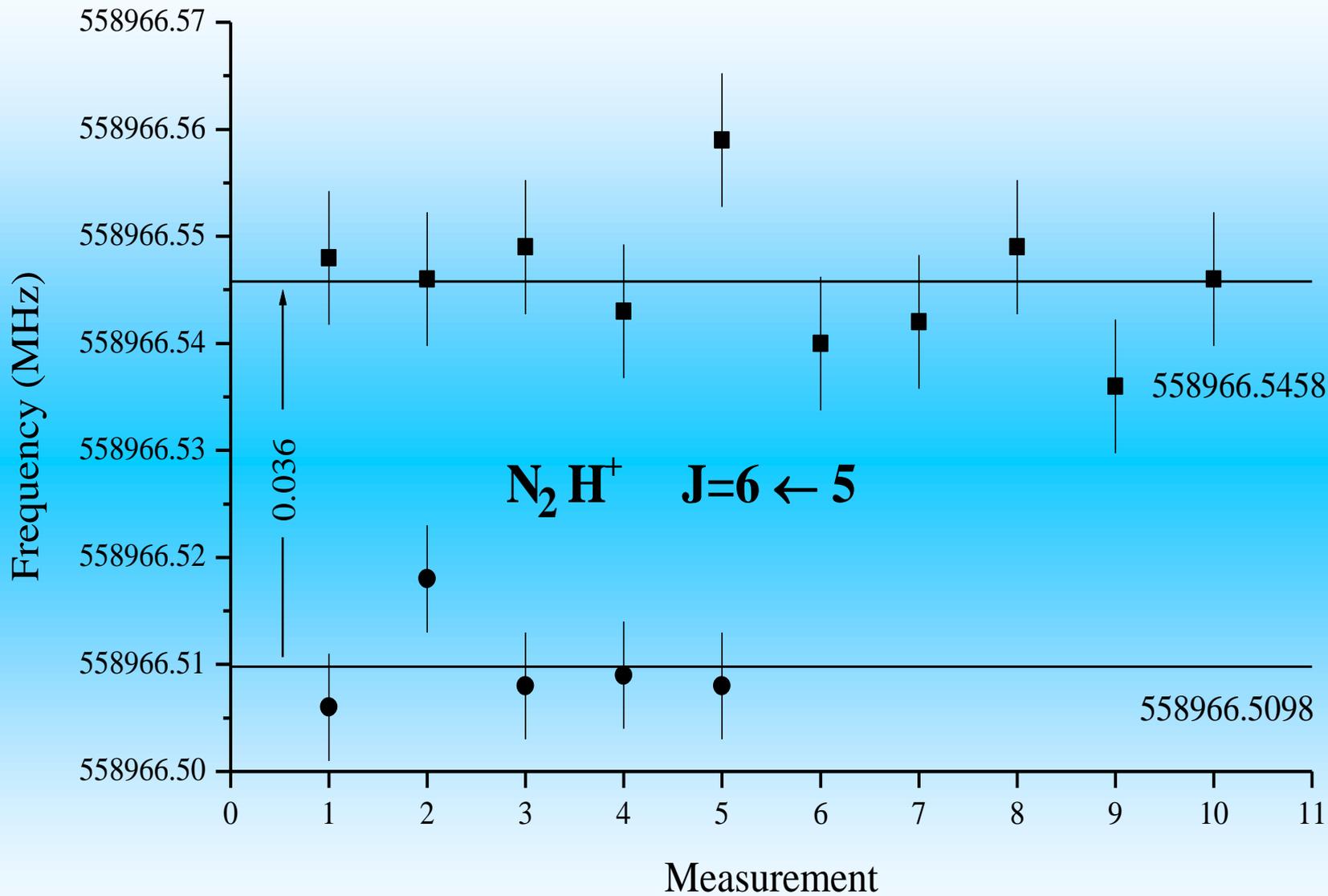
Frequency[MHz]

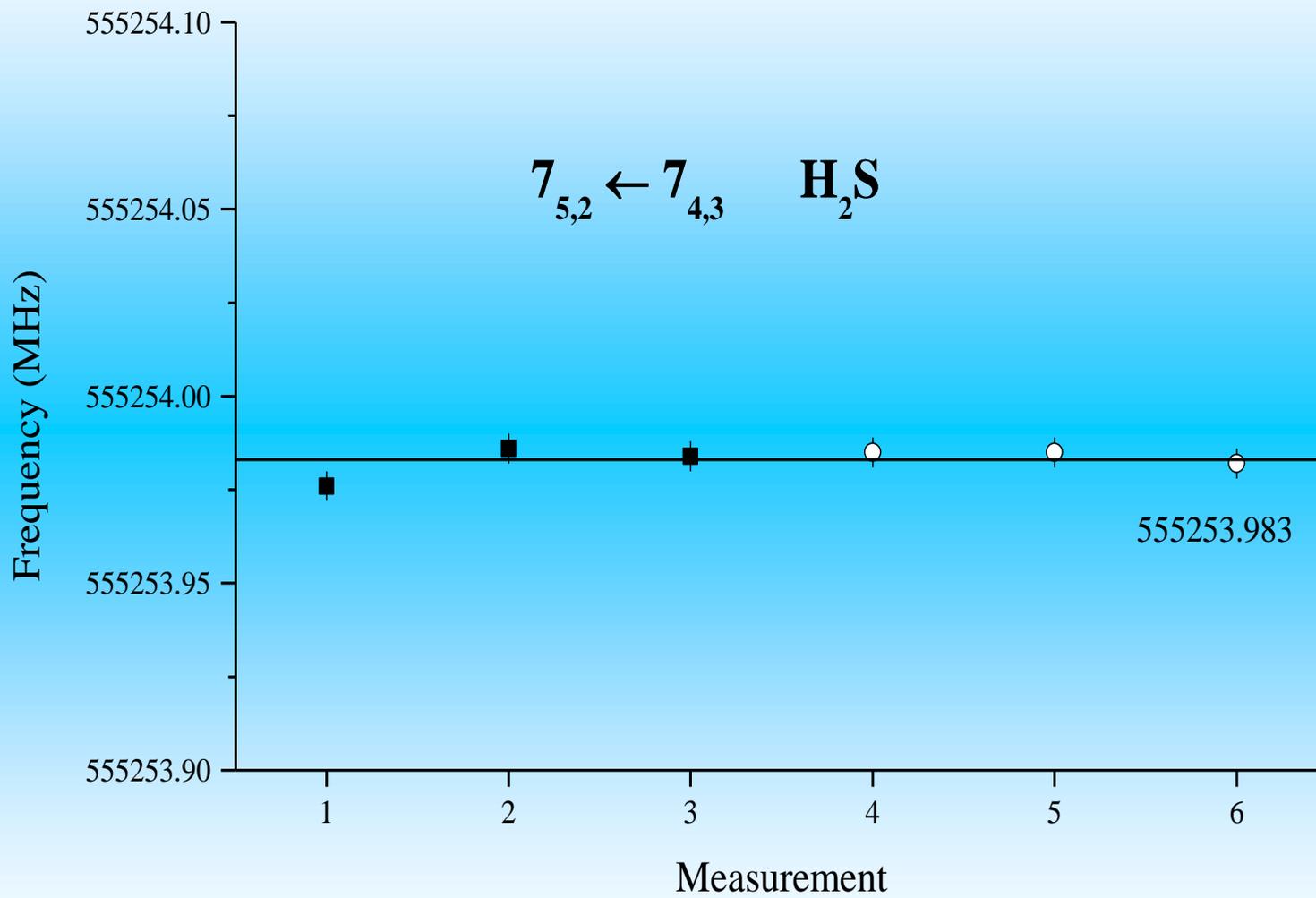




Frequency[MHz]

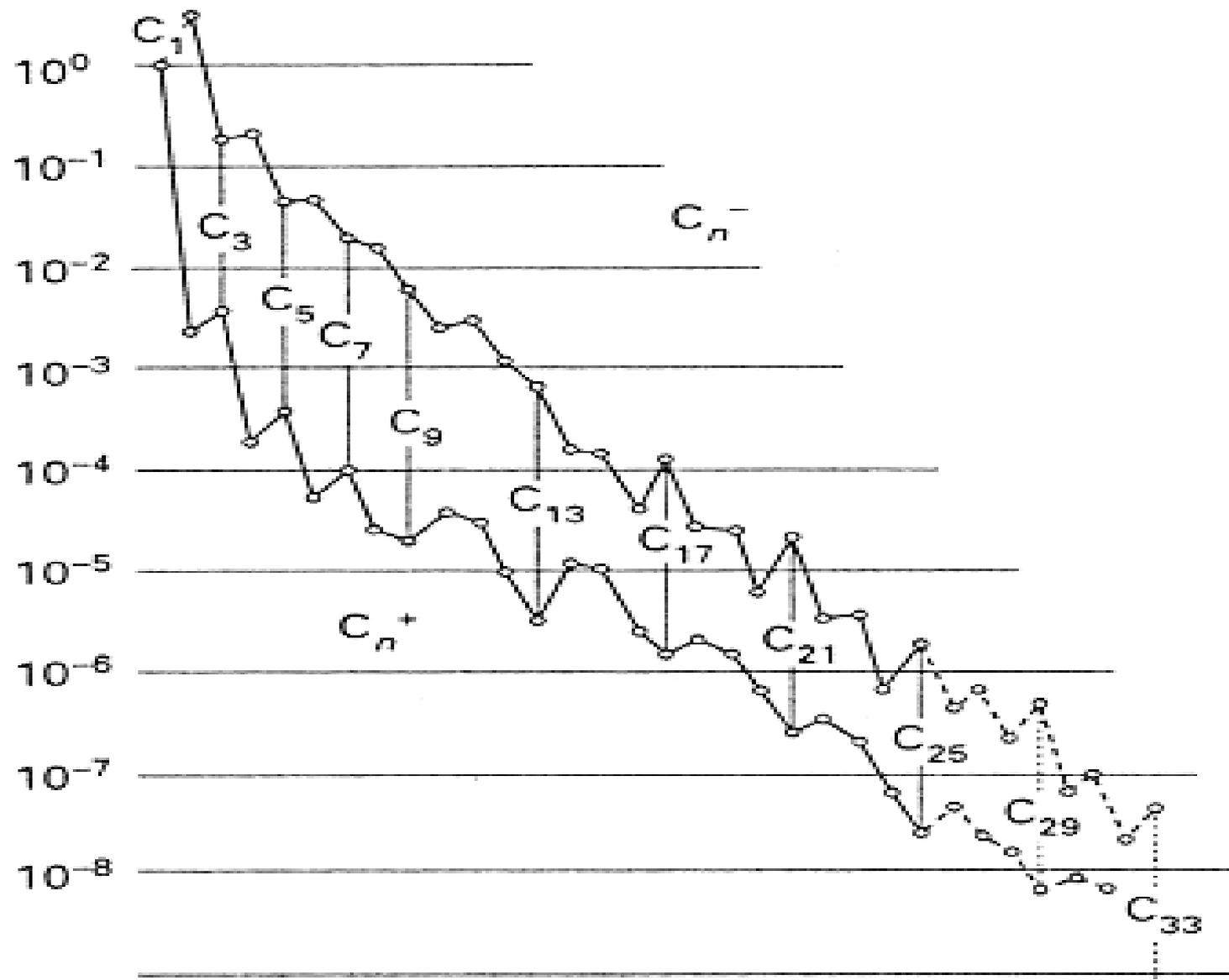






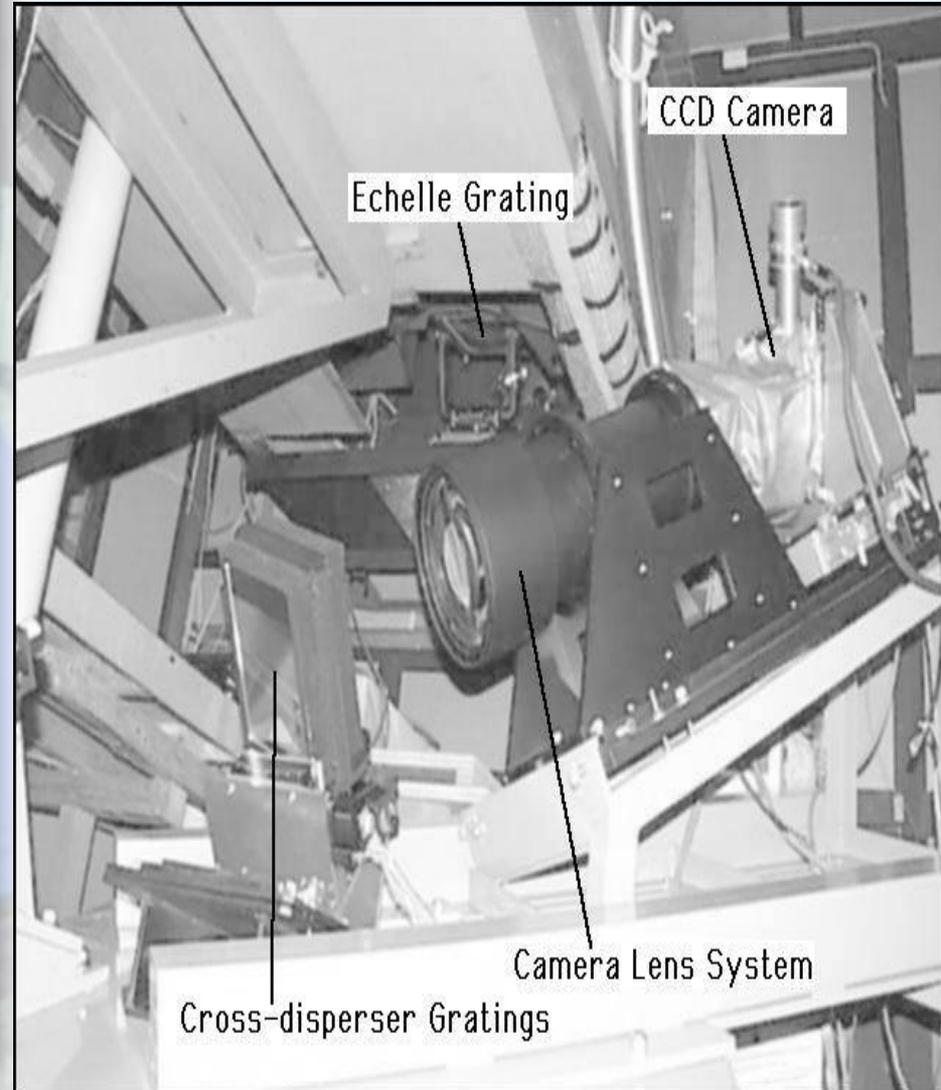
Oka: C₇⁻ Bands as DIB Carrier, 4I

Civiš, S., Hosaki Y, Kagi E., Kawaguchi K.: Search for C₂⁻ in Diffuse Clouds and Examination of the C₇⁻ Bands as DIB Carrier, *Publ. Astron. Soc. Japan*, 2005, **57**, 605-609.

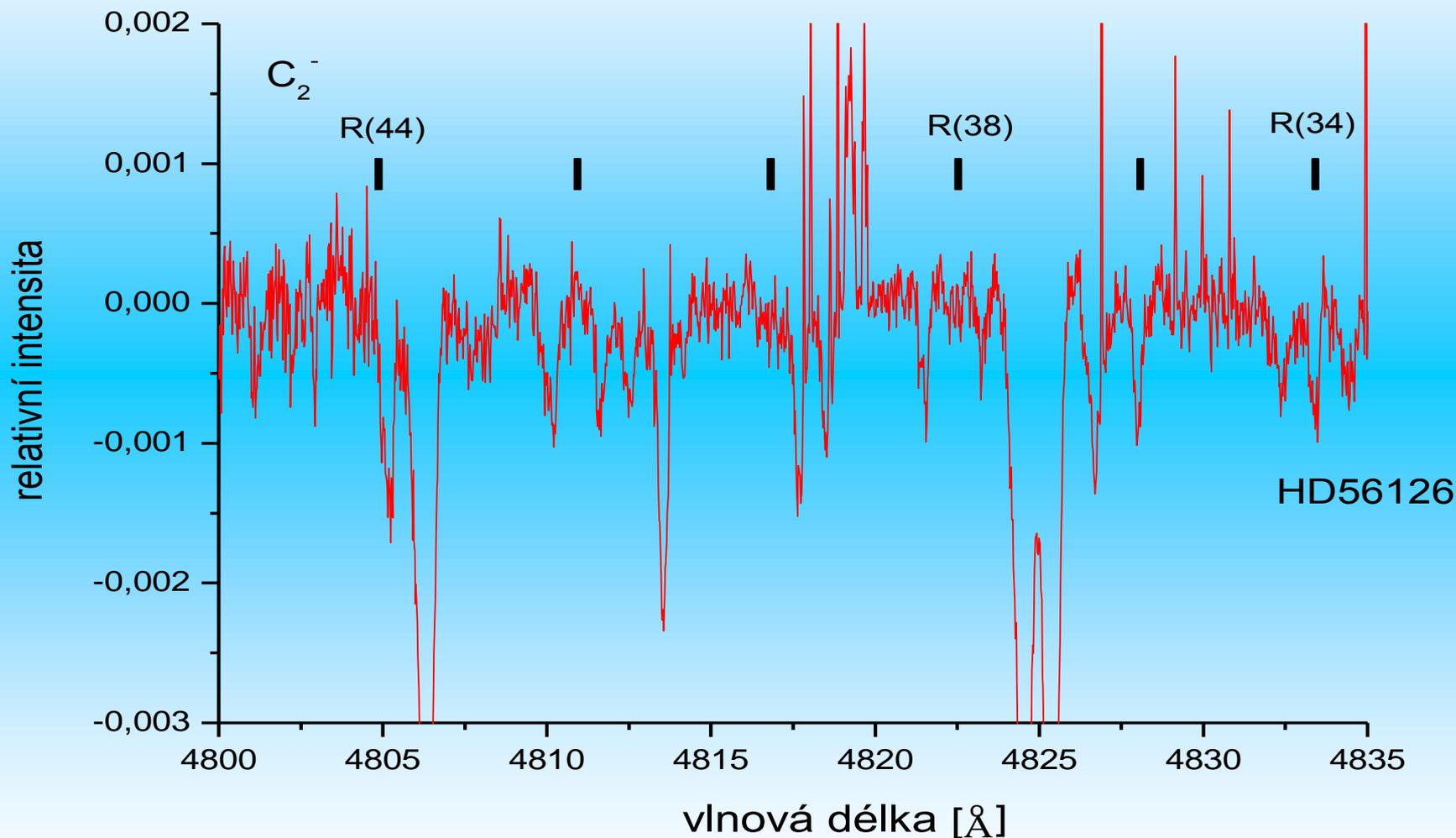


Optický teleskop v Okayamě, Japonsko 2003

Vysoce disperzní Echellův spektrograf

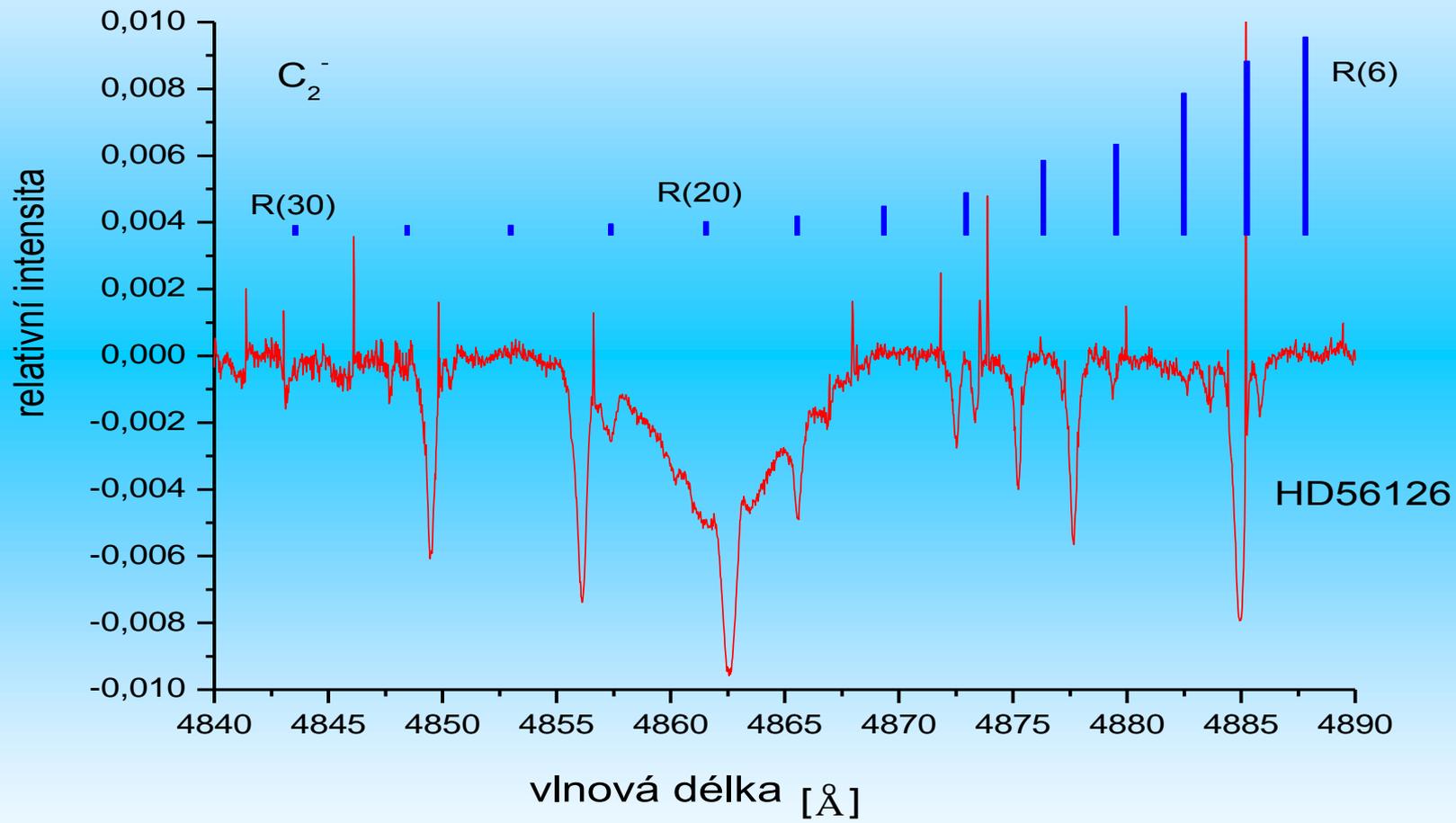


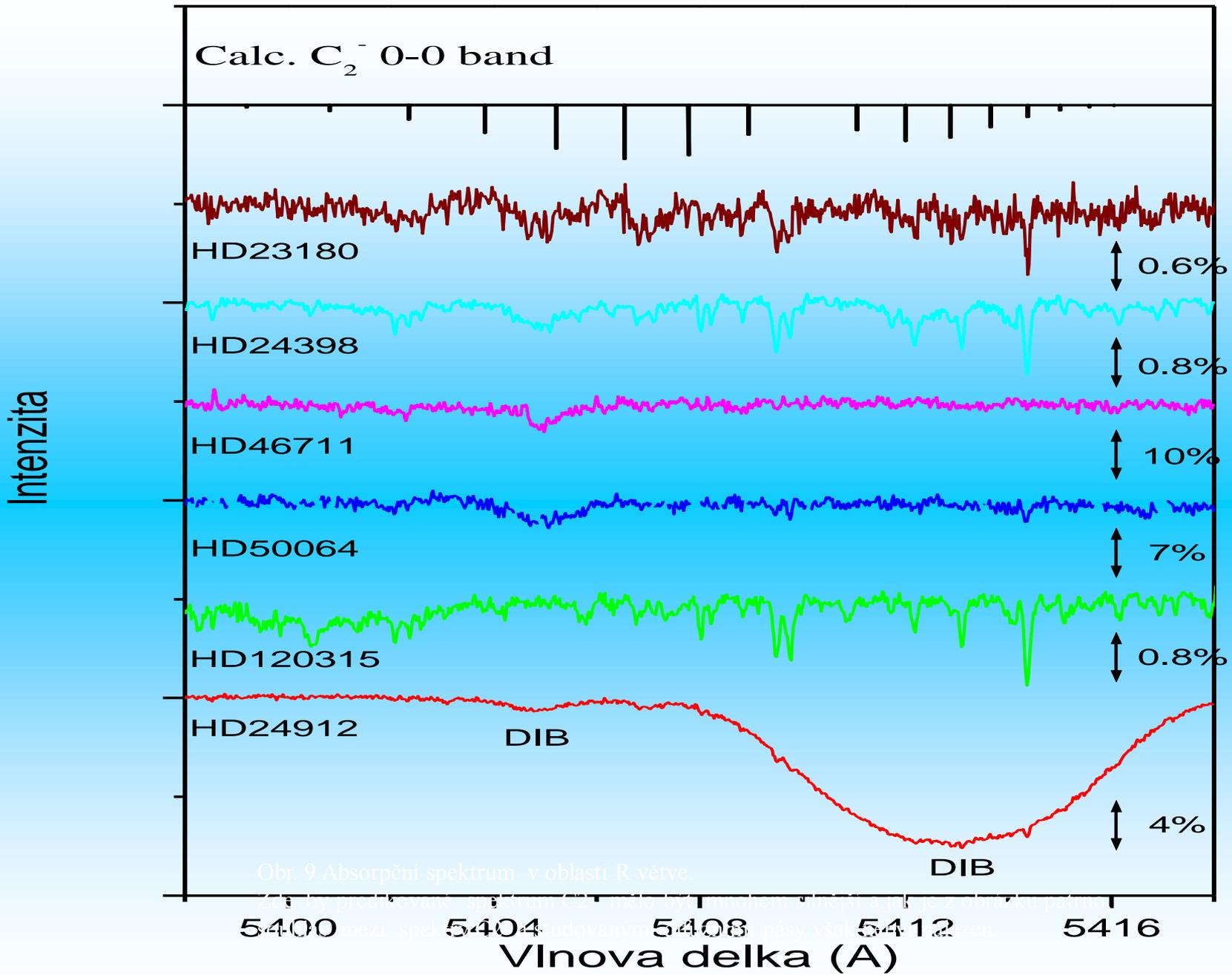
Na observatoři v Nobeyamě, vybavené 2 m optickým teleskopem, jsem měřil spektra objektů studovaných McCallem [47] ve spektrální oblasti absorpce C_2^- aniontu. Výsledky našeho měření shrnují obr., kde je zachyceno absorpční spektrum HD56126 a simulované spektrum C_2^- pro teplotu 240 K. Teplota byla určena na základě intenzit linií C_2 radikálu, přítomných ve spektru HD56126.



Část spektra, ve kterém několik absorpčních linií zdánlivě souhlasí s laboratorním spektrem C_2^-

Srovnání spekter v jiné oblasti vlnových délek





Obr. 9 Absorpční spektrum v oblasti R větve.

5400 5404 5408 5412 5416

Vlnova delka (A)

Search for C_2^- in Diffuse Clouds and Examination of the C_7^- Bands as DIB Carrier

S. Civiš¹, Y. Hosaki², E. Kagi³, H. Izumiura⁴,
K. Yanagisawa⁴, T. Šedivcová¹, and K. Kawaguchi²,

¹*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
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²*Department of Chemistry, Faculty of Science, Okayama University,
Tsushima-naka 3-1-1, Okayama 700-8530*

³*Department of Chemistry, Faculty of Information Sciences, Hiroshima City University,
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⁴*Okayama Astronomical Observatory, National Astronomical Observatory, Kamogata, Asakuchi,
Okayama 719-0232*

(Received 2003 October 0; accepted 2003 0)

Abstract

A search has been carried out for the C_2^- ion in diffuse clouds, toward HD 24398, HD 46711, HD 50064, HD 23180, HD 24912, HD 46711 using an Okayama 188-cm telescope HIDES spectrometer. The upper limit for C_2^- of $1.1 \times 10^{10} - 25 \times 10^{11} \text{ cm}^{-2}$ in column density has been reported, which is smaller than the C_7^- abundance obtained from the assumption that C_7^- is responsible for diffuse interstellar bands (DIBs). To examine the C_7^- assumption, we investigated the wavelength region where many vibrational bands for C_7^- can be expected. The results of all our observations indicate no evidence for the hypothesis that some diffuse bands originate from carbon chain such C_6^- , C_7^- and C_8^- .

Key words: molecular processes - ISM: molecules

Civiš, S., Hosaki Y, Kagi E., Kawaguchi K.: Search for C_2^- in Diffuse Clouds and Examination of the C_7^- Bands as DIB Carrier, *Publ. Astron. Soc. Japan*, 2005, **57**, 605-609.

Observational Studies Relating To Diffuse Interstellar Bands

H. Tada¹, K. Kawaguchi¹, H. Izumiura², T. Šedivcová³, and S. Civiš⁴

¹*Department of Chemistry, Faculty of Science, Okayama University,
Tsushimaoka 3-1-1, Okayama 700-8530, Japan*

²*Okayama Astrophysical Observatory, National Astronomical Observatory,
Kamogata, Asakuchi, Okayama 719-0232, Japan*

³*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
Flemingovo náměstí 2, CZ-166 10 Prague 6, Czech Republic*

⁴*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
Dolejškova 3, CZ-18223 Prague 8, Czech Republic*

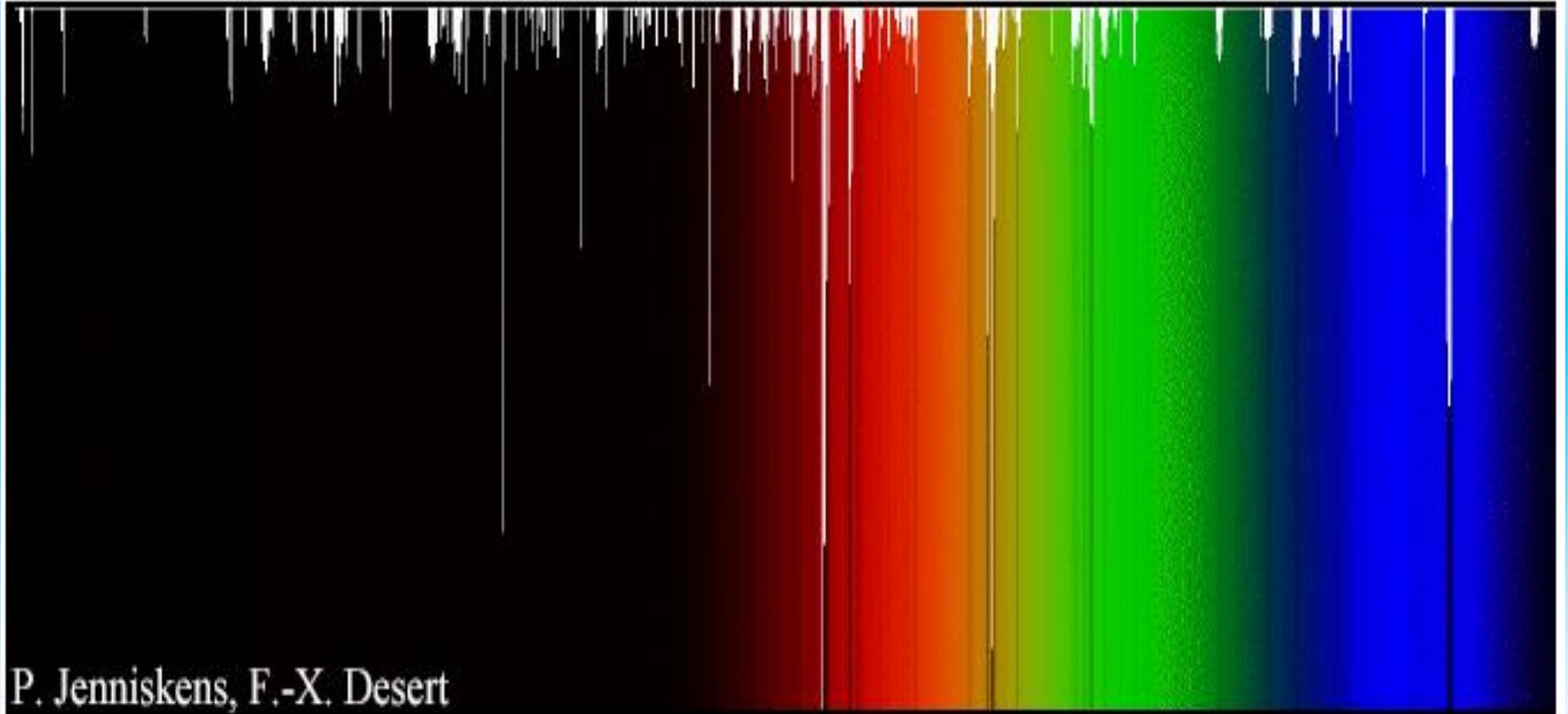
Abstract. We observed a series of five or six DIBs lines with a nearly constant spacing of about 35 cm^{-1} around 6800 Å by using a spectrometer with a wavelength resolution of $\lambda/\Delta\lambda=75000$. We obtained similar intensities in HD 21389, HD 41117, HD 43384, HD 198478, and HD 206165. As a candidate of these DIBs carrier, a perpendicular vibronic band of CH_2X type molecules has been proposed by Glinski et al., where X is a heavy atom or linear carbon chain. Although the 35 cm^{-1} intervals are interpreted by assuming only ortho lines are detected, we could find none of the spectral lines originating from para levels. For further confirmation we simulated the spectra of the C_7H_2 molecule as a typical CH_2X type molecule, and found that an extraordinarily high temperature is required for explanation of the observed spectra. Thus we concluded that the carrier of series of DIBs appeared near 6800 Å is not explained by the perpendicular vibronic band of CH_2X type molecules. Other candidates are discussed.

Keywords: line: identification – ISM: molecules – ISM: temperatures

PACS: 95.85.Kr

Tada H., Kawaguchi K., Izumiura H., Civiš S., Šedivcová T.: Observational Studies Relating to Diffuse Interstellar Bands, CP855, Astrochemistry, From Laboratory Studies to Astronomical Observations, edited by R.I. Kaiser, P. Bernath, Y. Osamura, S. Petrie, and A.M. Mebel, Astrochemistry, From laboratory studies to astronomical observation, 2006, American Institute of Physics, 219-224, 978-0-7354-0351-2/06

Difúzní interstelární pásy



Nobeyama, Japonsko, 2000-2003



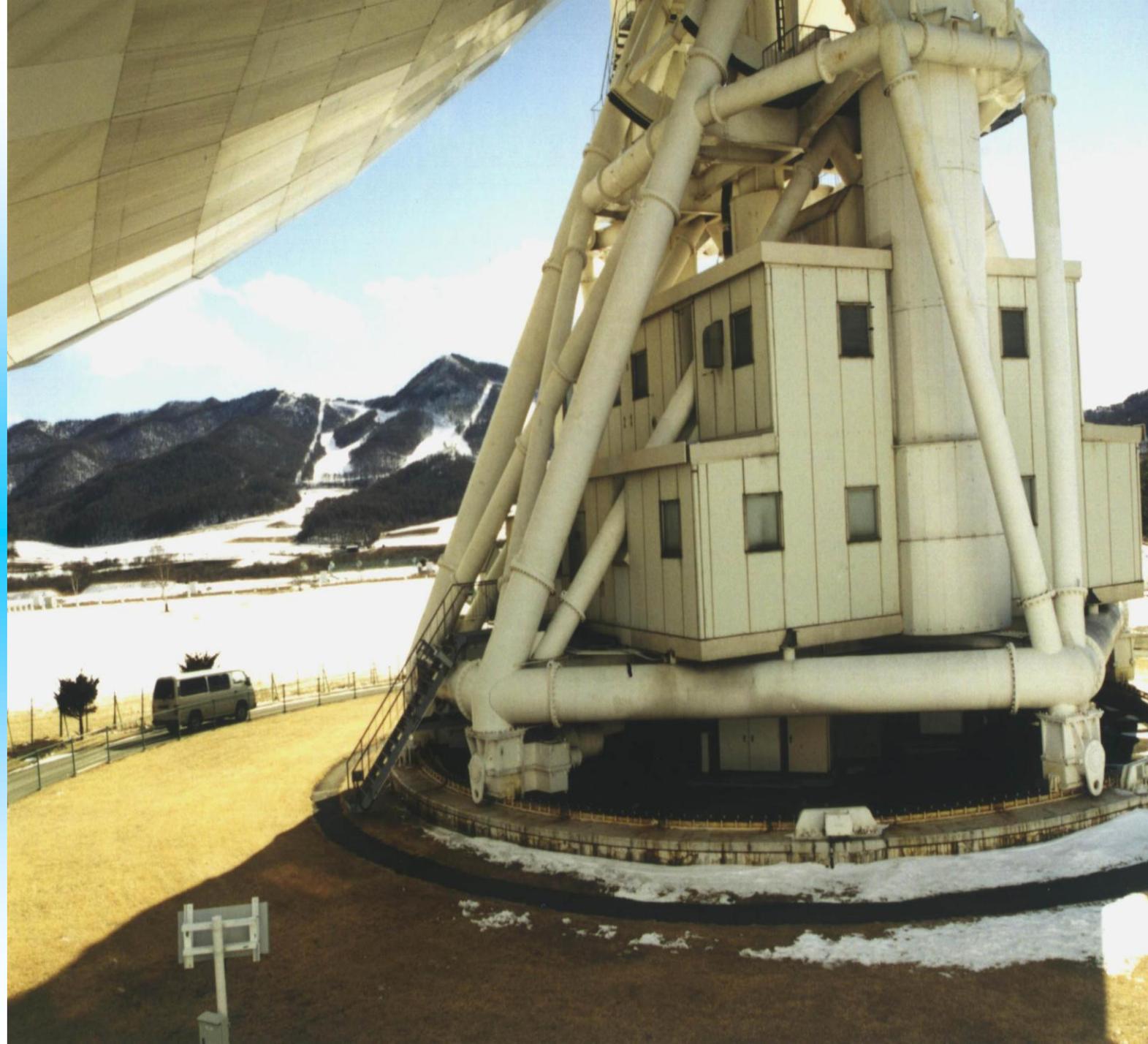
Nobeyama, Japonsko, 2000-2003

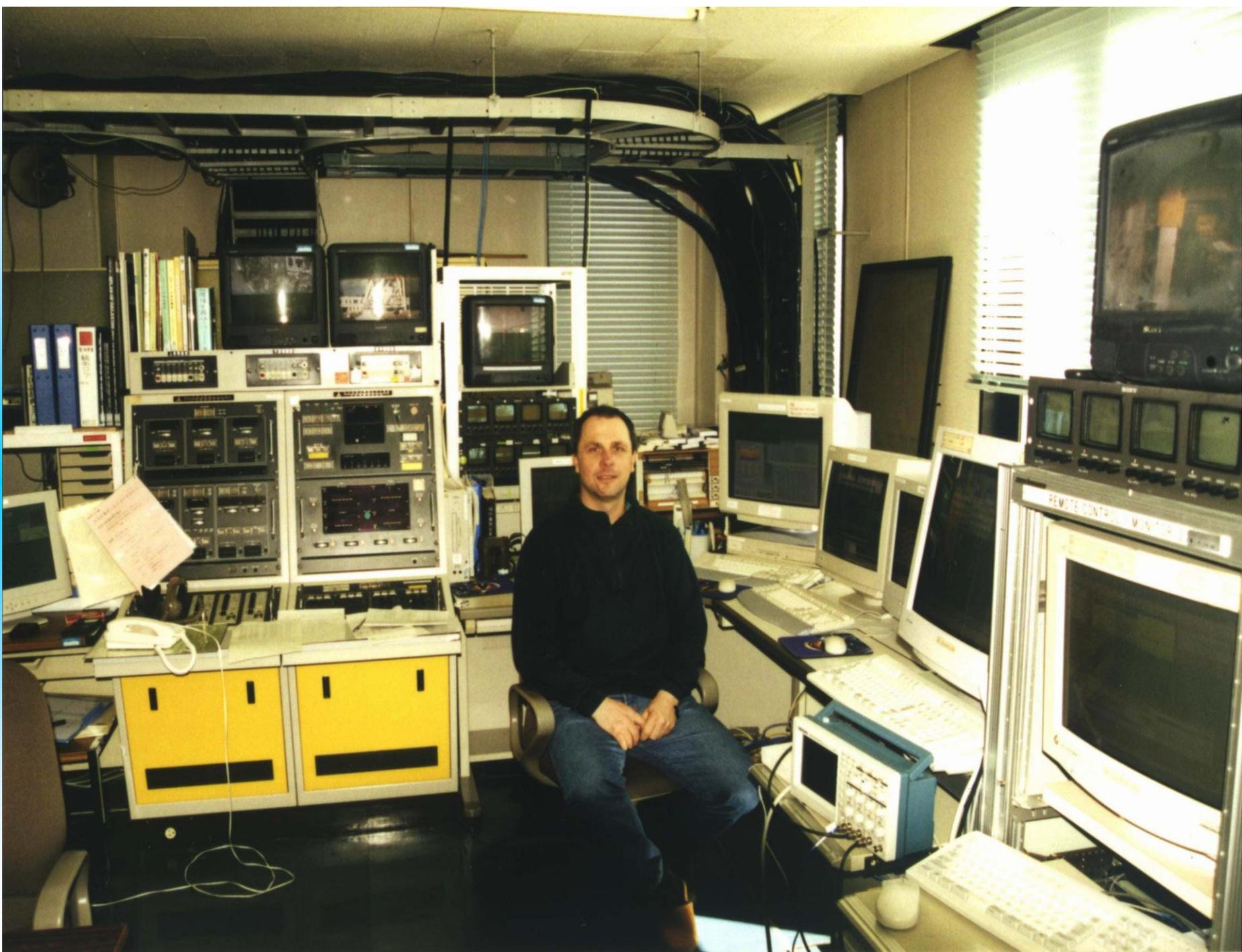
45 m radioteleskop

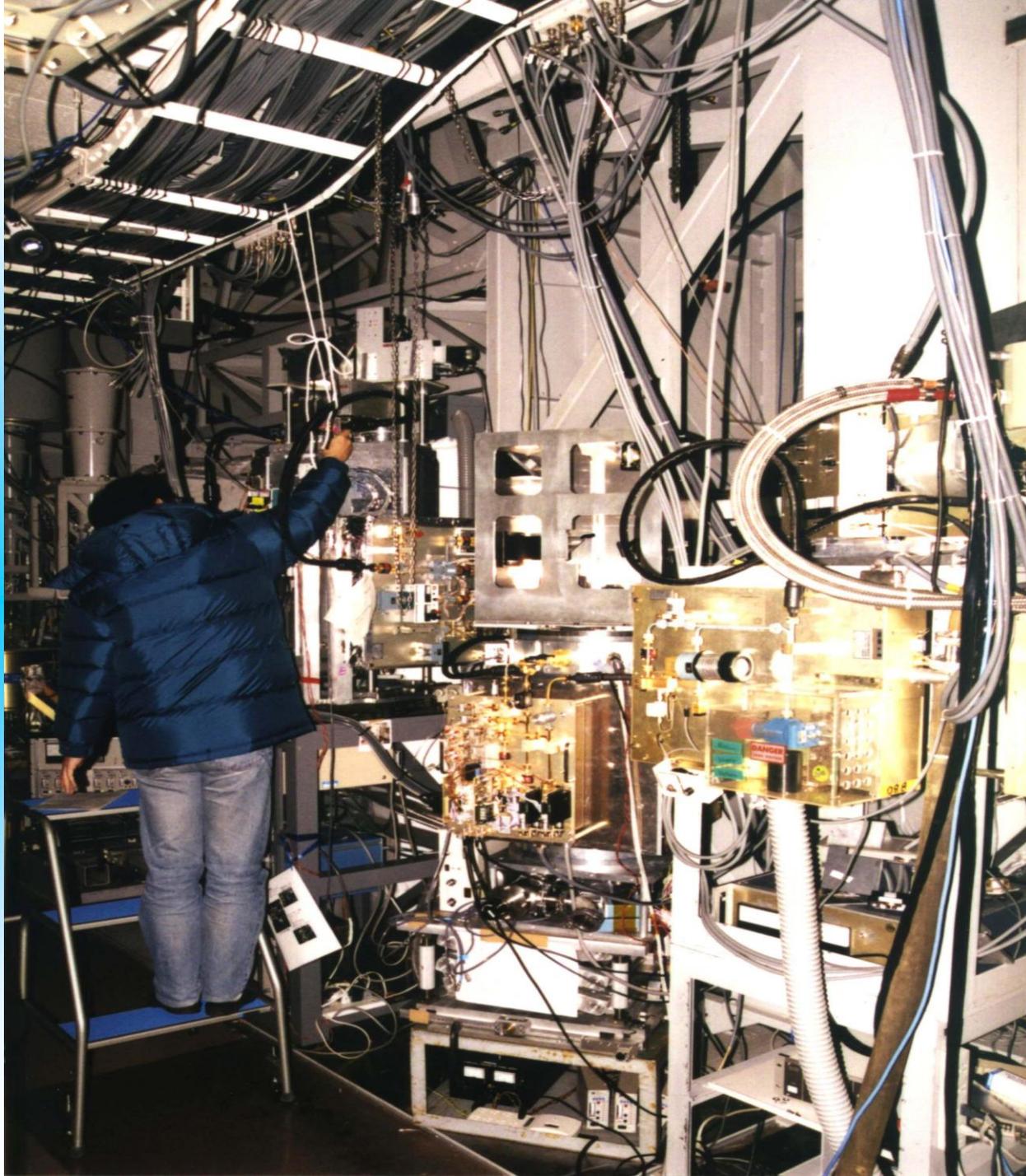
Hledání: NCO-
NCS-

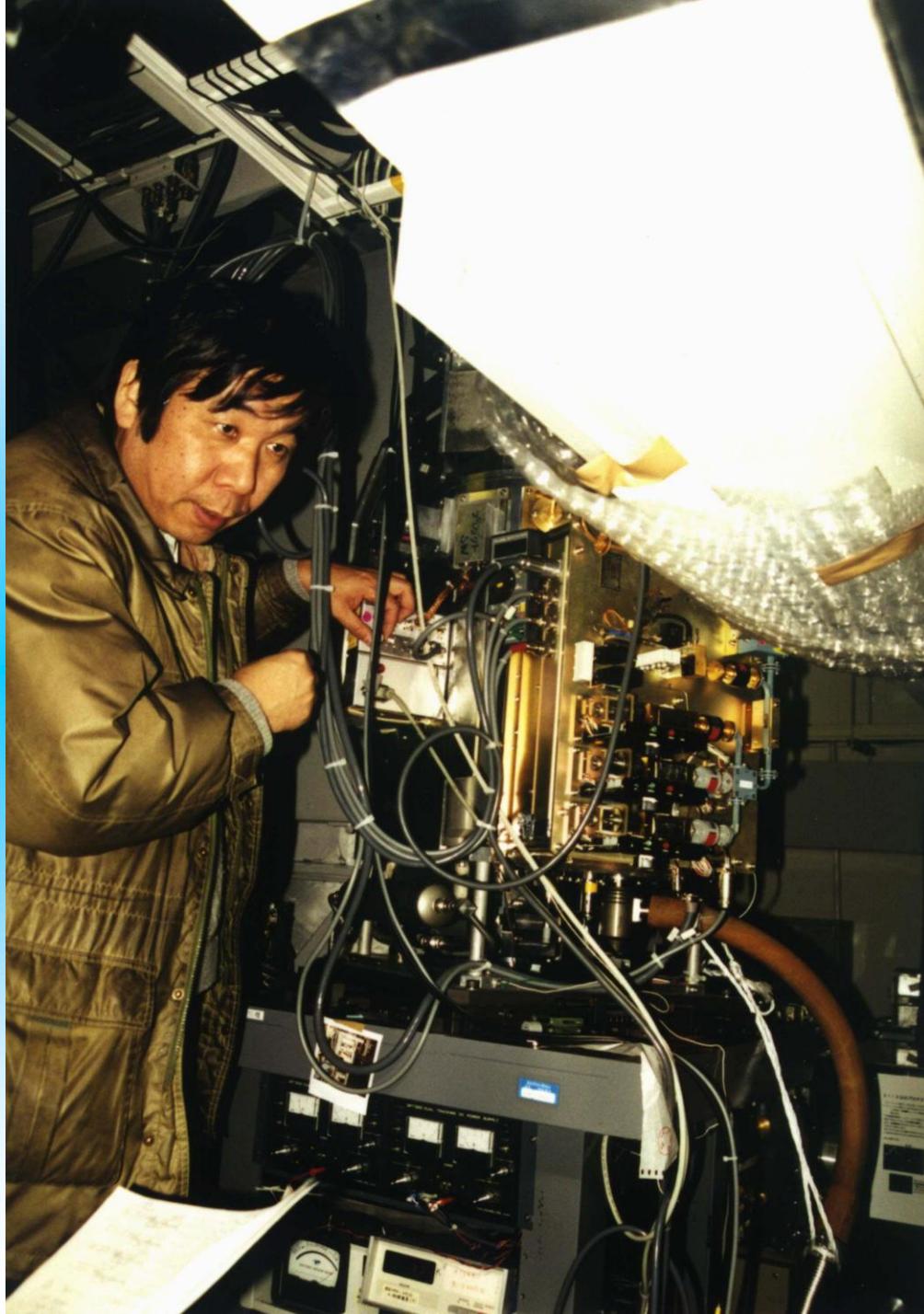
Na základě publikovaných infračervených spekter











CN RADIKÁL-mikrovlnné spektrum

Taurus molecular clauds

měřeno 40 metrovým teleskopem v Nobeyamě 2000

HC3NA TMC-1(CP)

#HC3NA_H.SMTHG

Comments

Spectrum-id = 00004 ()
Ref. coordinate = RA,DEC
X offset = -00d24'34.5"
Y offset = +00d21'36.0"
Center freq. = 113.504000(GHz)
r.m.s. = 0.1187(K)
Baseline order = 05

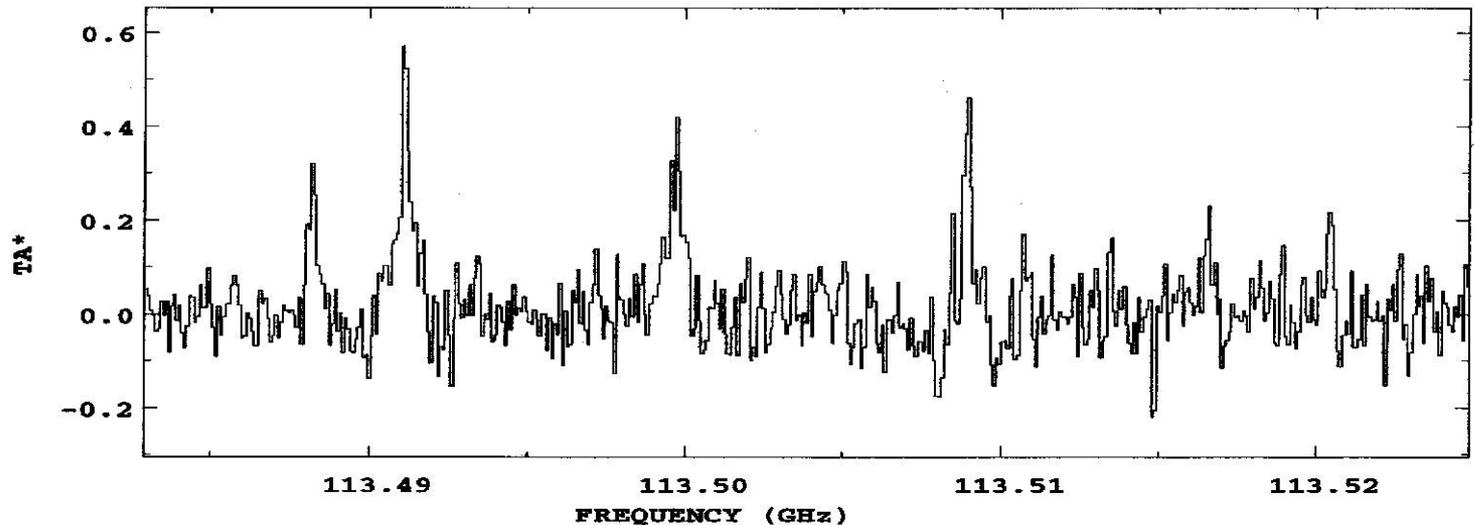
: DATE(M D Y) = 02 16 00
: P.A. = 0.000d
: RA (1950) = +04h36m49.3s : l = 173.822D
: DEC(1950) = +25d57'21.0" : b = -13.525D
: AOS-H6
: Integ time = 00h44m00s
: Scaling factor = 1.00

no. peak T

x of peak

half width

integ. int.



Anion CN⁻

CN⁻ (¹Σ základní stav) má disociační energii 10.3 eV [53], vysokou elektronovou afinitu 3,82 eV a dipólový moment 0,62 D. Je izoelektronický s CO, který je přítomen ve vysoké koncentraci v mezihvězdných oblacích. Nejnovější molekulární parametry a spektroskopické konstanty získané pomocí ab-initio výpočtů predikují rotační linii J=1←0 113 GHz.

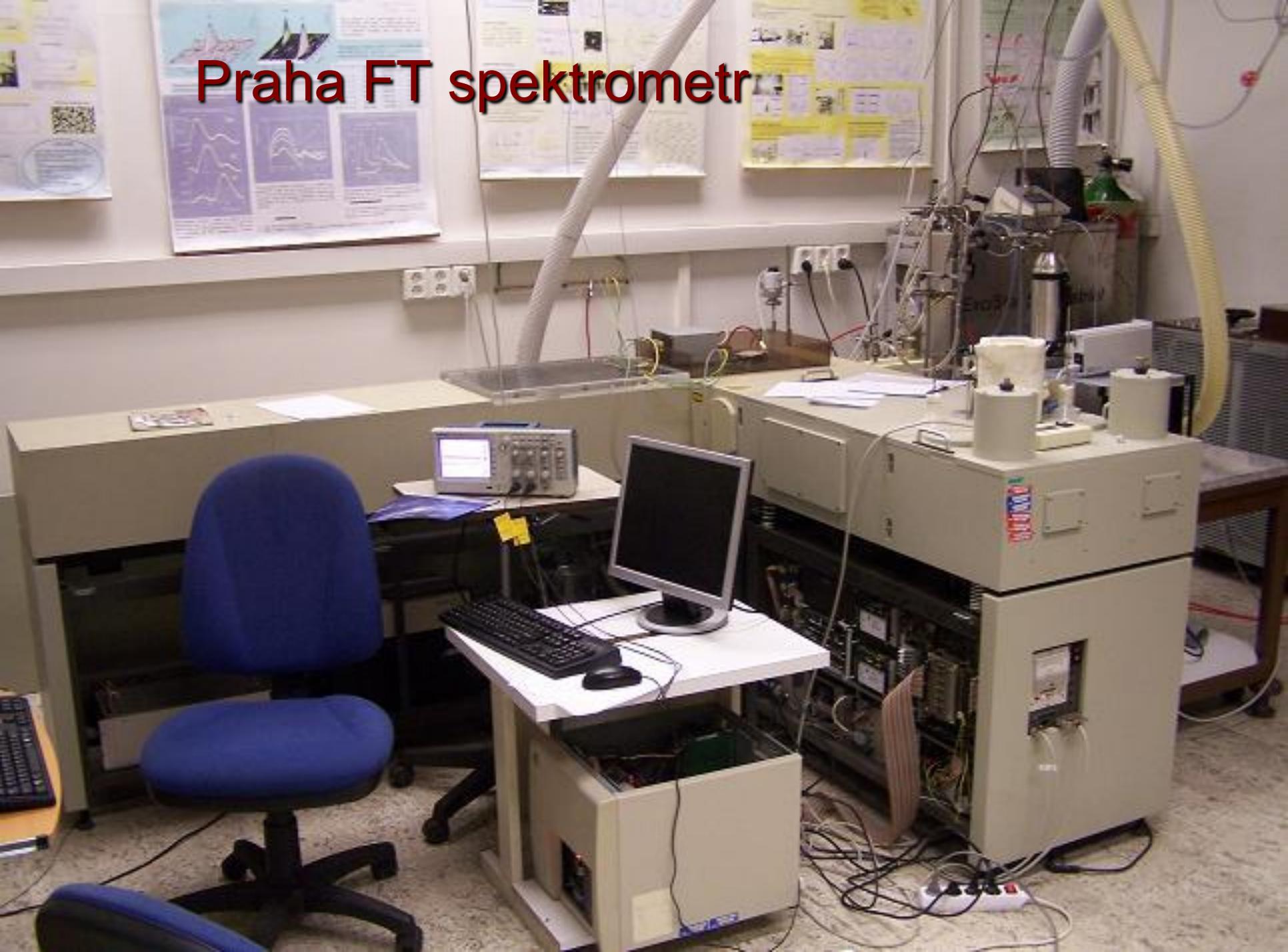
Fundamentální frekvence ν_0 rotačně-vibračního spektra CN⁻ spadá do oblasti

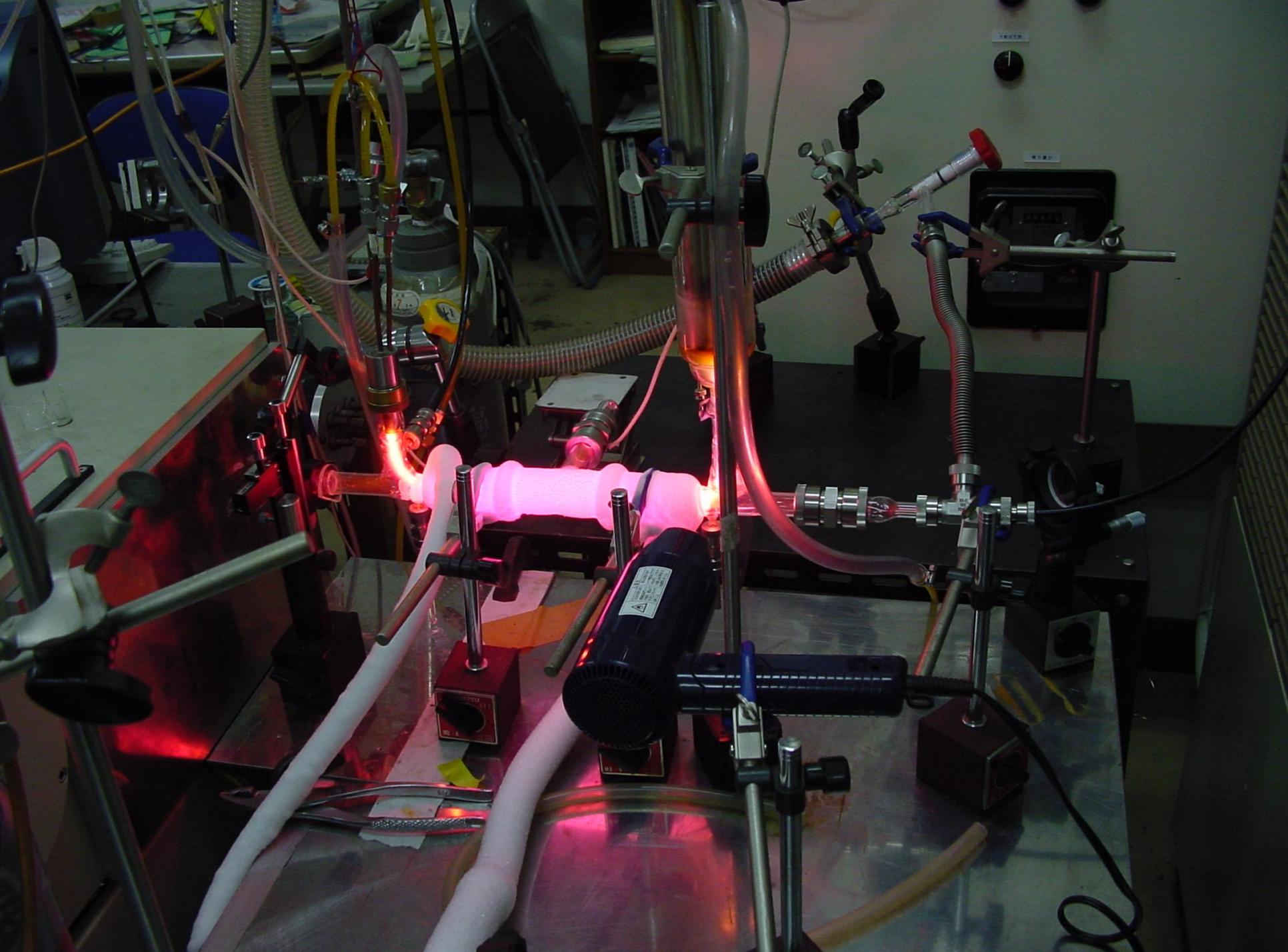
$$\omega_e - 2\omega_{exe} = 2044,6 \text{ cm}^{-1} .$$

Predikce ab-initio Špirko, Polák

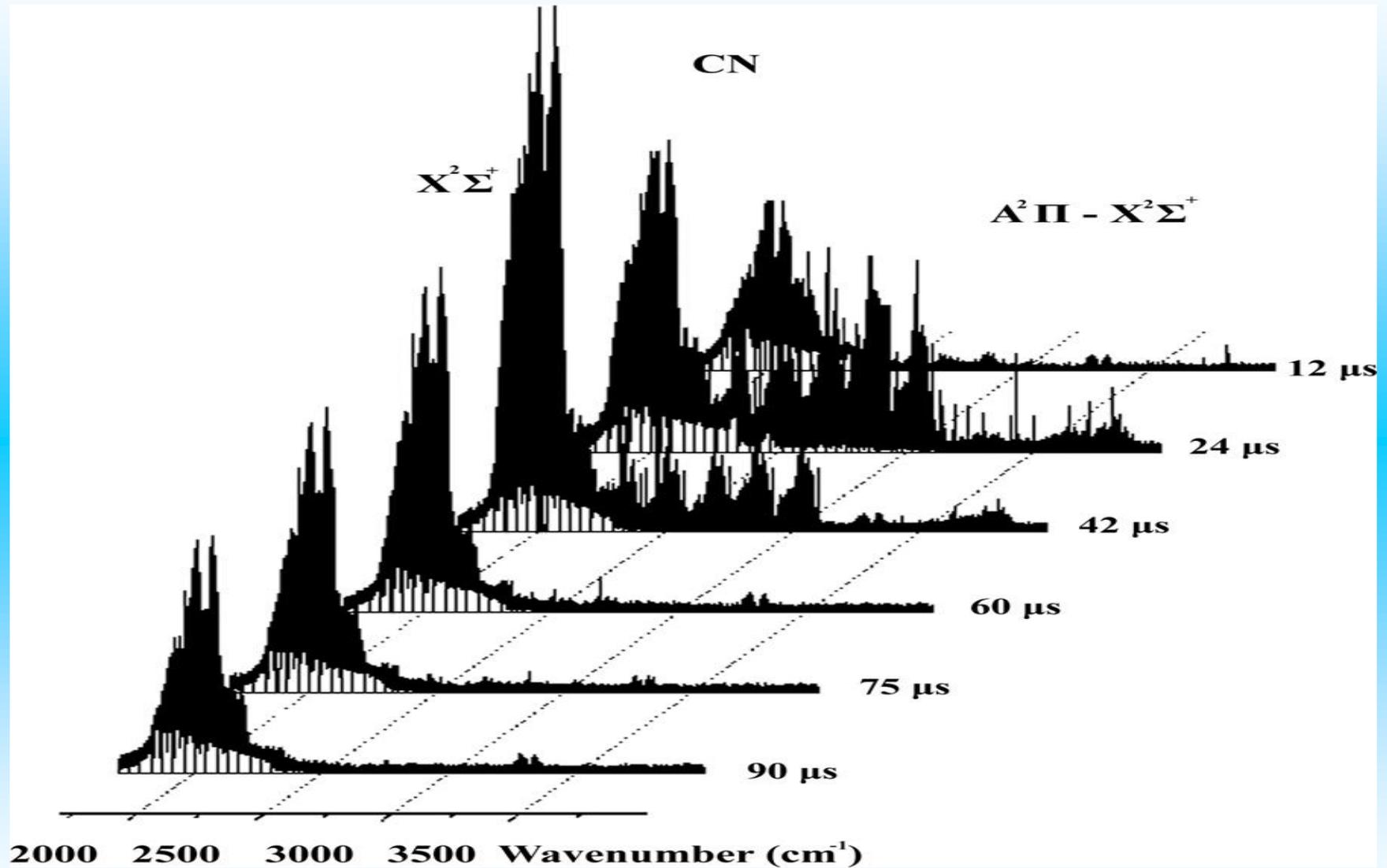
Civiš, S., Šedivcová, T.: „Detekce záporných iontů v mezihvězdném prostoru”,
Čs. čas. fyz., 2002, **52**, 152-159.

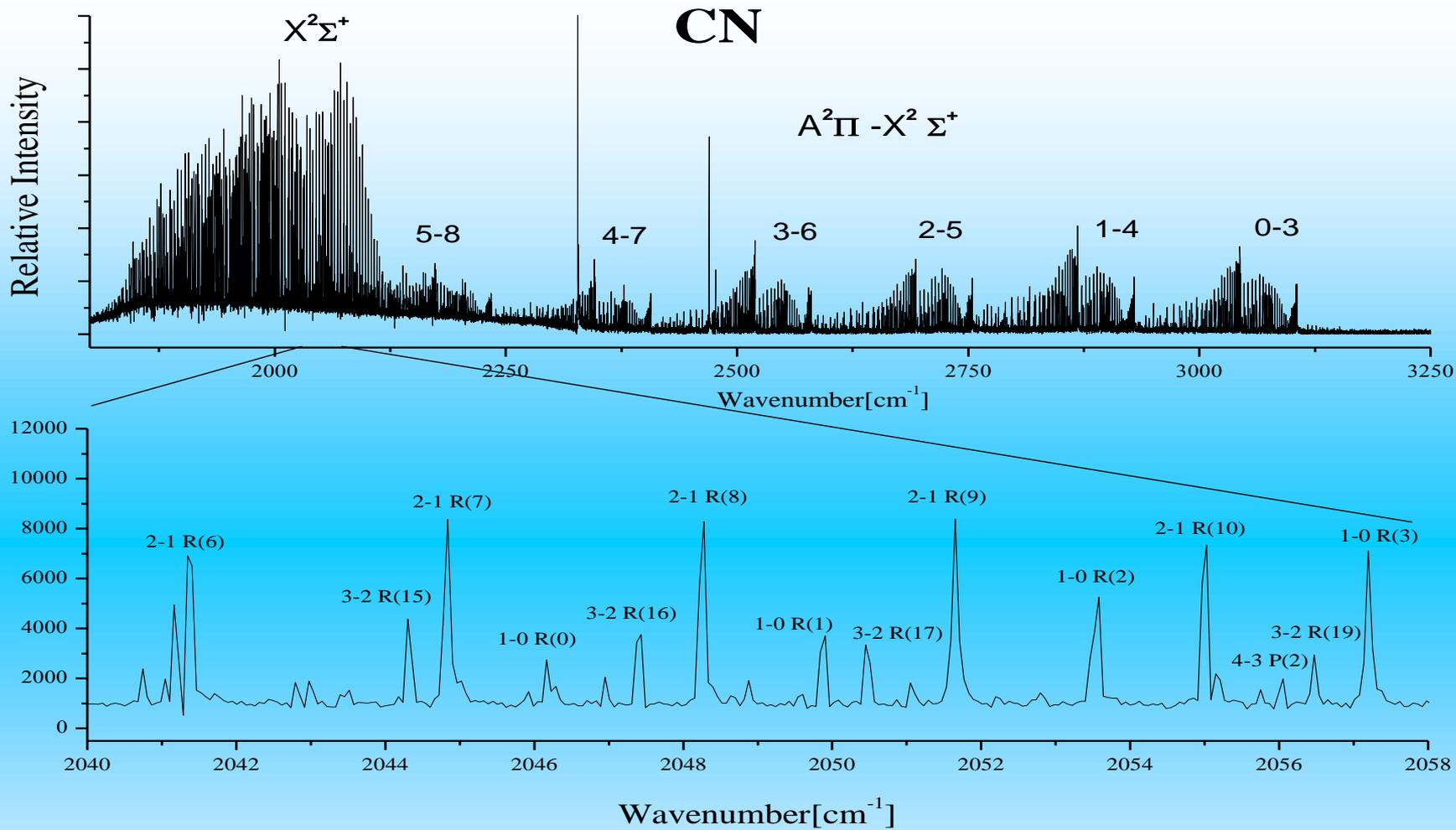
Praha FT spektrometr





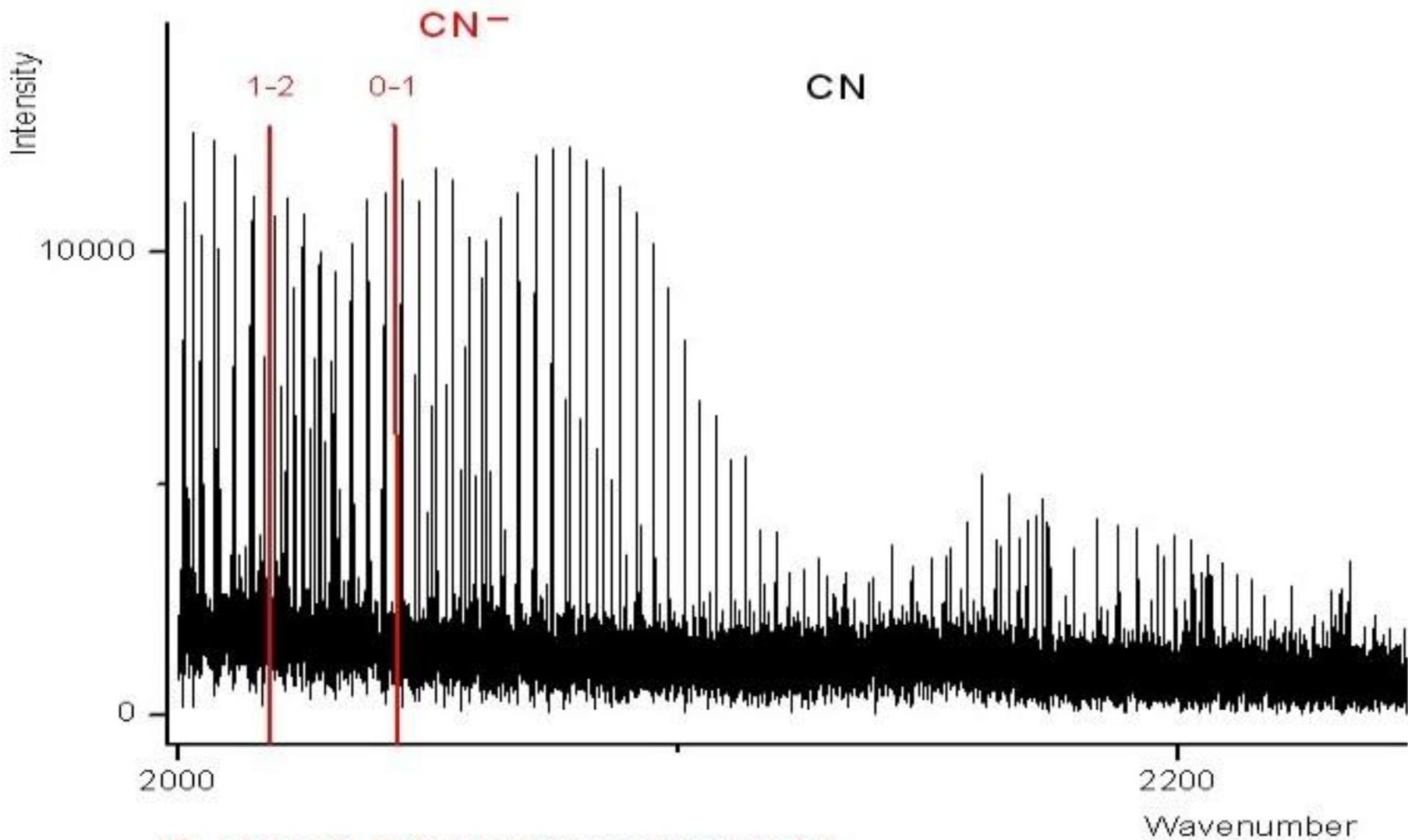
Ar + (CN)₂ discharge plasma





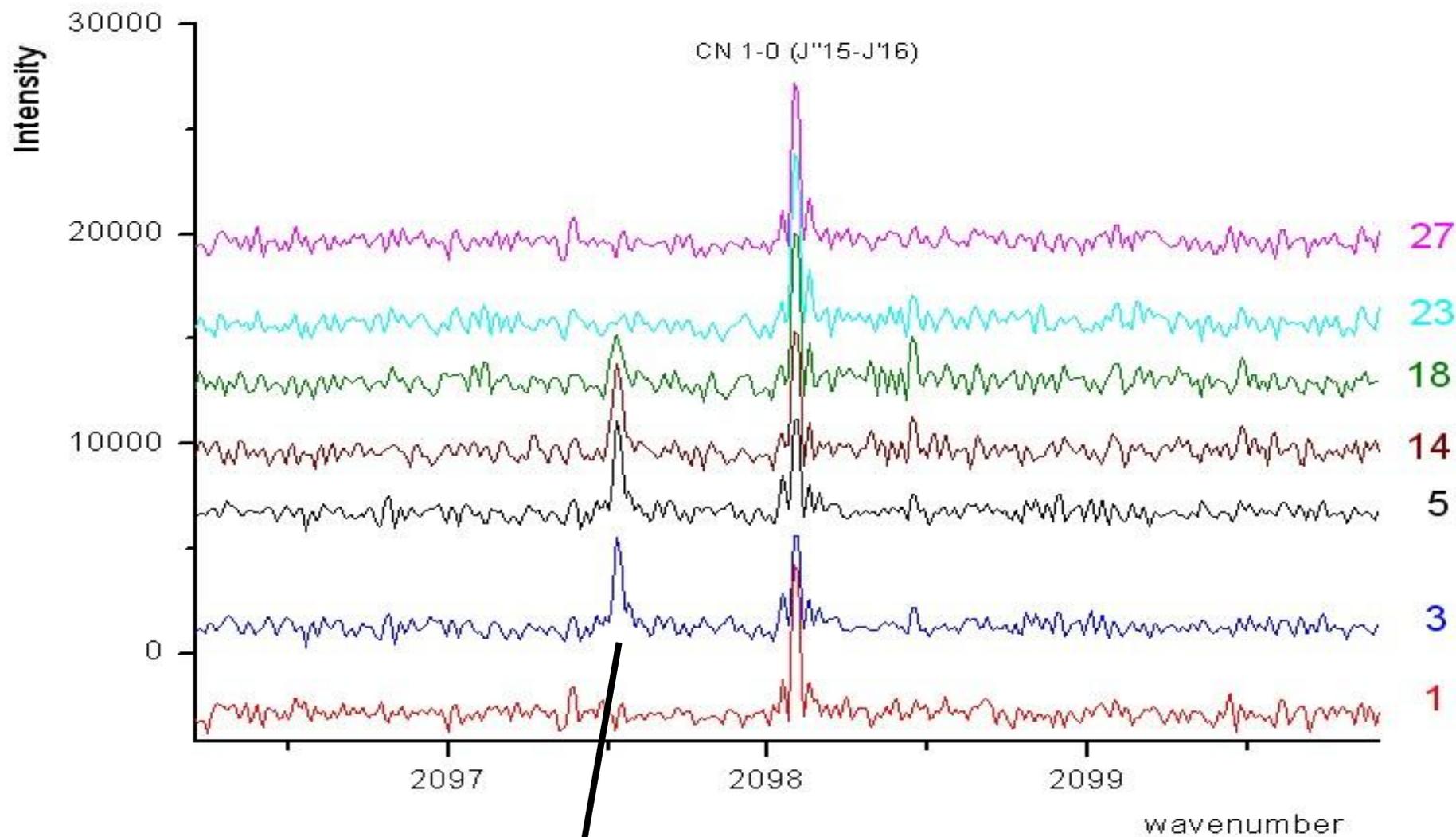
V. Horká, S. Civiš, V. Špirko, K. Kawaguchi: *Coll. Czech. Chem. Commun.*, 2004, **69**, 73-89

Civiš, S; Šedivcová-Uhliková, T; Kubelik, P. et al.: *J. Mol. Spectrosc*, 2008, **250**, 20-26



(T. J. Lee, Ch. E. Dateo; *Spectrochimica Acta*)

(V. Horká, S. Civiš; *Collect. Czech. Chem. Commun.*)



Nové neznámé linie

Search for rotational spectrum of CN^-

2003, Mito, Japonsko

J= 4-3 transition 449416.6 MHz

Discharge (He buffer gas) and Mg flame, booster pump, He pressure 100 mTorr through electrodes and Mg oven (total 300 mTorr)

Conditions:

Mg 63 V, 8.5 A

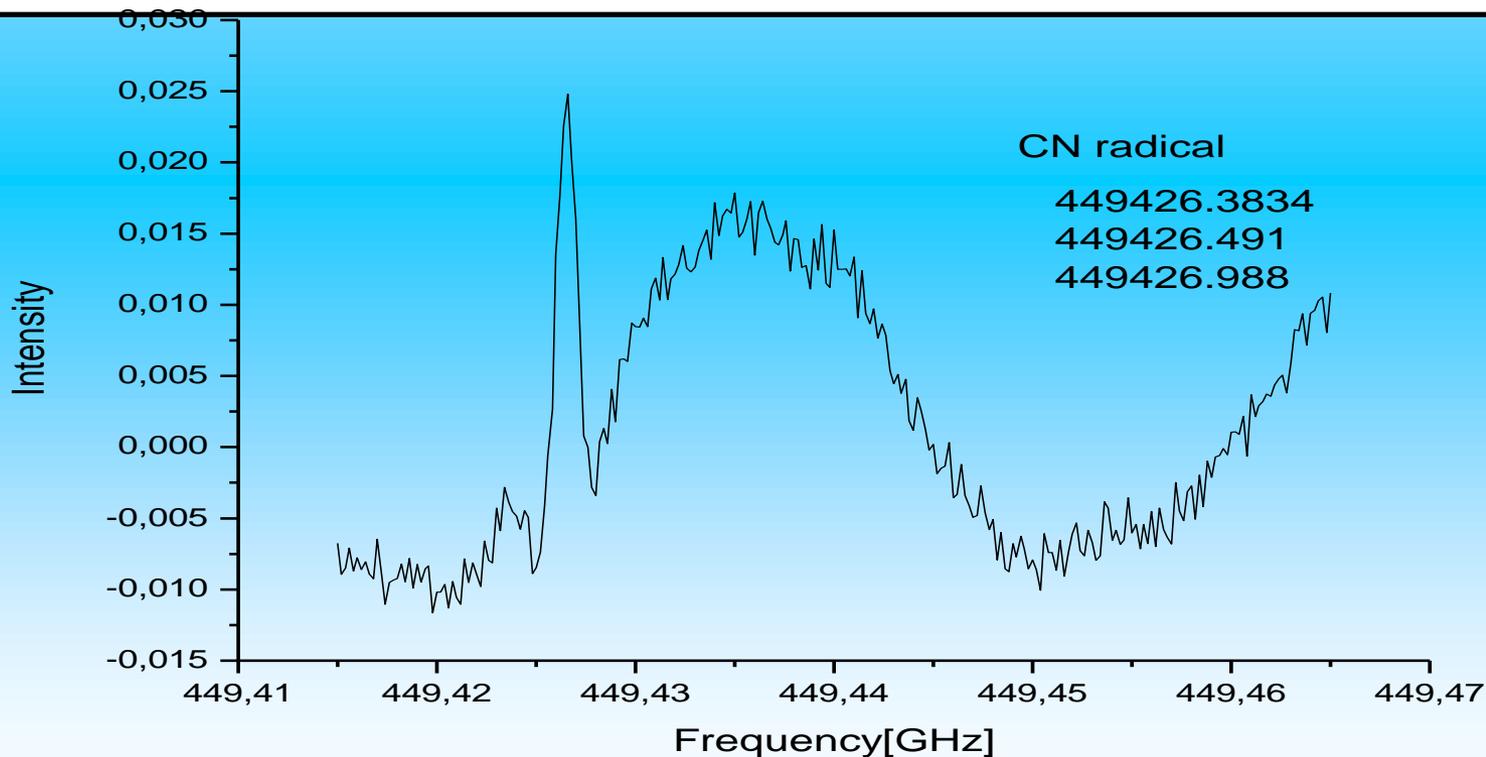
Discharge: 2 kV at the beginning, later 500V, current 10 mA

Blue flame of Mg

After adding $(\text{CN})_2$ change into green

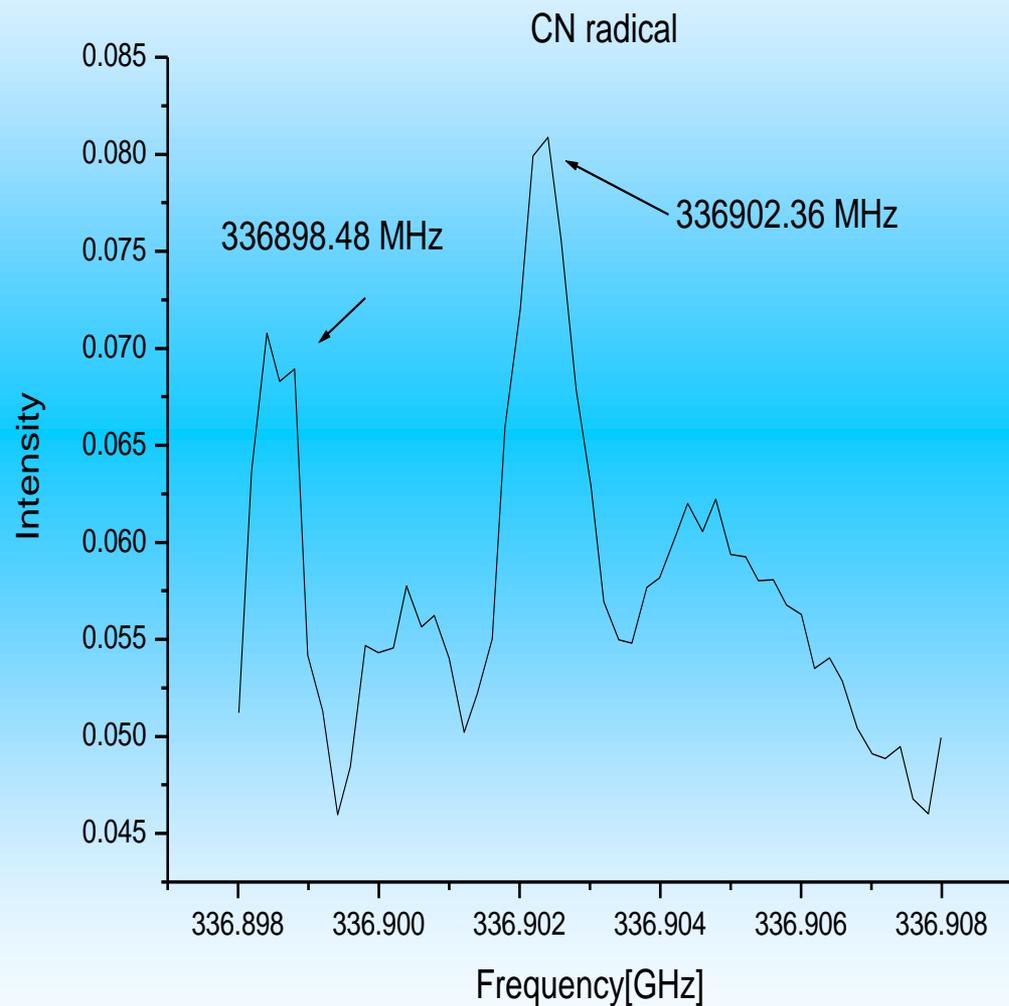
He + Mg + $(\text{CN})_2$

Scan interval : 449100- 449597 MHz (*J=4←3 449 014.351 MHz*)



Search for $J=3\leftarrow 2$ transition (Prediction 337078 MHz)

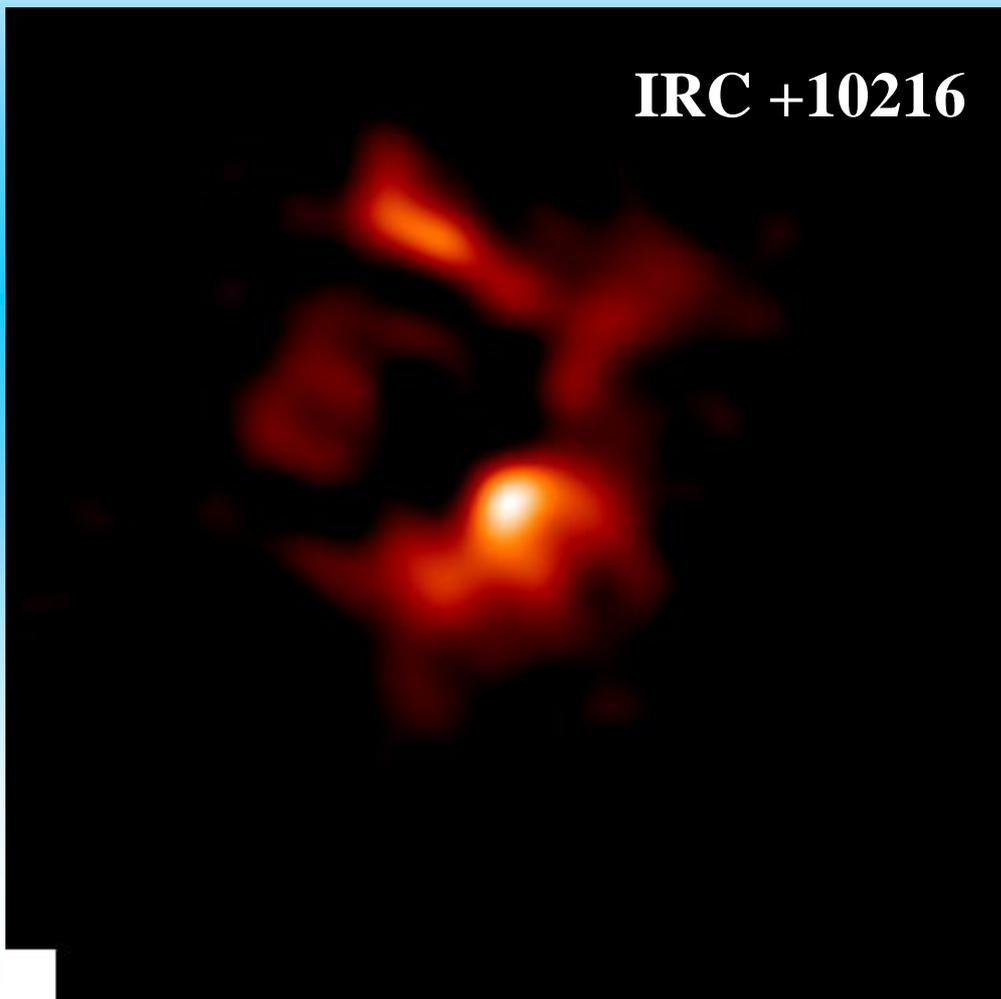
From 336900- 337300 MHz



Zlom: rok 2006

Malá exkurze do minulosti (rok 1995)
Nobeyama, Japonsko

IRC +10216



K.Kawaguchi

Two well-known astronomical sources: the molecular shell of the **evolved carbon star IRC 10216** and the **rich molecular cloud TMC-1** in the Taurus complex of dark nebulae and in IRC 10216 .

Puzzle of the unidentified harmonic sequence of lines discovered by **Kawaguchi et al. (1995)** and designated **B1377** because it is apparently from a closed-shell linear molecule with a rotational constant **B of 1377 MHz.**

LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION C_6H^-

M. C. McCarthy,¹ C. A. Gottlieb, H. Gupta, and P. Thaddeus

*Received 2006 September 28; accepted 2006 October 17; published
2006 November* ABSTRACT

The negative molecular ion C_6H^- has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC 10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that C_6H^- is the carrier of the series of lines with rotational constant **1377 MHz first observed by K. Kawaguchi et al. in IRC 10216**. The column density of C_6H^- toward both sources is 1%–5% that of neutral C_6H . These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

ROTATIONAL SPECTRA OF THE CARBON CHAIN NEGATIVE IONS C_4H^- AND C_8H^-
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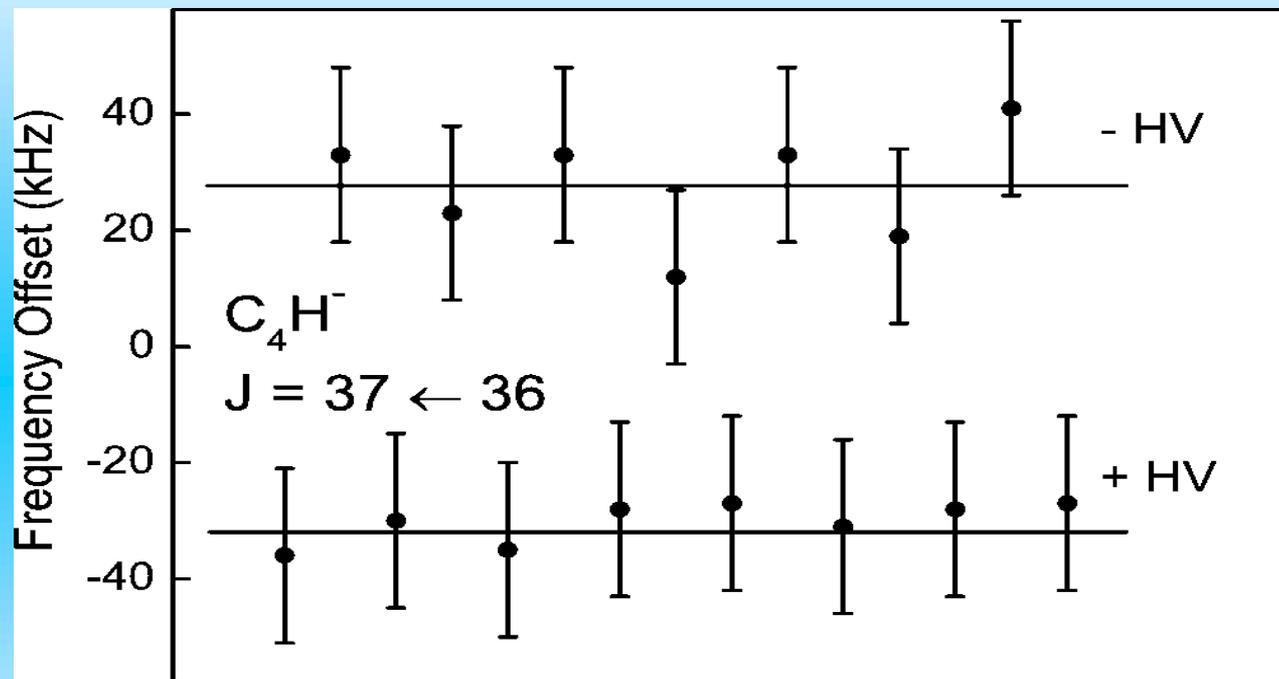
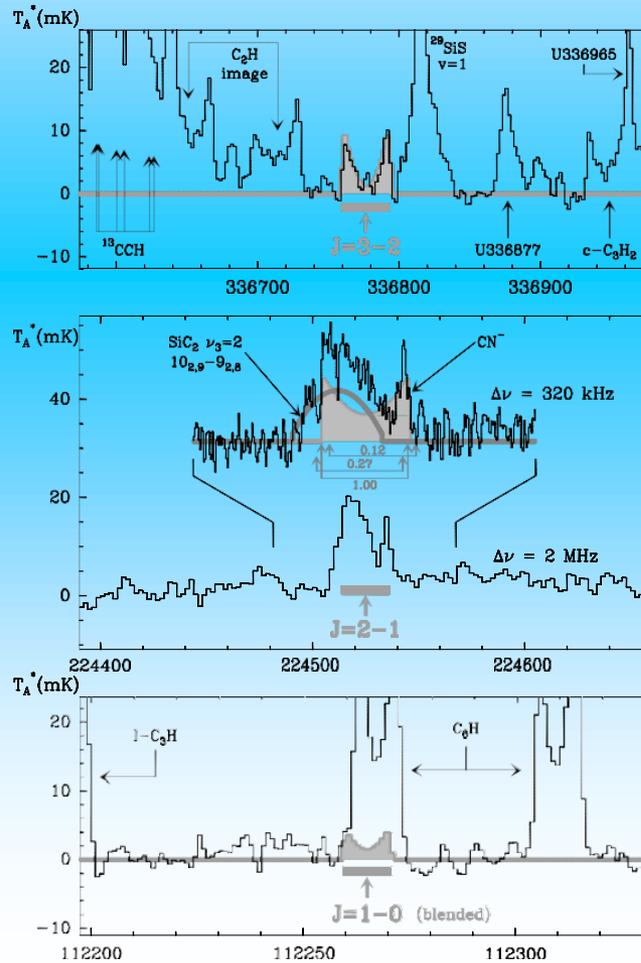


Fig. 3.—Ion drift measurements of C_4H^- . Plotted are a series of measurements of the $J_p 37 R 36$ line with either positive or negative high voltage (HV) applied to the electrode near the radiation source; the electrode on the detector side was at ground potential in either case. The frequency shift (relative to a center frequency of 344,346.874 MHz) corresponds to a drift velocity of 25 m s^{-1} .

Letter to the Editor

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

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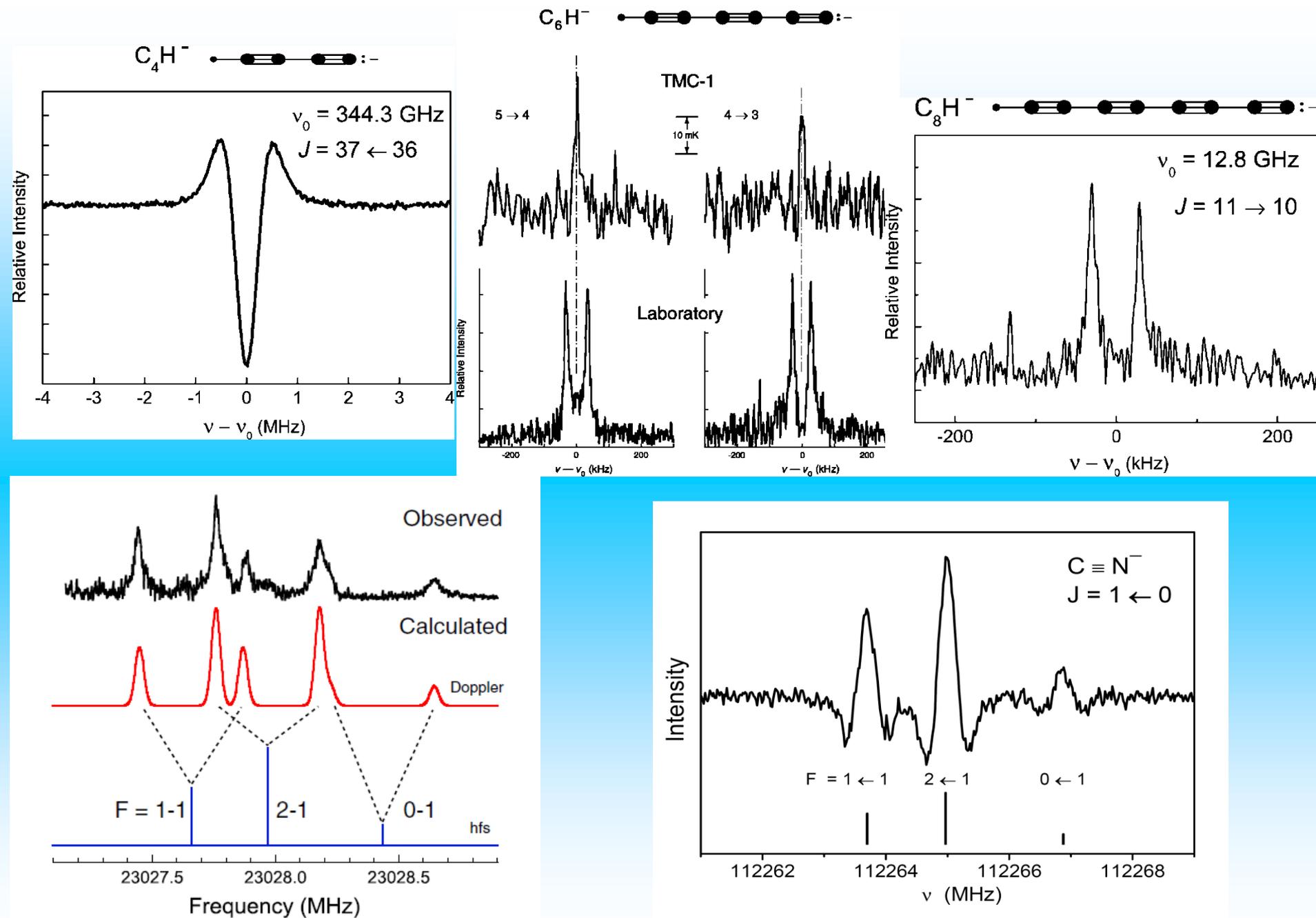
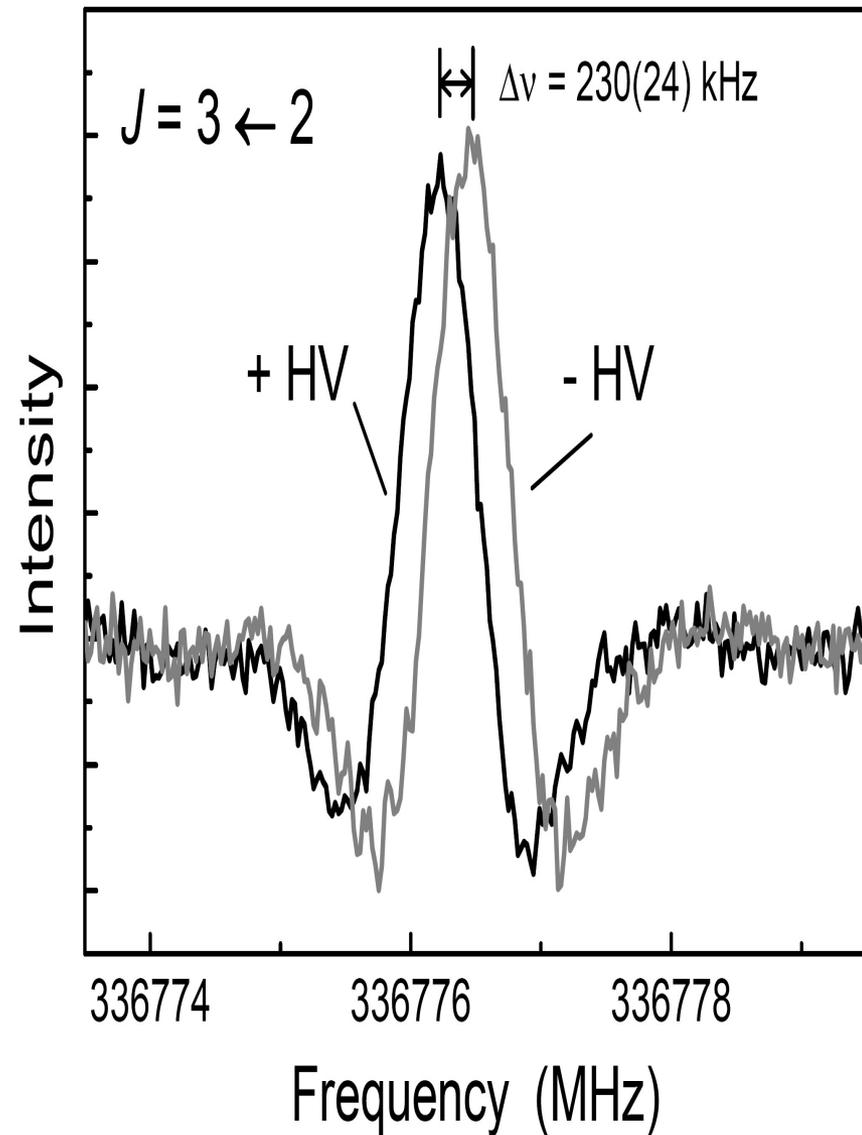
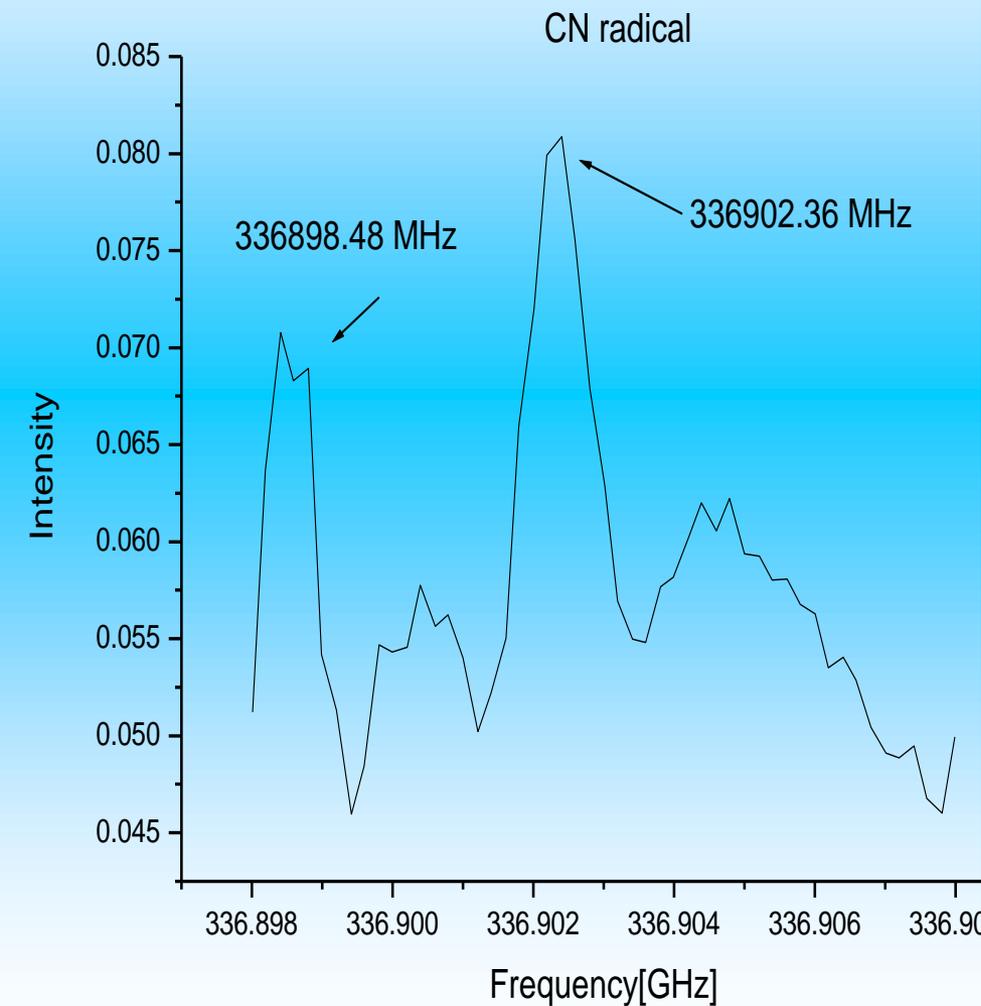


Figure 1. $J = 1 \rightarrow 0$ transition of NCO^- showing the well-resolved triplet

Search for $J=3\leftarrow 2$ transition CN^- (Predikce 337078 MHz)

From 336900- 337300 MHz



Přehled molekul a iontů detegovaných v mezihvězdném prostoru

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	13 atoms
H ₂	C ₃ [*]	c-C ₃ H	C ₅ [*]	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	C ₆ H ₆	HC ₁₁ N
AlF	C ₂ H	I-C ₃ H	C ₄ H	I-H ₂ C ₄	CH ₂ CHCN	HC(O)OCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	C ₂ H ₅ OCH ₃	
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄ [*]	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	n-C ₃ H ₇ CN	
C ₂ ^{**}	C ₂ S	C ₃ O	I-C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO			
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	CH ₃ CHO	H ₂ C ₆	HC ₇ N				
CH ⁺	HCN	C ₂ H ₂ [*]	H ₂ CCN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H				
CN	HCO	NH ₃	CH ₄ [*]	CH ₃ SH	c-C ₂ H ₄ O	I-HC ₆ H [*]	CH ₃ C(O)NH ₂				
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO	C ₈ H ⁻				
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN	C ₃ H ₆				
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO		H ₂ NCH ₂ CN					
SiC	H ₂ O	HNCS	H ₂ CNH	C ₅ N							
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	I-HC ₄ H [*]							
KCl	HNC	H ₂ CO	H ₂ NCN	I-HC ₄ N							
NH	HNO	H ₂ CN	HNC ₃	c-H ₂ C ₃ O							
NO	MgCN	H ₂ CS	SiH ₄ [*]	H ₂ CCNH							
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻							
NaCl	N ₂ H ⁺	c-SiC ₃	C ₄ H ⁻								
OH	N ₂ O	CH ₃ [*]	HC(O)CN								
PN	NaCN	C ₃ N ⁻									
SO	OCS	PH ₃									
SO ⁺	SO ₂	HCNO									
SiN	c-SiC ₂	HOCN									
SiO	CO ₂ [*]	HSCN									
SiS	NH ₂										
CS	H ₃ ^{**}										
HF	H ₂ D ⁺										
SH [*]	HD ₂ ⁺										
HD	SiCN										
FeO	AlNC										
O ₂	SiNC										
CF ⁺	HCP										
SiH	CCP										
PO											

Cations

Anions



Diffuse Interstellar Bands

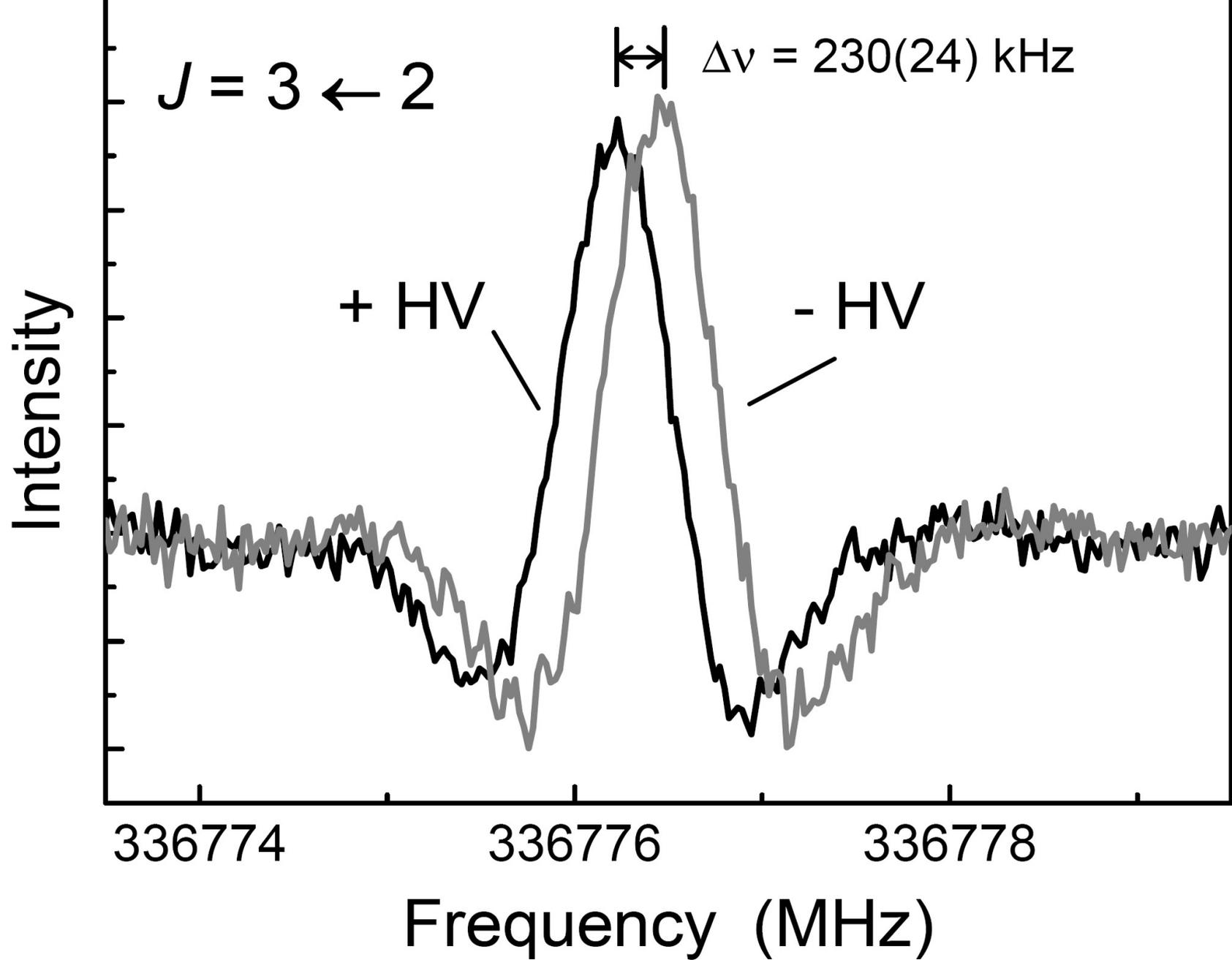
Závěr

- 20 let studia záporných iontů v laboratoři
Měření rotačně-vibračních, mikrovlnných spekter
- Hledání iontů v mezihvězdných oblacích (45 m teleskop v Nobeyamě, a 2 m optický teleskop v Okayamě, Japonsko)

<http://www.jh-inst.cas.cz/~ftirlab/>



Zleva: M. Ferus, M. Kamas, J. Cihelka, P. Kubelík, S. Civiš, K. Sovová, I. Matulková.



A Spectral-Line Survey Observation of IRC +10216 between 28 and 50 GHz

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Abstract

We report on a spectral-line survey of the circumstellar envelope of IRC +10216 between 28 and 50 GHz using the Nobeyama 45-m telescope with a sensitivity of < 10 mK. A total of 188 spectral lines were observed, 150 of which have been assigned to 22 molecules and their isotopic variants. We derived the column densities and excitation temperatures of the observed species by using a local thermodynamic equilibrium approximation. The observed frequency range is characterized by many long carbon chain molecules, up to HC₉N, as well as by 38 unidentified lines.

Key words: Atomic and molecular processes — Circumstellar matter — Interstellar:molecules — Radio sources: lines — Stars: individual (IRC +10216)

1. Introduction

As is well known, the late-type carbon star IRC +10216 is one of the brightest celestial objects in the 10–20 μ m region, and has a very rich molecular envelope, as shown by many radio and infrared observations. So far, 47 molecular species have been identified in IRC +10216, 15 of which were only detected in this source. One chemical feature of IRC +10216 is that many carbon chain molecules are synthesized in a mass-loss process from the central carbon star. On the other hand, only two oxygen-bearing molecules, CO and SiO, have been detected. Metal compounds, such as NaCl, AlF, AlCl, NaCN, KCl, MgNC, and MgCN, are also found

The Nobeyama 45-m telescope has been applied for line-survey observations of four typical molecular sources: IRC +10216, TMC-1, Sgr-B2, and Orion-KL. A large acousto-optical spectrometer in our observatory makes it possible to cover a wide frequency range (up to 2 GHz) simultaneously. These observations aim at obtaining molecular-line data in the frequency range of 9–115 GHz in order to determine the molecular abundances and to clarify the chemistry of these objects. Through these unbiased survey observations many un-identified lines have been detected, and eleven new molecular species, namely C₆H, CCS, C₃S, C₄Si, cyclic-C₃H, CH₂CN, CCO, HCCNC, HNCCC, HC₃NH⁺, and MgNC, have been identified. In the present paper we report on obser-

The Rotational Spectrum of CN^-

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(Dated: April 20, 2007)

The rotational spectrum of the molecular negative ion CN^- has been detected in the laboratory at high resolution. The four lowest transitions were observed in a low pressure glow discharge through C_2N_2 and N_2 . Conclusive evidence for the identification was provided by well-resolved nitrogen quadrupole hyperfine in the lowest rotational transition, and a measurable Doppler shift due to the ion drift in the positive column of the discharge. Three spectroscopic constants (B , D , and eQq) reproduce the observed spectrum to within 1 part in 10^7 or better, allowing the entire rotational spectrum to be calculated well into the far IR to within 1 km s^{-1} in radial velocity. CN^- is an excellent candidate for astronomical detection, because the CN radical is observed in many galactic molecular sources, the electron binding energy of CN^- is large, and calculations indicate CN^- should be detectable in IRC+10216 — the carbon star where C_6H^- has recently been observed. The fairly high concentration of CN^- in our discharge implies that other molecular anions containing the nitrile group may be within reach.

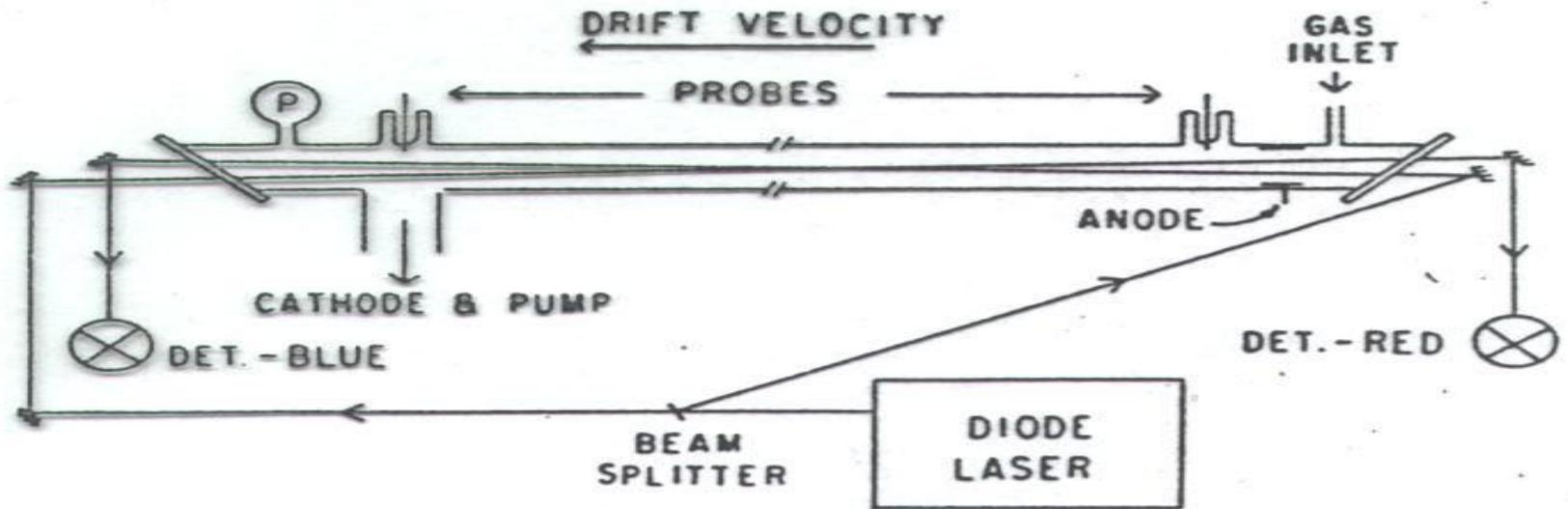


FIG. 1. Doppler-shift discharge cell and optical arrangement.

1576

