MAX PLANCK INSTITUTE
FOR EXTRATERRESTRIAL PHYSICS

# MOLECULAR SPECTROSCOPY FOR ASTROCHEMISTRY

## Part II — From Theory to Lab to Space

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# MENU OF THE DAY

- Let’s get real: from rigid rotor approximation to centrifugal distortion.
- Other perturbations on molecular spectra.

- Some examples.
- Connecting dots: theory - lab - space.

# ROTATION-VIBRATION INTERACTION

- Real molecules are not rigid!
- While rotating, molecules stretch —> larger moments of inertia —> shift of the rotational energies.
- Need to evaluate vibrational effects.
- Let’s start with the simplest case: Diatomic Molecule

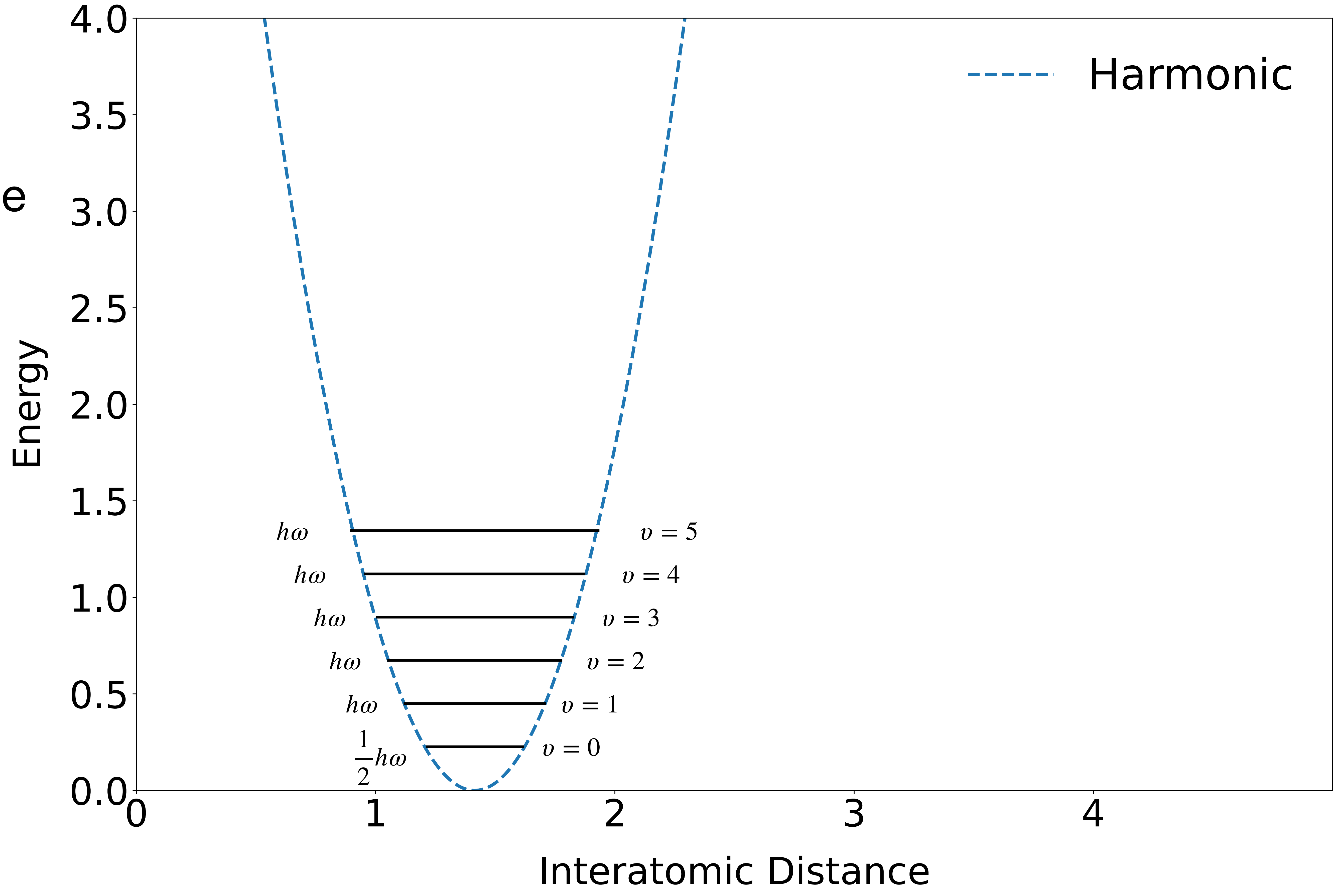
# ROTATION-VIBRATION INTERACTION

1. First approximation: **HARMONIC OSCILLATOR**

- from quantum mechanical treatment we have discrete vib. levels identified by $\upsilon$

$$E_\upsilon = \hbar(\upsilon + \frac{1}{2})\sqrt{\frac{k}{\mu}} = (\upsilon + \frac{1}{2})h\omega$$

- with $\upsilon$ = 0, 1, 2, …, and $\Delta E = h\omega$.



# ROTATION-VIBRATION INTERACTION

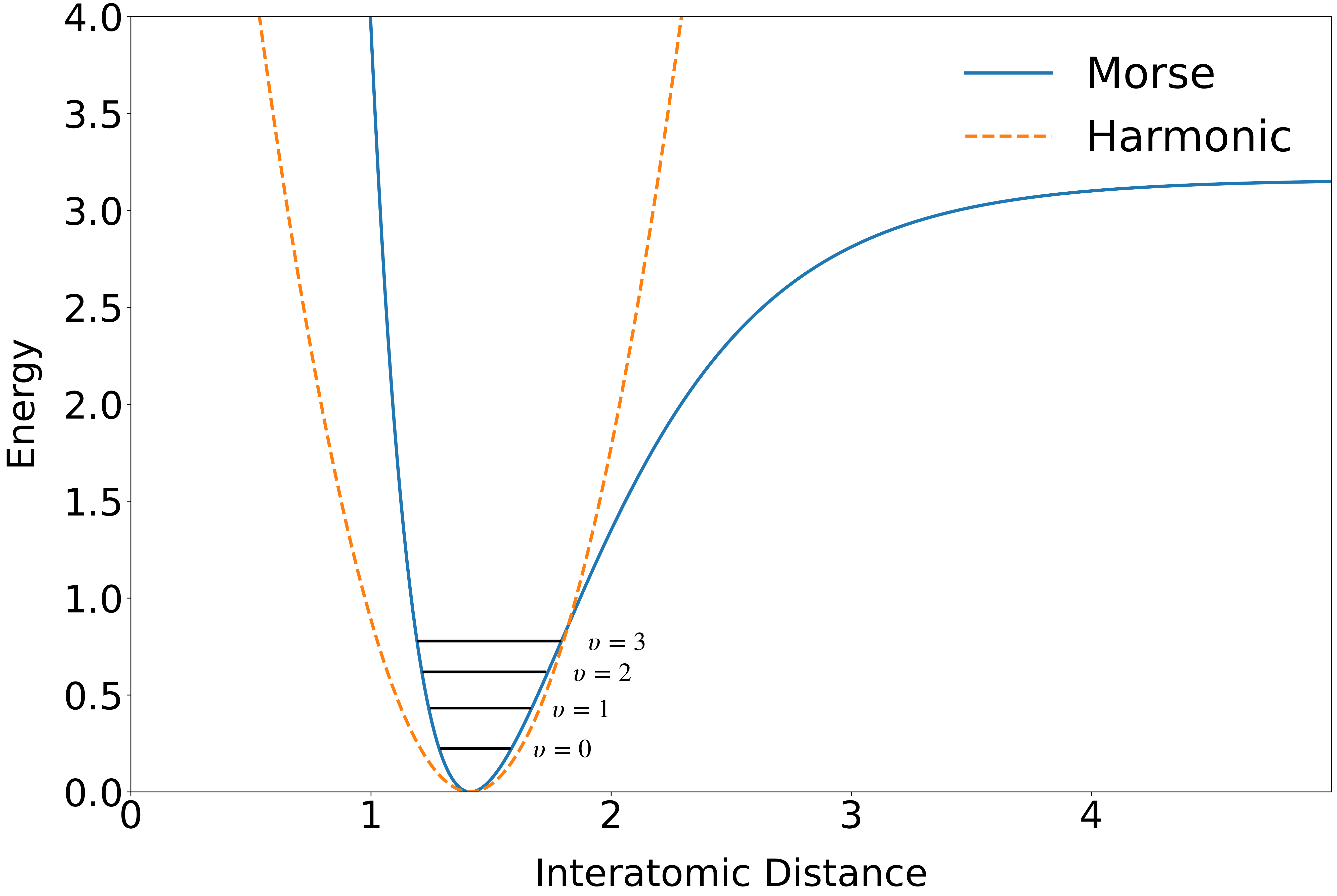
2. Harmonic oscillator is **not realistic**.
   - Close nuclei higher potential (repel each other);
   - Larger distance —> molecule dissociates.
3. Morse Potential (empirical function):

$$V(r) = D_e[1 - e^{-\beta(r-r_e)}]$$

with $D_e$ the depth of the potential well, $\beta$ curvature parameter, and $r_e$ equilibrium interatomic distance.

$$E_\upsilon/h = \omega_e(\upsilon + \frac{1}{2}) - \omega_e x_e(\upsilon + \frac{1}{2})^2$$

$\omega_e$ being the **fundamental harmonic frequency** and $\omega_e x_e$ the **anharmonic correction**.



# CENTRIFUGAL DISTORTION

- Due to energy/frequency considerations, “we” are usually interested in rotational transitions, eventually occurring in excited vibrational states (“ro-vibrational transitions”, $\Delta \upsilon = 0, J \rightarrow J+1$) but not to pure vibrational transition ($\Delta \upsilon = \pm 1$).

- Taking into account the effect of the modified structure (due to the vibration) to the rotational energies, the rotational frequency for a vibrational level $\upsilon$ will be:

$$\nu = 2B_\upsilon(J+1) - 4D_\upsilon(J+1)^3 + H_\upsilon(J+1)^3[(J+2)^3 - J^3] + \ldots$$

with

$$B_\upsilon = B_e - \alpha_e(\upsilon + \frac{1}{2}) + \gamma_e(\upsilon + \frac{1}{2})^2 + \ldots$$

$$D_\upsilon = D_e + \beta_e(\upsilon + \frac{1}{2}) + \ldots$$

# CENTRIFUGAL DISTORTION — DIATOMIC & LINEAR

$$\nu = 2B_\upsilon(J+1) - 4D_\upsilon(J+1)^3 + H_\upsilon(J+1)^3[(J+2)^3 - J^3] + \ldots$$

$$B_\upsilon = B_e - \alpha_e(\upsilon + \frac{1}{2}) + \gamma_e(\upsilon + \frac{1}{2})^2 + \ldots$$

$$D_\upsilon = D_e + \beta_e(\upsilon + \frac{1}{2}) + \ldots$$

- $\alpha_e$ and $\gamma_e$ represent rotation-vibration interaction constants.
- $D_\upsilon$ represents the first-order centrifugal stretching term ("**quartic centrifugal distortion parameter**"), and the term $\beta_e(\upsilon + \frac{1}{2})$ corrects for the effects of vibration on the centrifugal stretching constant.
- $H_\upsilon$ is the second-order centrifugal stretching term, the "**sextic centrifugal distortion parameter**"

# CENTRIFUGAL DISTORTION — SYMMETRIC TOP

- For symmetric rotors expression is similar to linear and diatomic molecules.

- For the ground state of a prolate symmetric top the rotational energies are:

$$E_{J,K}/h = B_0J(J+1) + (A_0 - B_0)K^2 - D_JJ^2(J+1)^2 - D_{JK}J(J+1)K^2 + D_KK^4$$

- Now, taking into account the selection rule $J \rightarrow J+1, K \rightarrow K$, and adding also the sextic corrections, the rotational frequencies are:

$$\nu = 2B_0(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 + H_J(J+1)^3[(J+2)^3 - J^3] + 4H_{JK}(J+1)^3K^2 + 2H_{KJ}(J+1)K^4 + \ldots$$

# CENTRIFUGAL DISTORTION — ASYMMETRIC TOP

- Extending to any class of molecules things get a bit more complex…

- Effect can be treated as a series of perturbation terms: $\hat{H} = \hat{H}_r + \hat{H}_d^4 + \hat{H}_d^6 + \ldots$, where

$$\hat{H}_d^4 = \frac{\hbar^4}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} \hat{J}_\alpha \hat{J}_\beta \hat{J}_\gamma \hat{J}_\delta$$

$$\hat{H}_d^6 = \hbar^6 \sum_{\alpha\beta\gamma\delta\epsilon\eta} \upsilon_{\alpha\beta\gamma\delta\epsilon\eta} \hat{J}_\alpha \hat{J}_\beta \hat{J}_\gamma \hat{J}_\delta \hat{J}_\epsilon \hat{J}_\eta$$

with $\alpha, \beta, \gamma, \delta, \epsilon, \eta = x, y,$ or $z$.

- $\tau_{\alpha\beta\gamma\delta}$ and $\upsilon_{\alpha\beta\gamma\delta\epsilon\eta}$ are the **quartic and sextic centrifugal distortion constants**.

# CENTRIFUGAL DISTORTION — ASYMMETRIC TOP

- For asymmetric rotors, these constants amounts to a total number of **81 quartic and 729 sextic coefficients**!
- Nevertheless, the eigenvalues may depend on only certain linear combinations of these parameters.
- “Reduced” Hamiltonians are usually used to fit experimental data.
- Widely used are the Watson’s reduced Hamiltonians — ***Asymmetric (A)*** or ***Symmetric (S) Top Reduction***.

# CENTRIFUGAL DISTORTION — ASYMMETRIC TOP

**WATSON'S A REDUCTION:**

$$\hat{H}_d^{\;4,A} = -\Delta_J \hat{J}^4 - \Delta_{JK} \hat{J}^2 \hat{J}_z^2 - \Delta_K \hat{J}_z^4 - \frac{1}{2}[(\delta_J \hat{J}^2 + \delta_K \hat{J}_z^2), (\hat{J}_+^2 + \hat{J}_-^2)]_+$$

$$\hat{H}_d^{\;6,A} = \Phi_J \hat{J}^6 + \Phi_{JK} \hat{J}^4 \hat{J}_z^2 + \Phi_{KJ} \hat{J}^2 \hat{J}_z^4 + \Phi_K \hat{J}_z^6 + \frac{1}{2}[(\phi_J \hat{J}^4 + \phi_{JK} \hat{J}_z^2 + \phi_K \hat{J}^2 \hat{J}_z^2), (\hat{J}_+^2 + \hat{J}_-^2)]_+$$

**WATSON'S S REDUCTION:**

$$\hat{H}_d^{\;4,S} = -D_J \hat{J}^4 - D_{JK} \hat{J}^2 \hat{J}_z^2 - D_K \hat{J}_z^4 + d_1 \hat{J}^2 (\hat{J}_+^2 + \hat{J}_-^2) + d_2 (\hat{J}_+^4 + \hat{J}_-^4)$$

$$\hat{H}_d^{\;6,S} = H_J \hat{J}^6 + H_{JK} \hat{J}^4 \hat{J}_z^2 + H_{KJ} \hat{J}^2 \hat{J}_z^4 + H_K \hat{J}_z^6 + h_1 \hat{J}^4 (\hat{J}_+^2 + \hat{J}_-^2) + h_2 \hat{J}^2 (\hat{J}_+^4 + \hat{J}_-^4) + h_3 (\hat{J}_+^6 + \hat{J}_-^6)$$

- with $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$, and $[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$

# ADDITIONAL PERTURBATIONS

- So far we have seen the “simplest” cases.

- It can get waaaaay more messy in presence of other perturbations which can generate splitting of the rotational levels.

- In particular if we are in the presence of:
  - electronic angular momentum (e.g. $CN$)
  - internal specular symmetry (e.g. $NH_3$)
  - large amplitude motions (e.g. $CH_3OH$)
  - nuclear spin (e.g. $DCN$)
  - degenerate vibrational modes (l-type doubling)

- Or if we have a combination of multiple effects!

# LINEWIDTH OF ROTATIONAL LINES

# BROADENING EFFECTS — I

- ***Natural line width:***

— From uncertainty principle $\Delta t \Delta E \approx \hbar$ => $FWHM = \dfrac{\Delta E}{h} \approx \dfrac{1}{2\pi(\Delta t)}$

e.g.: if $\mu \approx 1\, D$ and in ground vib. state, $FWHM \approx 10^{-5}\, Hz\, (@3mm) / 10^{-8}\, Hz\, (@3cm)$

if excited vib. state $FWHM \approx 10s\, Hz$

=> USUALLY NEGLIGIBLE

- ***Doppler Broadening:***

— Frequency of radiation absorbed by a molecule moving at v depends on the velocity of the molecule relative to that of the radiation. If $\nu_0$ is the resonant absorption frequency at rest, the absorbed frequency then will be:

$$\nu = \nu_0(1 + v/c)$$

Assuming Maxwell-Boltzmann distribution of velocities: $FWHM_D = 7.15 \times 10^{-7}\sqrt{\dfrac{T}{M}}\nu_0$

e.g. @300K: $NH_3\ @24\, GHz$ => $FWHM_D \sim\ 72\, kHz$ / $NH_3\ J = 0 \rightarrow 1\ @572\, GHz$ => $FWHM_D \sim\ 1.7\, MHz$

# BROADENING EFFECTS — II

- ***Pressure Broadening:***

— Very complex: depends on intermolecular potential between colliding molecules.

— Collision break the "life" of the molecule in a rotational energy state.

— In general: $FWHM_P \sim bP$, where P is the pressure and $b \propto [\sigma, M, T]$

— $b \approx 10\, MHz/Torr$

— Also PRESSURE SHIFT on $\nu$, usually $\sim\ 1\, MHz/Torr$

- ***Other minor contributions:***

— Power effects: Saturation -> Distortion -> Line broadening.

— Collision with cell walls: When pressure is so low that cell dimensions are comparable to the mean free path.

# FROM THEORY TO LAB

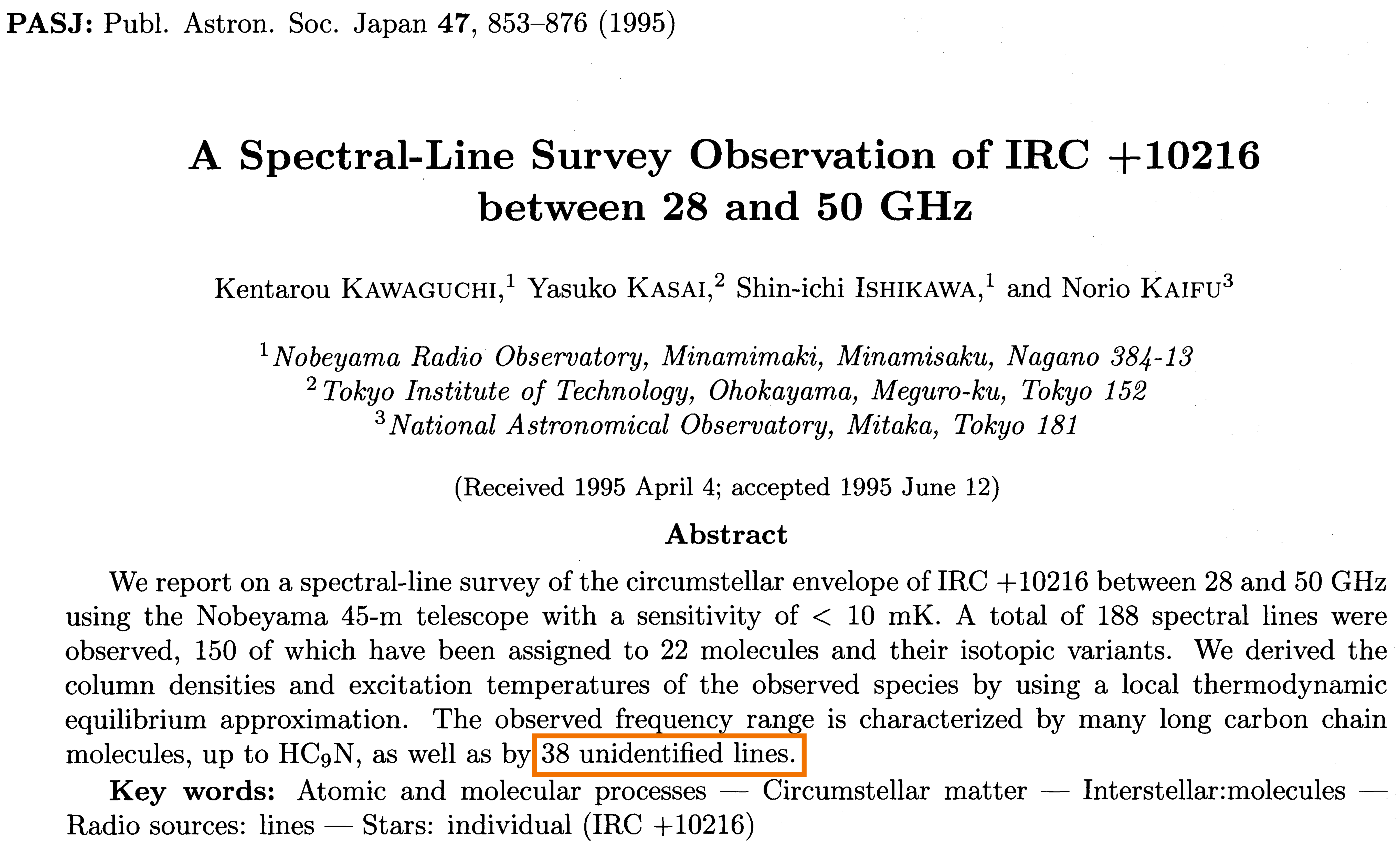
# TYPICAL LABORATORY WORKFLOW

- …
- Measure rotational transitions.
- Line profile fitting of the different experimental features.
- Build a collection of quantum number vs frequency line list.
- Statistical fit over molecular model (Hamiltonian).
- Derive Rotational and Distortion parameters of the molecule.
- Predict a global database based on the experimental fitted parameters.

- This will be the focus of the practical work.

# THE CURIOUS CASE OF B1377

# U-LINES IN IRC+10216



**PASJ:** Publ. Astron. Soc. Japan **47**, 853–876 (1995)

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

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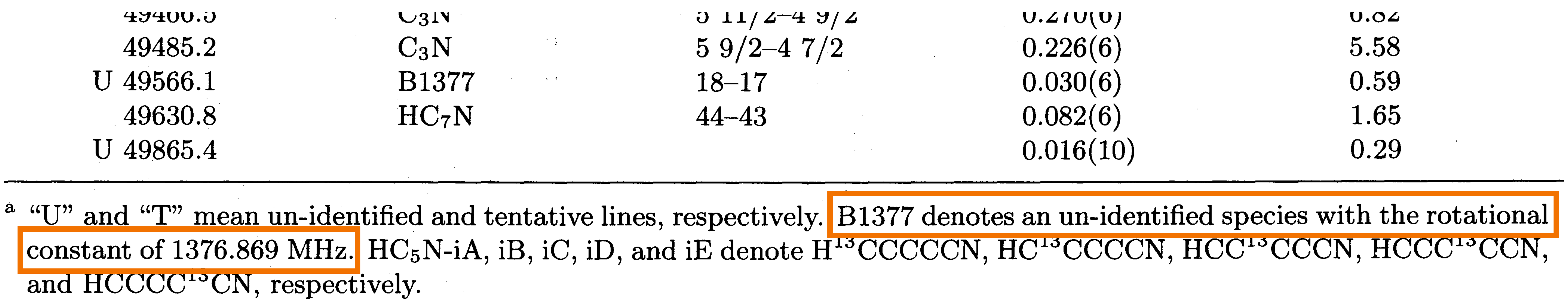
### Abstract

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 $HC_9N$, as well as by 38 unidentified lines.

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

# U-LINES IN IRC+10216



| | | | | |
|---|---|---|---|---|
| 49466.5 | $C_3N$ | 5 11/2–4 9/2 | 0.270(6) | 6.82 |
| 49485.2 | $C_3N$ | 5 9/2–4 7/2 | 0.226(6) | 5.58 |
| U 49566.1 | B1377 | 18–17 | 0.030(6) | 0.59 |
| 49630.8 | $HC_7N$ | 44–43 | 0.082(6) | 1.65 |
| U 49865.4 | | | 0.016(10) | 0.29 |

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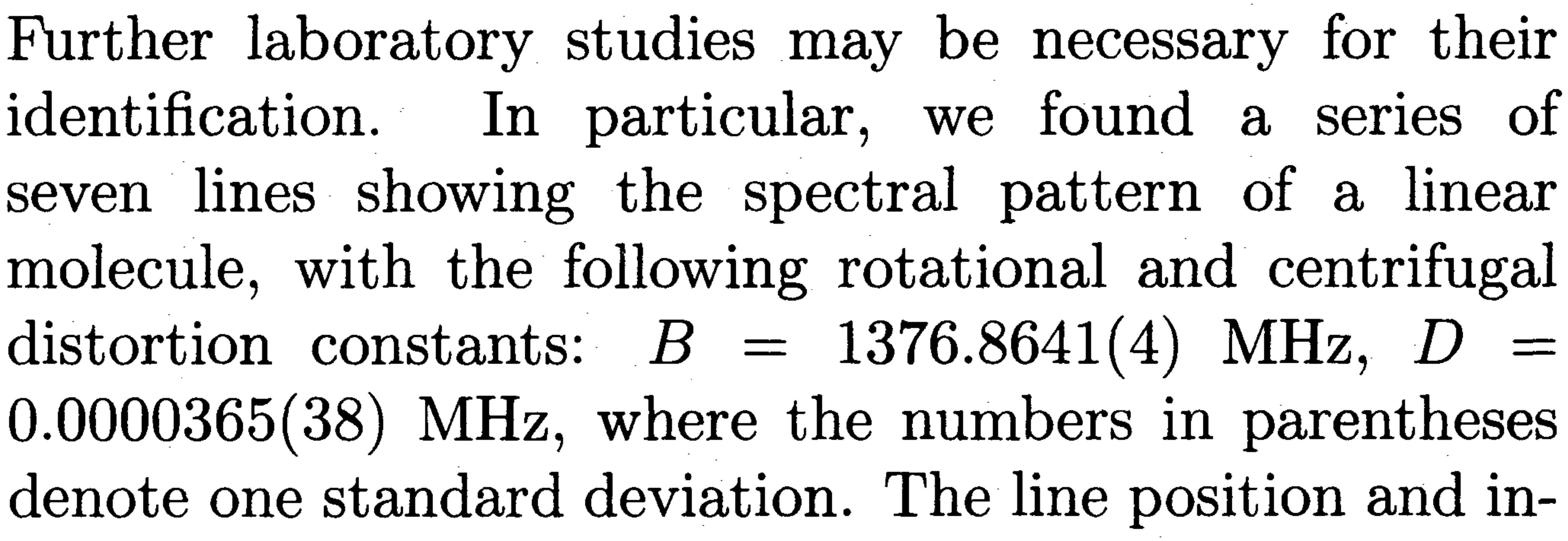
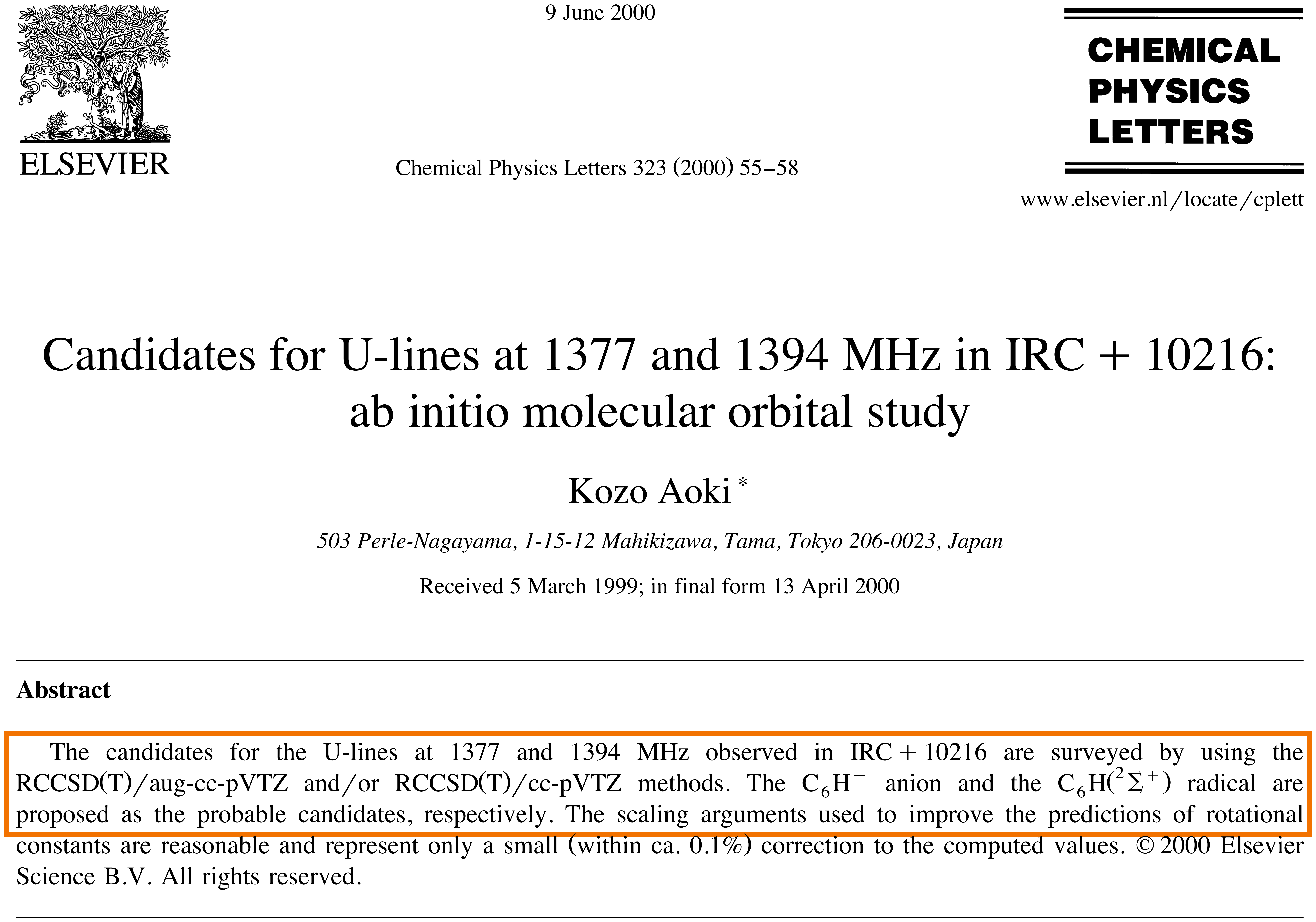
[a] “U” and “T” mean un-identified and tentative lines, respectively. B1377 denotes an un-identified species with the rotational constant of 1376.869 MHz. $HC_5N$-iA, iB, iC, iD, and iE denote $H^{13}CCCCCN$, $HC^{13}CCCCN$, $HCC^{13}CCCN$, $HCCC^{13}CCN$, and $HCCCC^{13}CN$, respectively.



Further laboratory studies may be necessary for their identification. In particular, we found a series of seven lines showing the spectral pattern of a linear molecule, with the following rotational and centrifugal distortion constants: $B = 1376.8641(4)$ MHz, $D = 0.0000365(38)$ MHz, where the numbers in parentheses denote one standard deviation. The line position and in-

# U-LINES IN IRC+10216



9 June 2000

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Chemical Physics Letters 323 (2000) 55–58

CHEMICAL PHYSICS LETTERS

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## Candidates for U-lines at 1377 and 1394 MHz in IRC + 10216: ab initio molecular orbital study

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Received 5 March 1999; in final form 13 April 2000

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**Abstract**

The candidates for the U-lines at 1377 and 1394 MHz observed in IRC + 10216 are surveyed by using the RCCSD(T)/aug-cc-pVTZ and/or RCCSD(T)/cc-pVTZ methods. The $C_6H^-$ anion and the $C_6H(^2\Sigma^+)$ radical are proposed as the probable candidates, respectively. The scaling arguments used to improve the predictions of rotational constants are reasonable and represent only a small (within ca. 0.1%) correction to the computed values.

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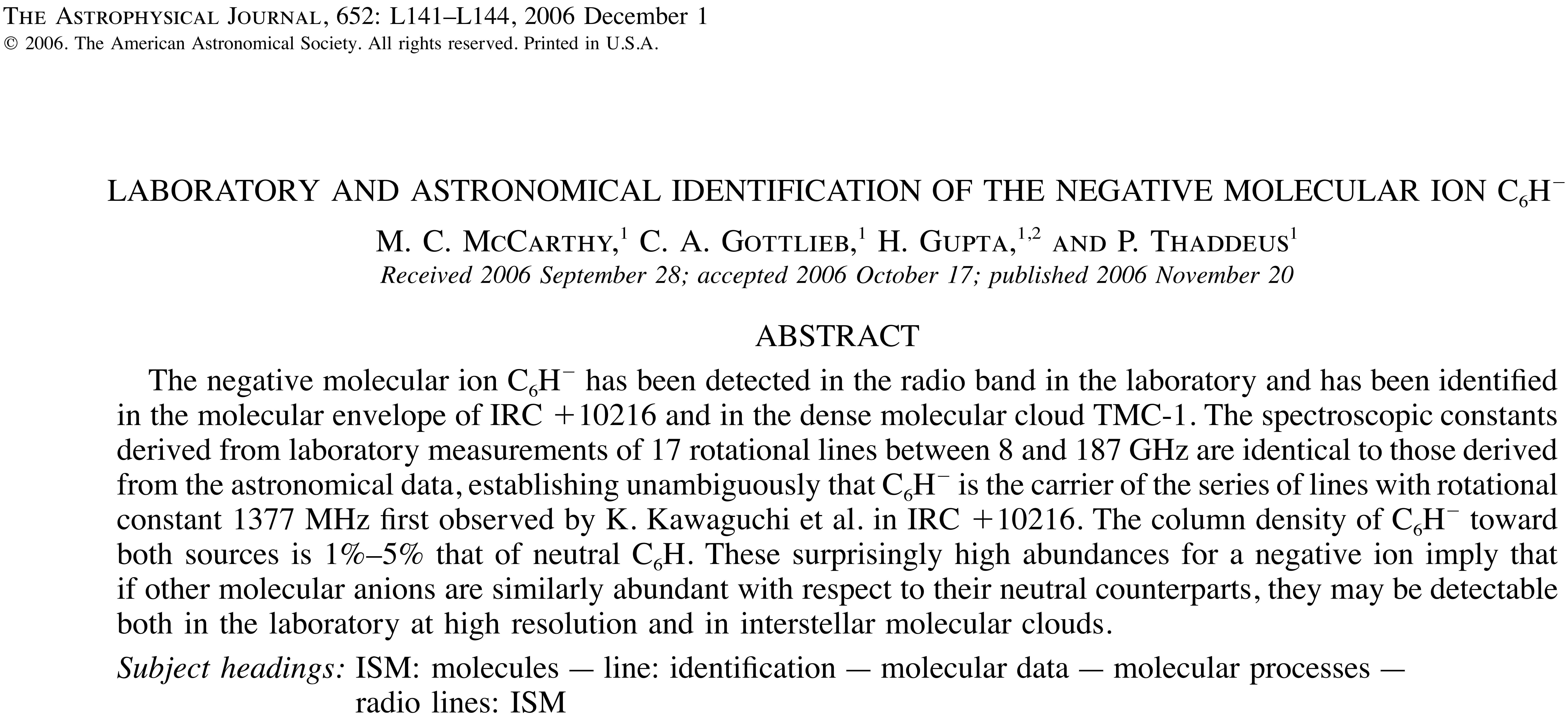
# DISCOVERY OF ANIONS IN SPACE



The Astrophysical Journal, 652: L141–L144, 2006 December 1

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

M. C. McCarthy,[1] C. A. Gottlieb,[1] H. Gupta,[1,2] and P. Thaddeus[1]

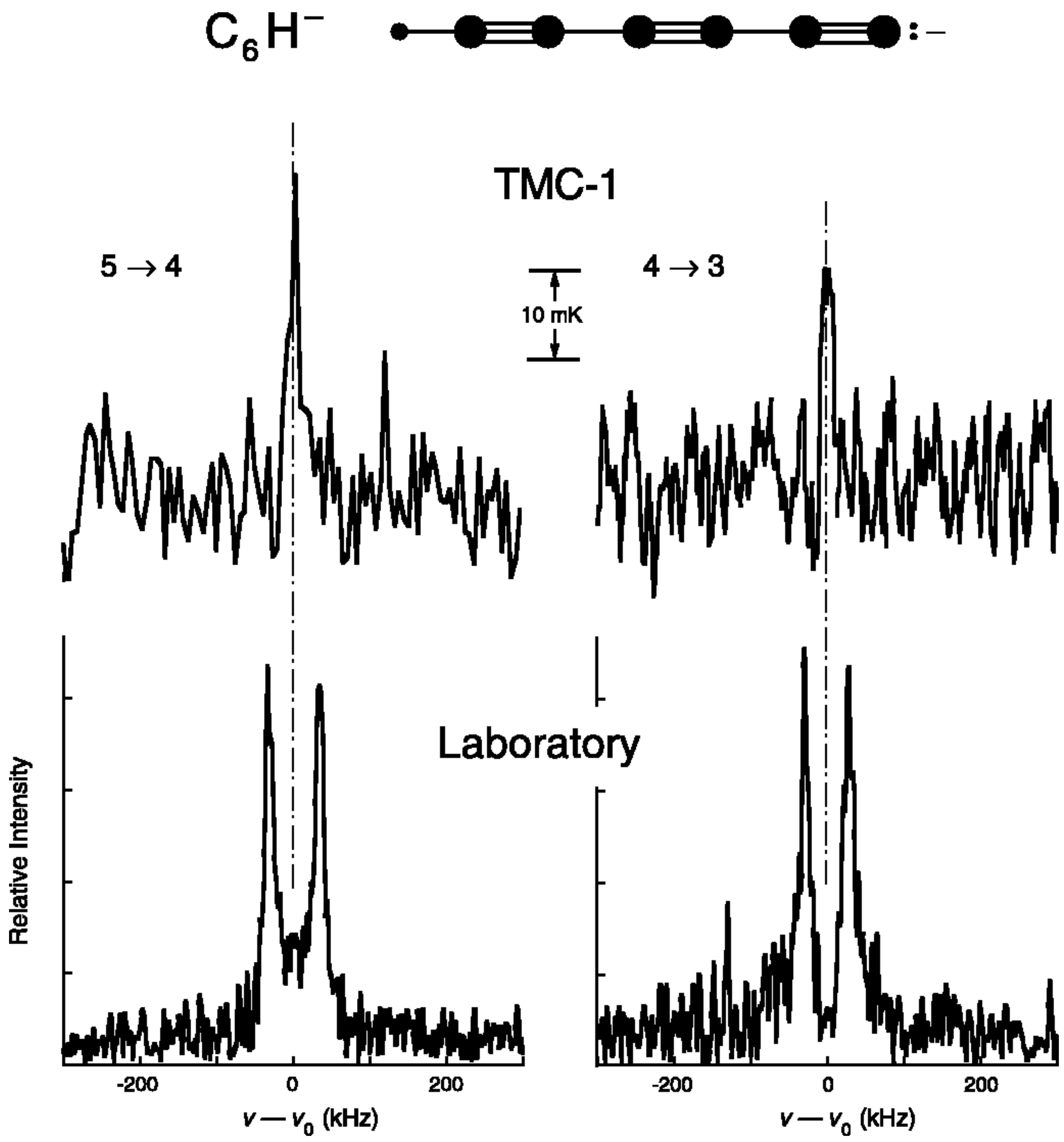
*Received 2006 September 28; accepted 2006 October 17; published 2006 November 20*

## 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.

*Subject headings:* ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

# DISCOVERY OF ANIONS IN SPACE



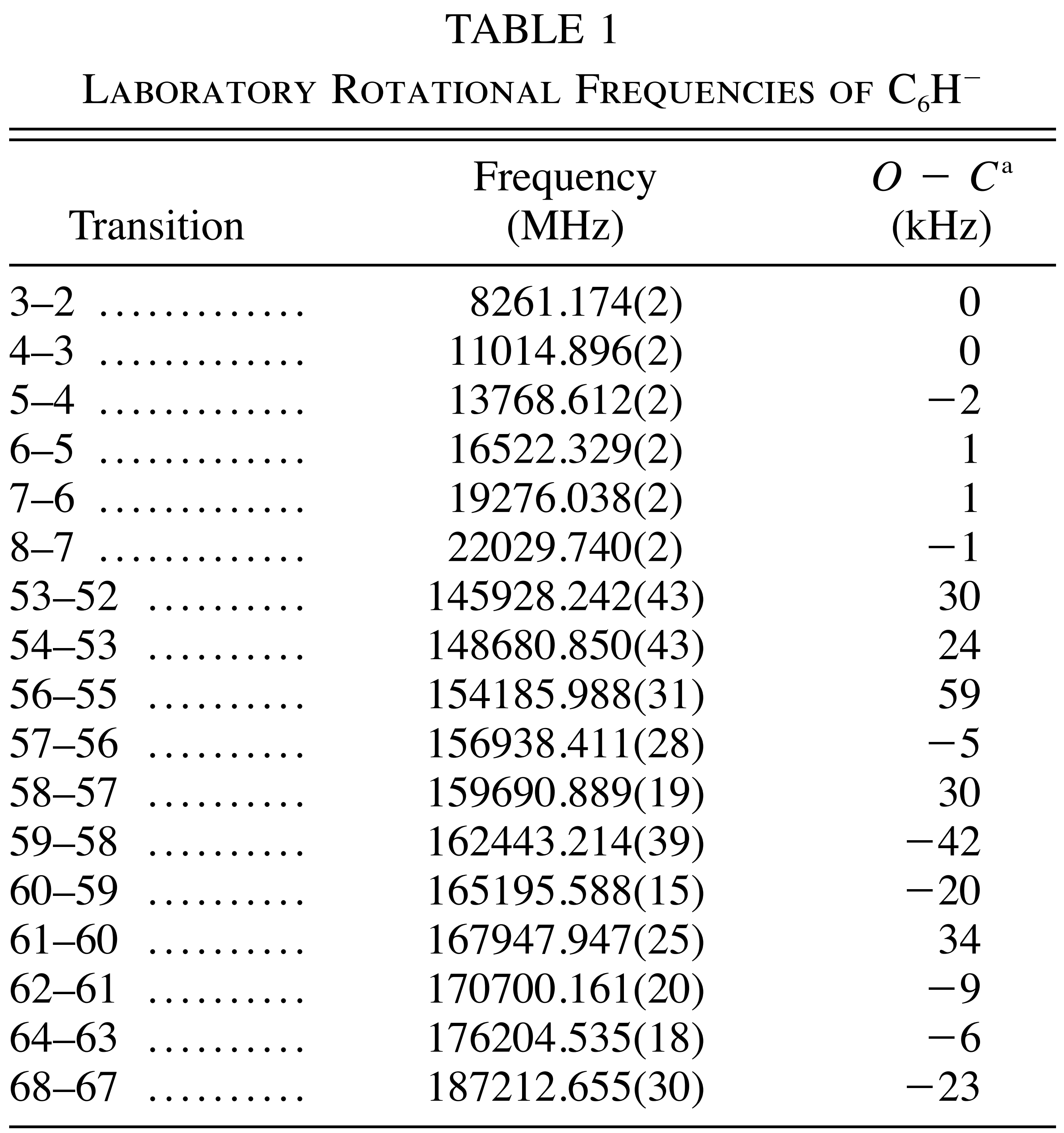


TABLE 1

LABORATORY ROTATIONAL FREQUENCIES OF $C_6H^-$

| Transition | Frequency (MHz) | $O - C^a$ (kHz) |
|---|---|---|
| 3–2 ............ | 8261.174(2) | 0 |
| 4–3 ............ | 11014.896(2) | 0 |
| 5–4 ............ | 13768.612(2) | −2 |
| 6–5 ............ | 16522.329(2) | 1 |
| 7–6 ............ | 19276.038(2) | 1 |
| 8–7 ............ | 22029.740(2) | −1 |
| 53–52 ......... | 145928.242(43) | 30 |
| 54–53 ......... | 148680.850(43) | 24 |
| 56–55 ......... | 154185.988(31) | 59 |
| 57–56 ......... | 156938.411(28) | −5 |
| 58–57 ......... | 159690.889(19) | 30 |
| 59–58 ......... | 162443.214(39) | −42 |
| 60–59 ......... | 165195.588(15) | −20 |
| 61–60 ......... | 167947.947(25) | 34 |
| 62–61 ......... | 170700.161(20) | −9 |
| 64–63 ......... | 176204.535(18) | −6 |
| 68–67 ......... | 187212.655(30) | −23 |

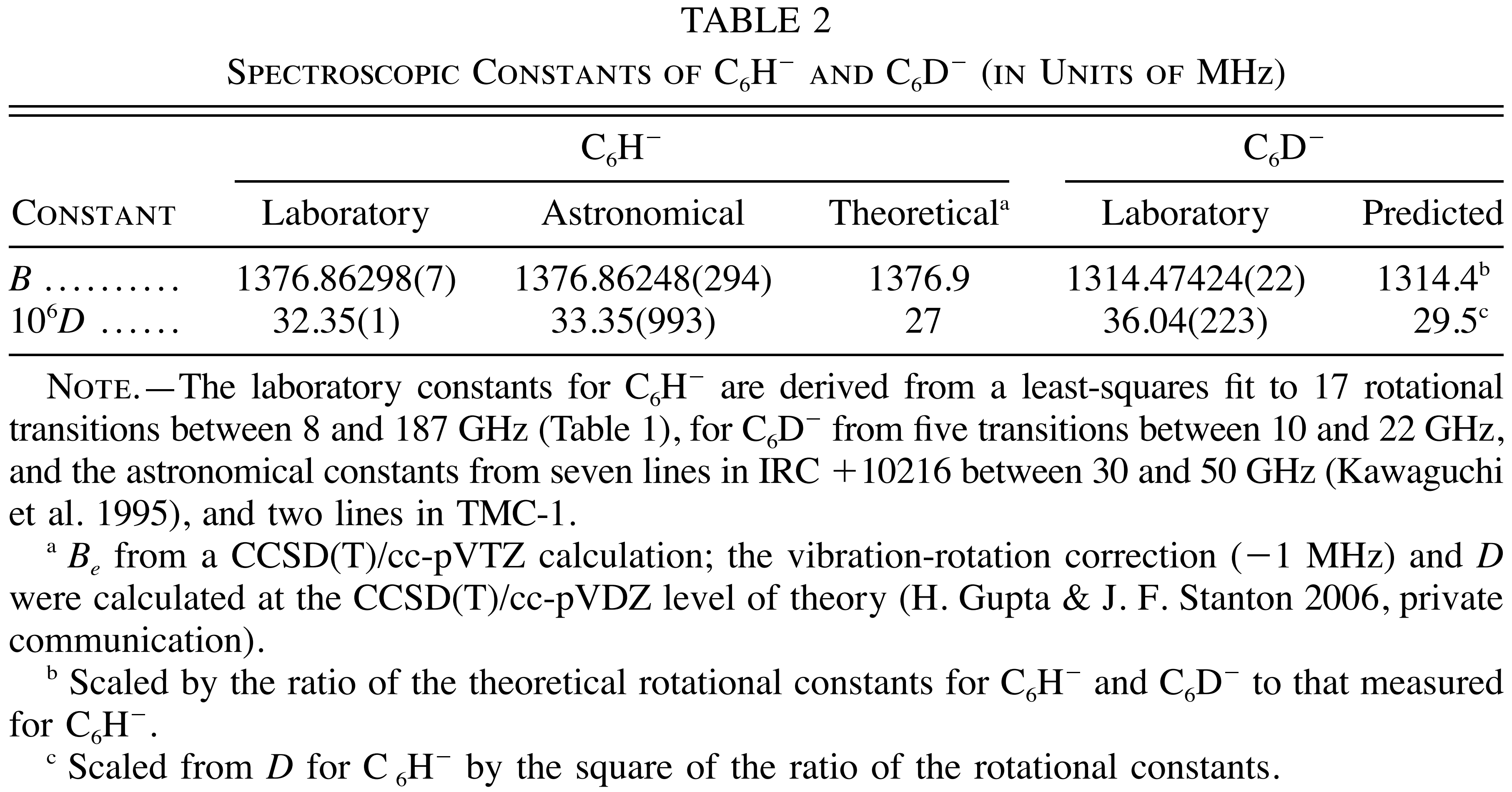


TABLE 2

SPECTROSCOPIC CONSTANTS OF $C_6H^-$ AND $C_6D^-$ (IN UNITS OF MHz)

| | $C_6H^-$ | | | $C_6D^-$ | |
|---|---|---|---|---|---|
| CONSTANT | Laboratory | Astronomical | Theoretical[a] | Laboratory | Predicted |
| $B$ .......... | 1376.86298(7) | 1376.86248(294) | 1376.9 | 1314.47424(22) | 1314.4[b] |
| $10^6D$ ...... | 32.35(1) | 33.35(993) | 27 | 36.04(223) | 29.5[c] |

NOTE.—The laboratory constants for $C_6H^-$ are derived from a least-squares fit to 17 rotational transitions between 8 and 187 GHz (Table 1), for $C_6D^-$ from five transitions between 10 and 22 GHz, and the astronomical constants from seven lines in IRC +10216 between 30 and 50 GHz (Kawaguchi et al. 1995), and two lines in TMC-1.

[a] $B_e$ from a CCSD(T)/cc-pVTZ calculation; the vibration-rotation correction (−1 MHz) and $D$ were calculated at the CCSD(T)/cc-pVDZ level of theory (H. Gupta & J. F. Stanton 2006, private communication).

[b] Scaled by the ratio of the theoretical rotational constants for $C_6H^-$ and $C_6D^-$ to that measured for $C_6H^-$.

[c] Scaled from $D$ for $C_6H^-$ by the square of the ratio of the rotational constants.

# ANIONS IN SPACE

- $C_6H^-$ first anion detected in space.
- Five more detected since: $C_4H^-, C_8H^-, C_3N^-, CN^-$, and $C_5N^-$ (+ $OCN^-$ detected in ices, via IR).
- $C_5N^-$ assigned w/o laboratory data!
- Electron radiative attachment $(X + e^- \rightarrow X^- + h\nu)$ most likely formation pathway in space.
- $CN^-$ however suggests other formation mechanism, such as the reaction $C_n^- + N$ (see *Agúndez+ 2010; Cordiner & Millar 2009*).

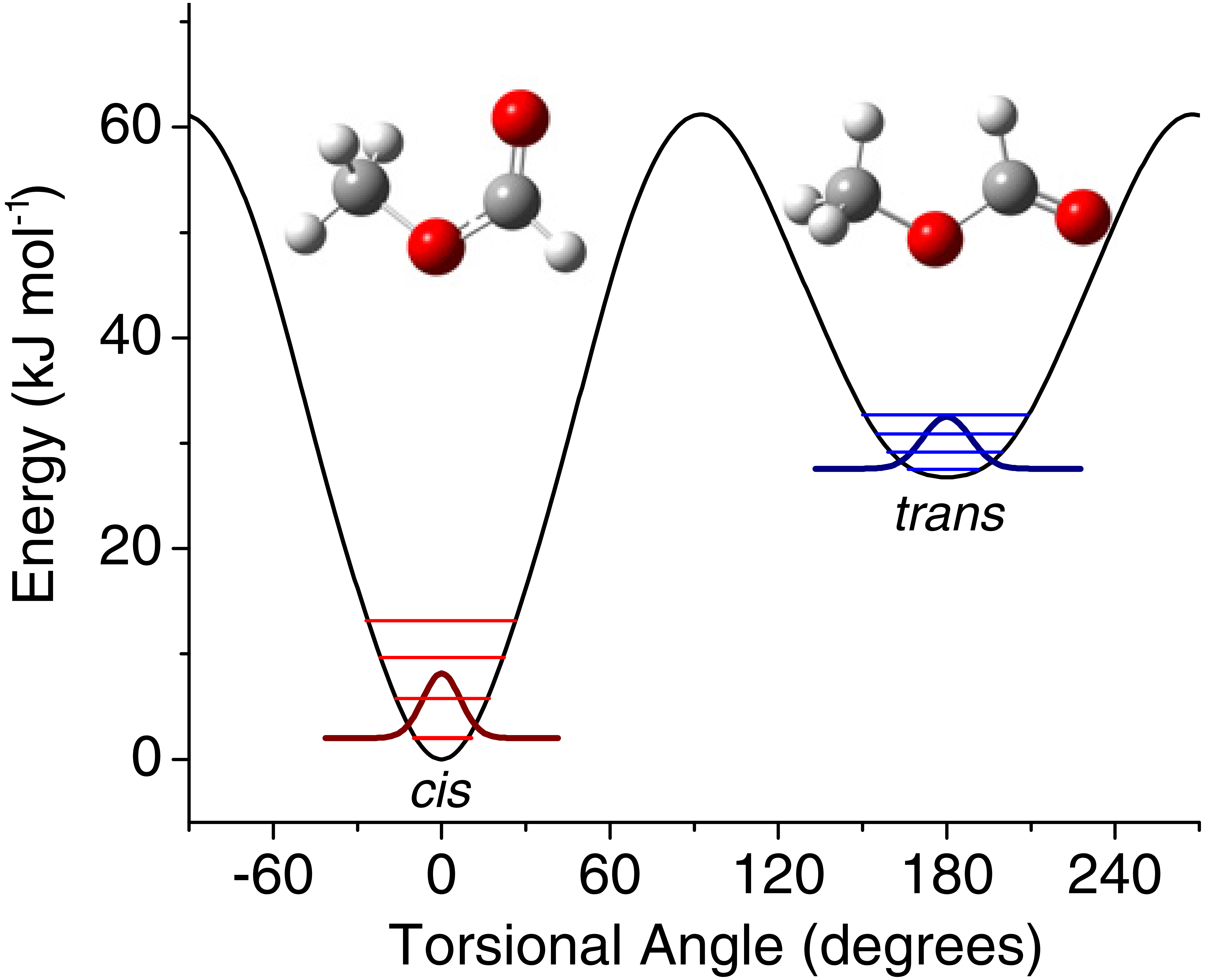
# CONFORMATIONAL ISOMERISMS

# METHYL FORMATE — $HCOOCH_3$

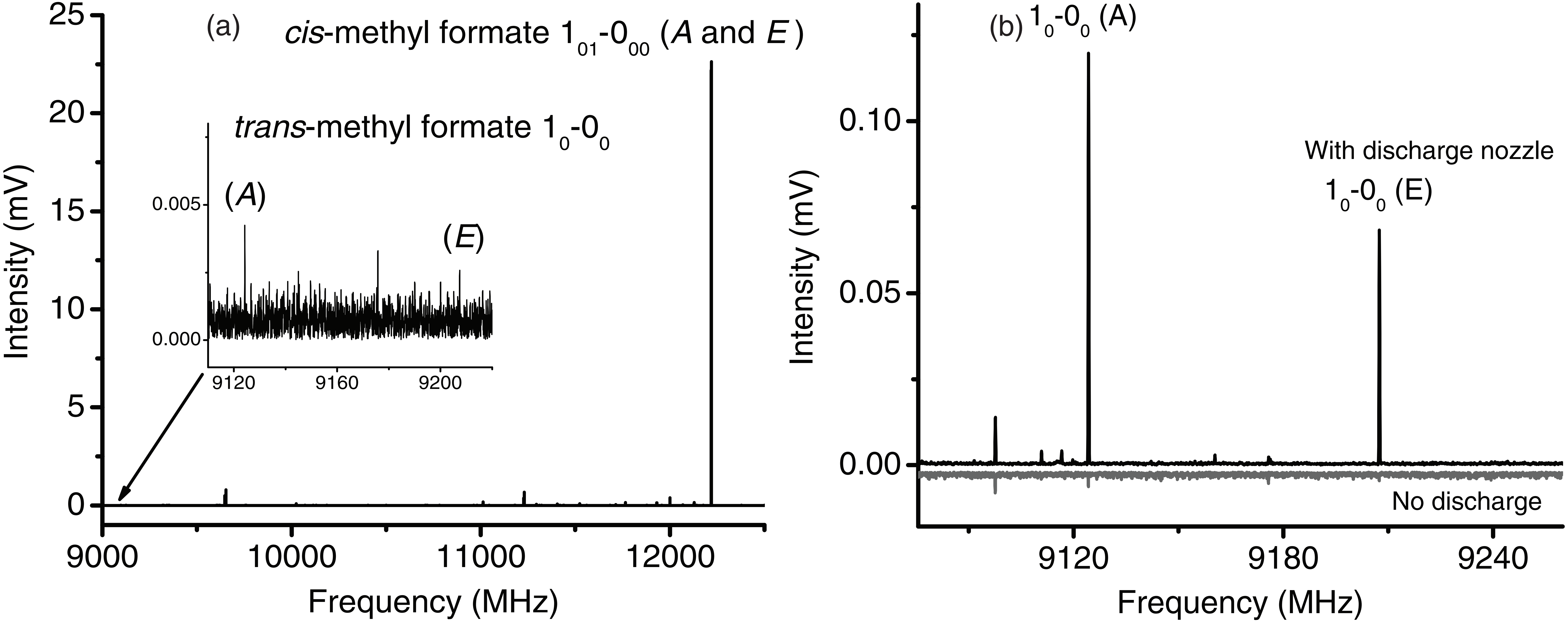
- The *cis* isomer is one of the most abundant iCOM (i.e. interstellar complex molecule) in space.
- Its abundance compared to that of its structural isomers acetic acid ($CH_3COOH$, most energetically stable) and glycolaldehyde ($HOCH_2CHO$) is especially surprising.
- Most likely formation involves grain chemistry, like many other iCOMs.
- Non-thermal desorption of iced methanol might also start a series of gas-phase reactions leading to formation of methoxy ($CH_3O$), dimethyl ether ($CH_3OCH_3$) and methyl formate (see *Balucani+ 2015*).
- High angular resolution observations help to disentangle the chemistry of different species.

# METHYL FORMATE – *$HCOOCH_3$*

- Trans isomer less stable by 25 kJ/mol (~3000K).
- @ 100K *cis/trans* ~ $10^{13}$ : 1 !!
- If trans detected non-thermal distribution.
- Relative abundances will reflect conformer-specific processes.
- Different spatial distribution (= high-angular resolution) and production mechanisms.

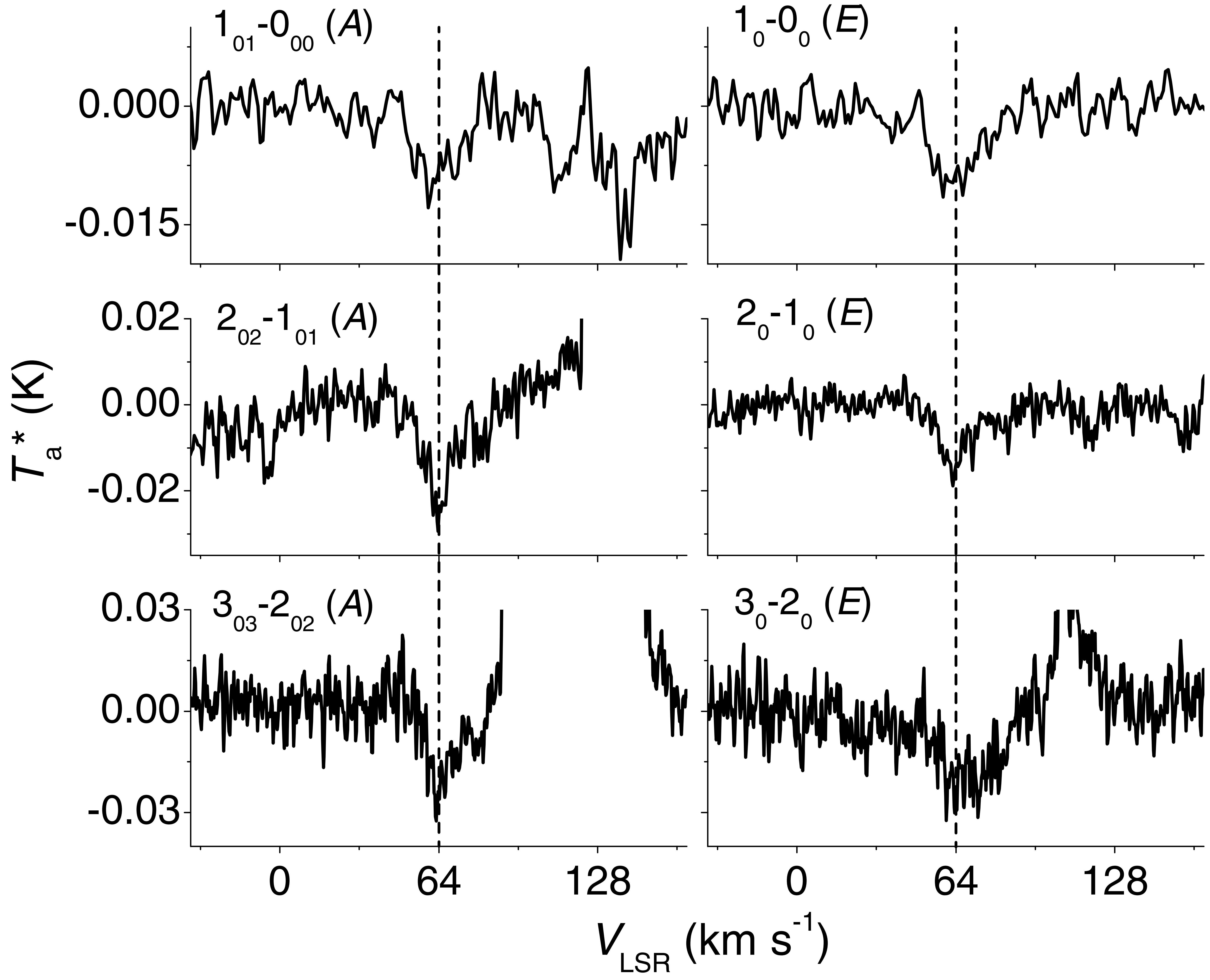


# *trans*-METHYL FORMATE — Lab



*Neill+ 2012*

# *trans*-METHYL FORMATE — SgrB2(N)

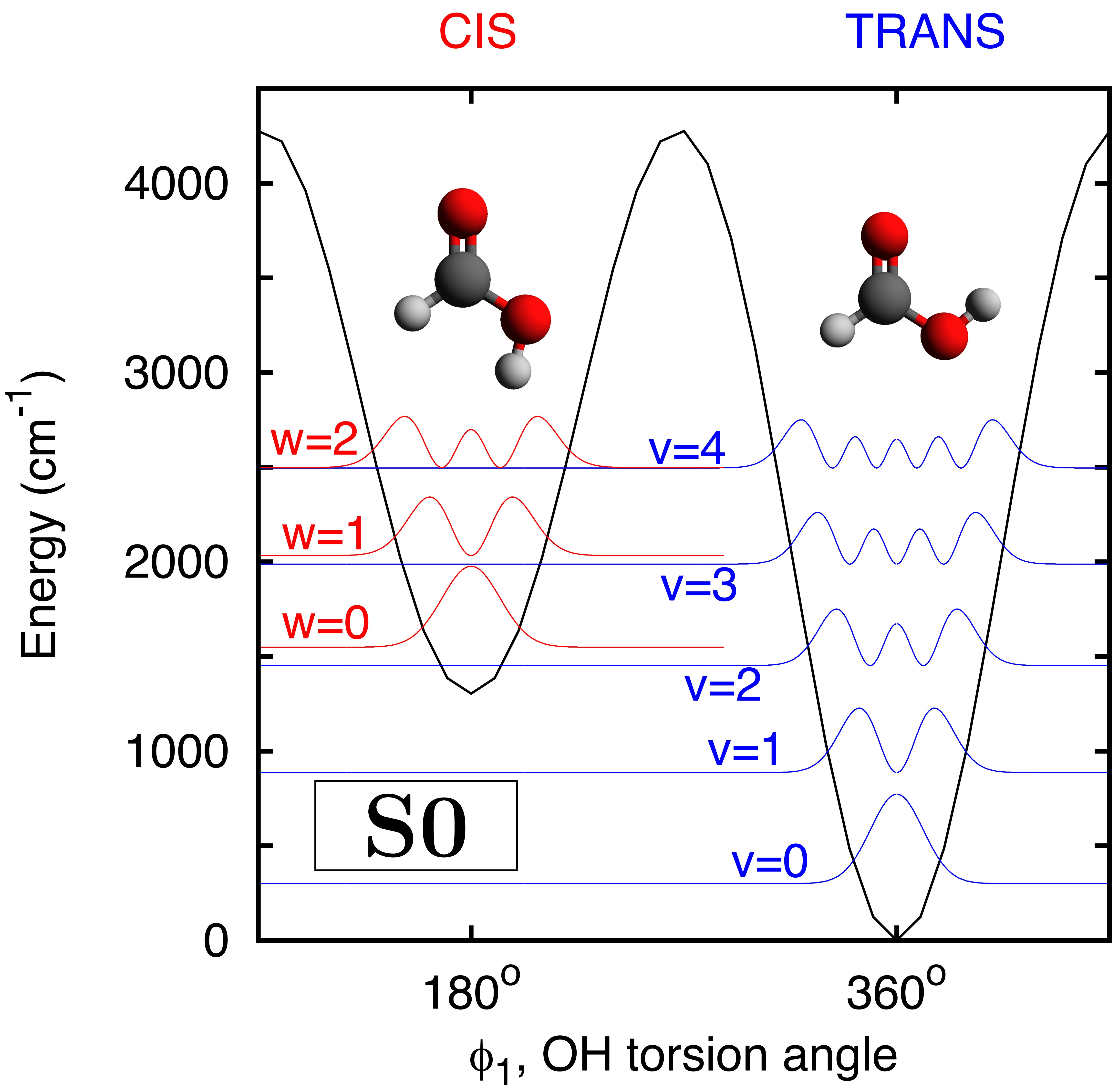


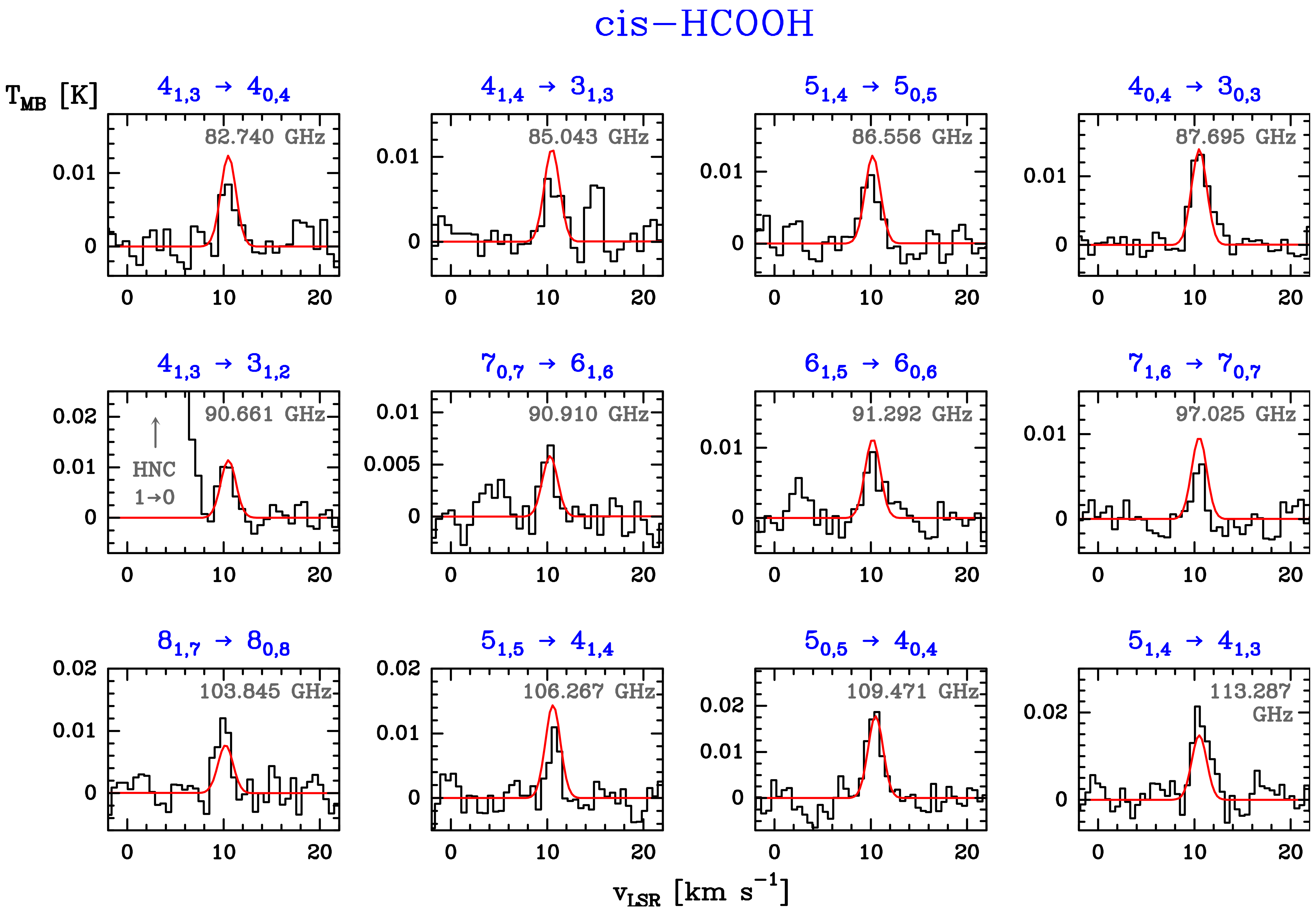
*Neill+ 2012*

# FORMIC ACID – $HCOOH$

- Few years later *Cuadrado+ (2016)* were able to detect *cis*-$HCOOH$ towards the Orion Bar photodissociation region.
- $HCOOH$ is the simplest organic acid.
- The most stable, *trans*, conformer was the first acid detected in the ISM (*Zuckerman+ 1971*) and since it has been detected in a variety of IS sources, including ices (*Keane+ 2001*) and chondritic meteorites (*Briscoe & Moore 1993*).
- *cis*-$HCOOH$ is ~2000K higher than the *trans* conformer, with an internal rotation barrier of ~ 7000K.

# FORMIC ACID – *HCOOH*





*Cuadrado+ 2016*

# FORMIC ACID – *HCOOH*

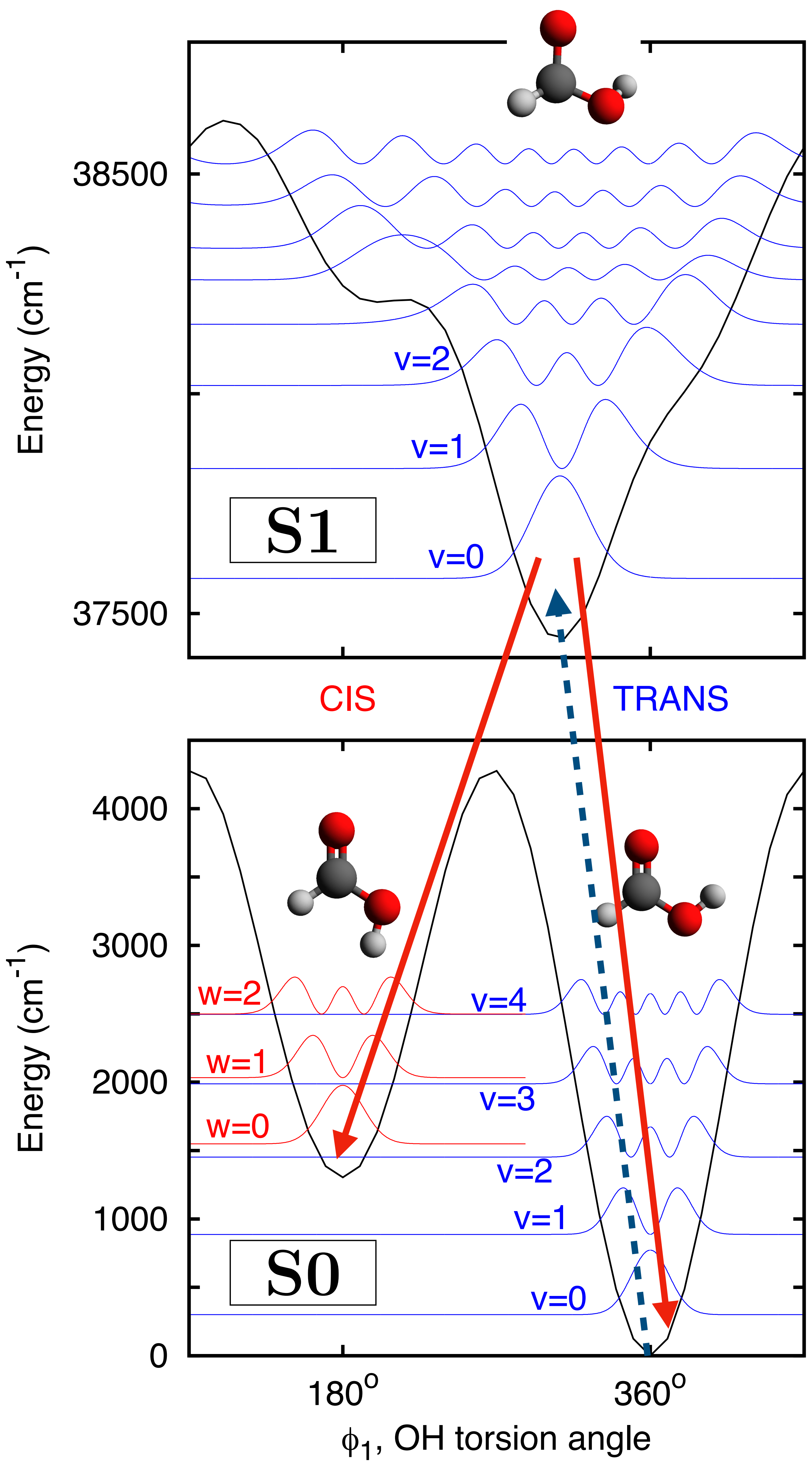
- Photoswitching in action:

  —a given conformer absorbs a stellar photon;

  — molecule is radiatively excited to high electronic state, above the interconversion barrier;

  — subsequent fluorescent decay leaves may leave the molecules in a different conformer form.

- New mechanism in space.
- May be important in UV irradiated environments.
- Other approaches to explain non-equilibrium ratio of different conformers in different IS environments are competitive chemical routes and quantum tunneling (*García de la Concepción+ 2021*).



# ISOTOPIC FRACTIONATION

## some recent results

# DEUTERIUM FRACTIONATION

- The number of D-species detected in the ISM is incredibly high if considering the local ISM $D/H = (2.0 \pm 0.1) \times 10^{-5}$.
- Including doubly (e.g. $CH_3OCHD_2$, *Richard+ 2021*) and triply-deuterated (e.g. $CD_3OH$, *Parise+2002*).
- Deuterium fractionation can be used a clock to trace molecules to the time and environment of their formation.
- $D_2/D$ ratios observed are higher than $D/H$ => multiple deuteration is more favourable, as confirmed by lab.
- From $D/H$ and $D_2/D$ column density ratios in 67P/Churyumov–Gerasimenko, singly deuterated methanol ($CH_2DOH$) is constrained to happen via the $H-D$ substitution of the main isotopologue, while, $CHD_2OH$ is deduced to form from the hydrogenation of doubly deuterated formaldehyde ($D_2CO$) (*Drozdovskaya et al. 2021*).

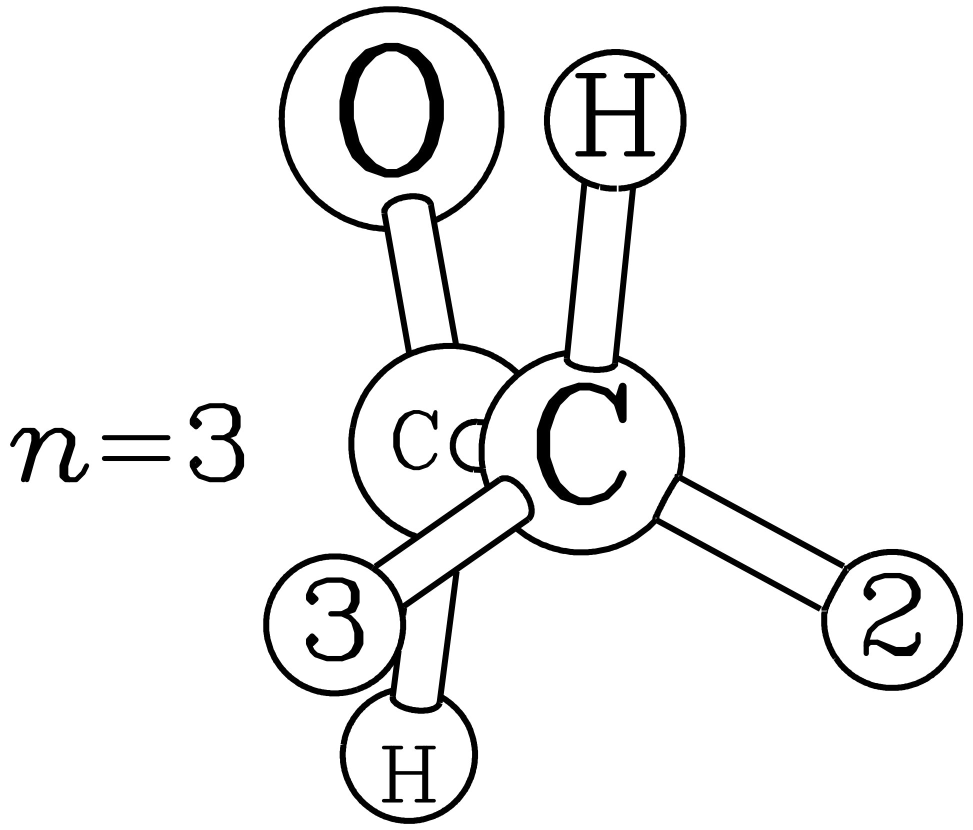
# DEUTERATED ACETALDEHYDE – $CHD_2CHO$

## Judit Ferrer PhD Student

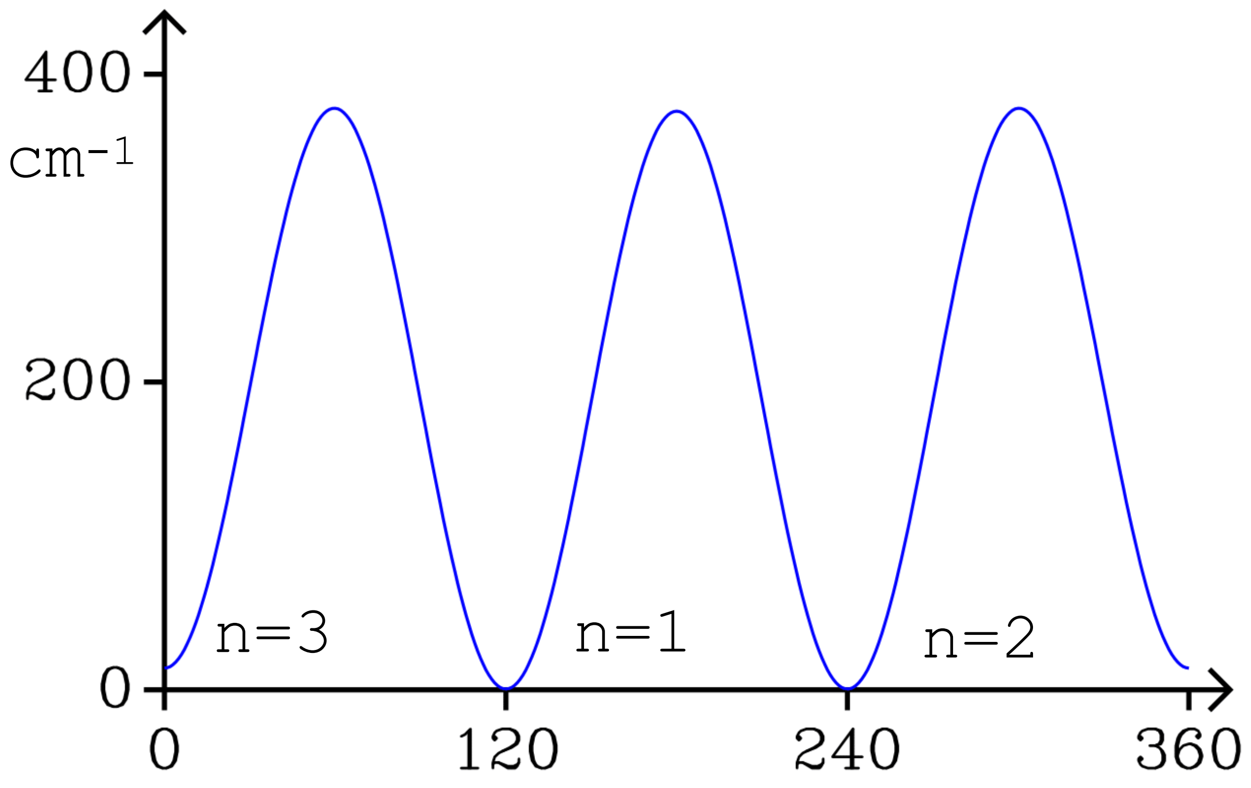
- Acetaldehyde one of the most abundant iCOMs in ISM.
- Singly-deuterated, both in the methyl ($CH_2DCHO$) and aldehyde group ($CH_3CDO$), both detected in ISM.
- Doubly-deuterated never detected in ISM and only one low frequency (8-40 GHz) lab study.

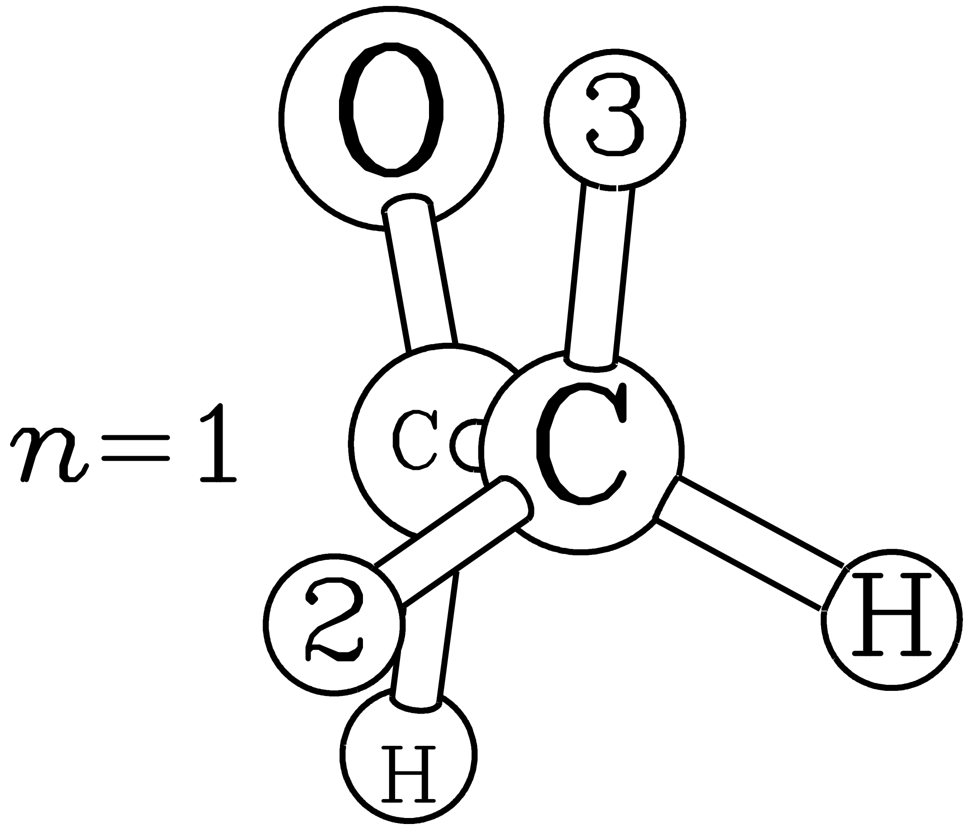
- New spectroscopy in 82-450 GHz in our labs, combining different techniques.
- More than 700 new rotational lines detected, both for the *In* and *Out* symmetries.
- Data analysis complex and specific Hamiltonian used to fit lab data.

# DEUTERATED ACETALDEHYDE – $CHD_2CHO$

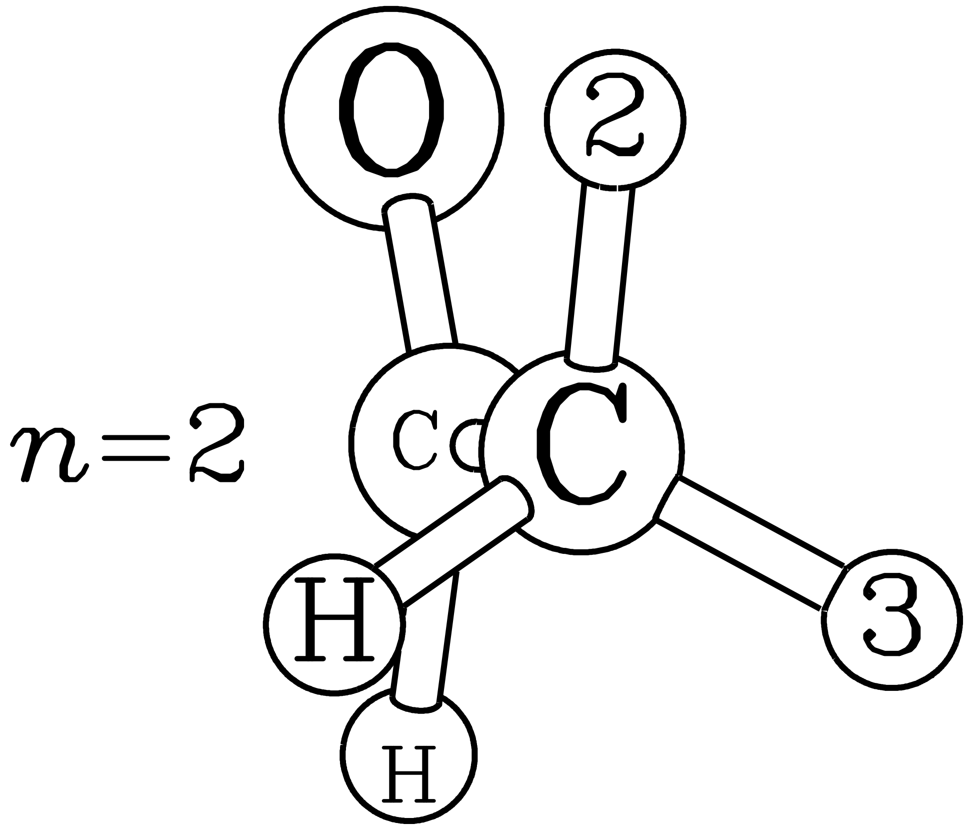


$\alpha_{\mathrm{eq}}^{(3)}=0°$ In

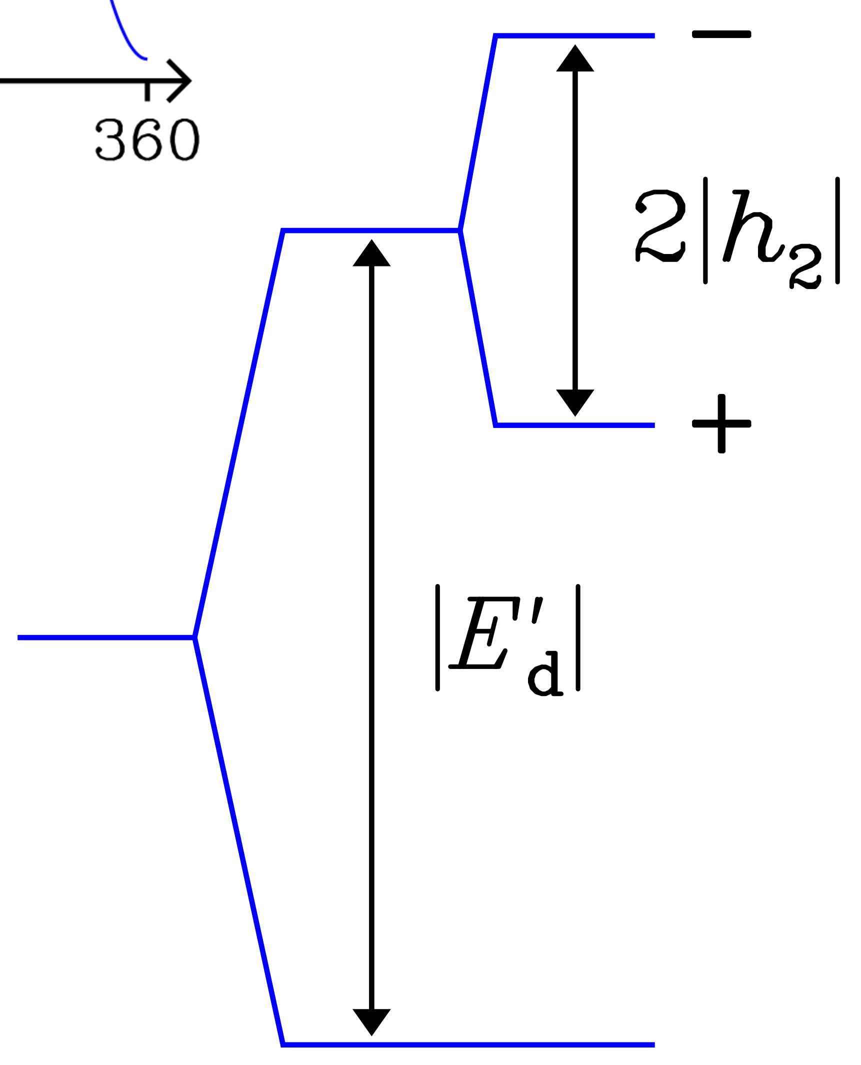




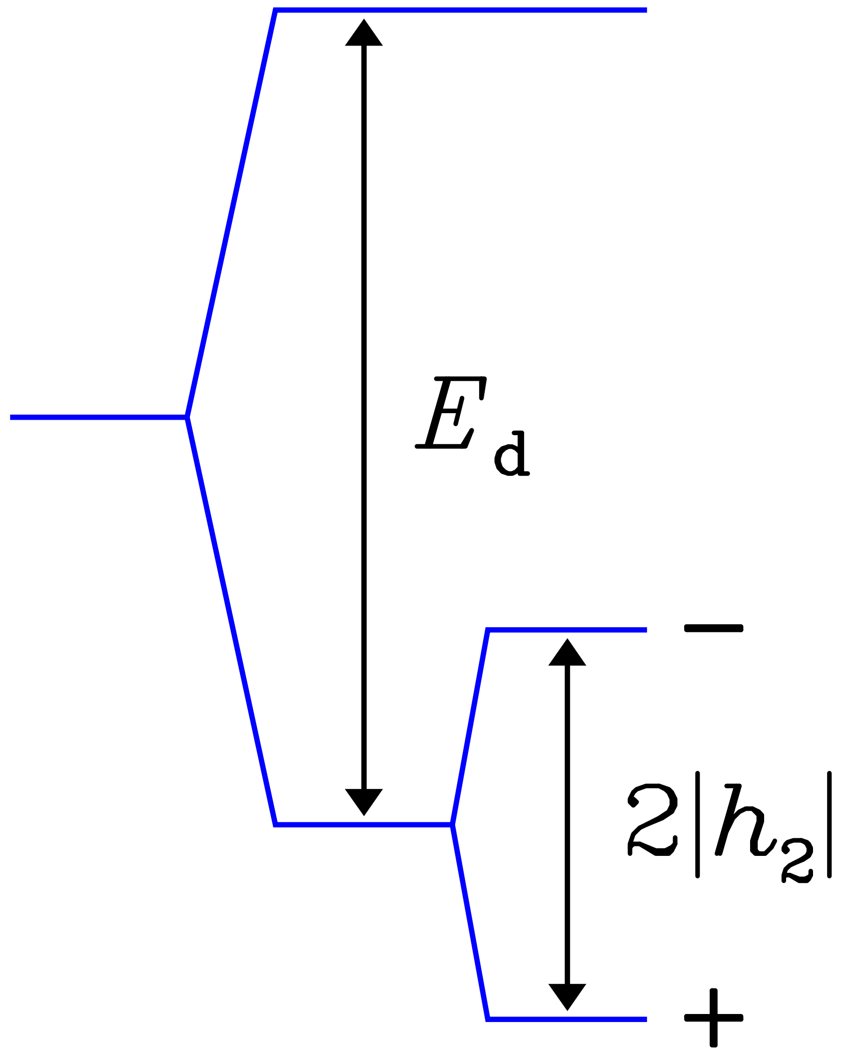
$\alpha_{\mathrm{eq}}^{(1)}=120°$ Out



$\alpha_{\mathrm{eq}}^{(2)}=240°$ Out



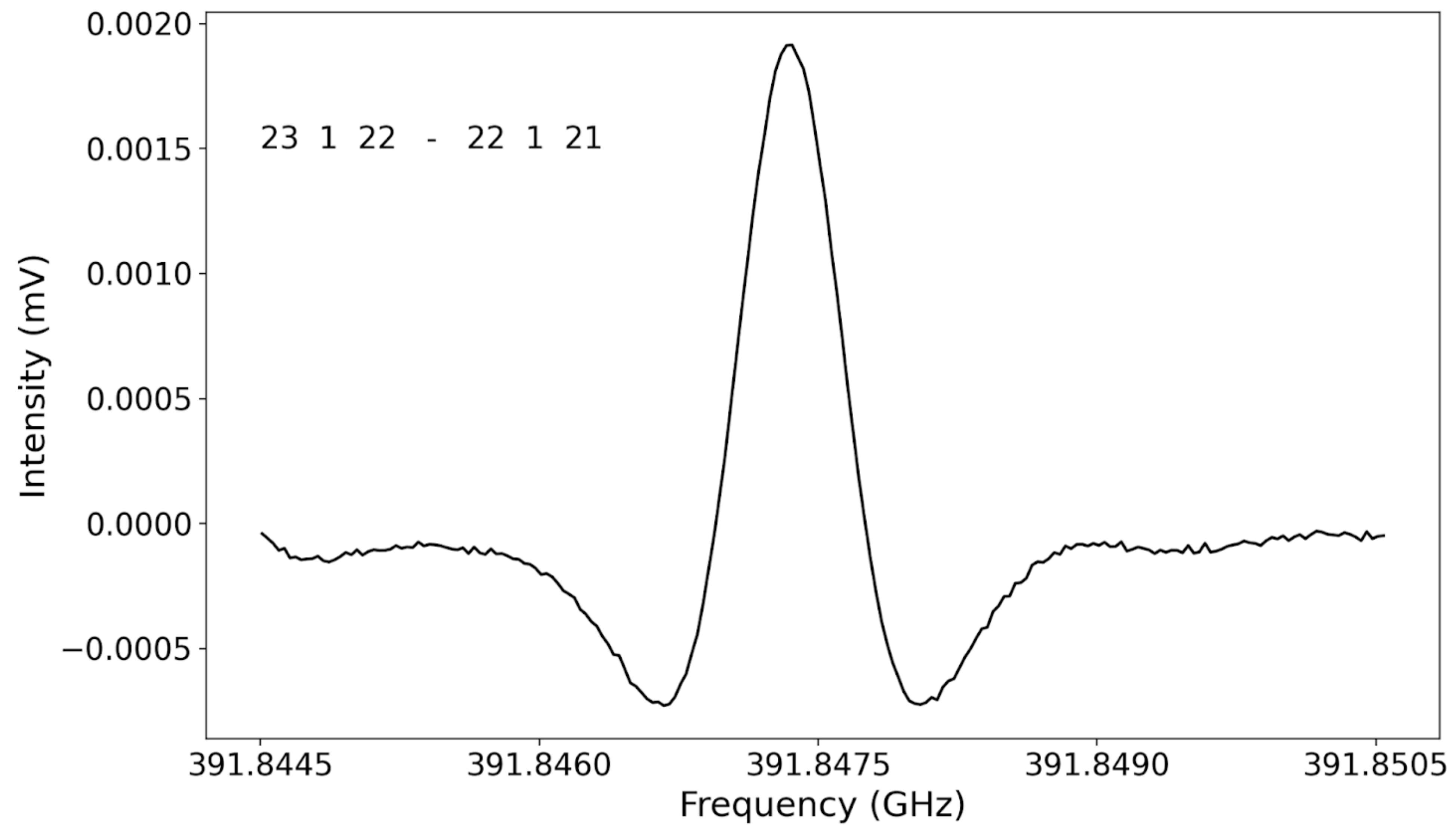
$CH_2DCOH$

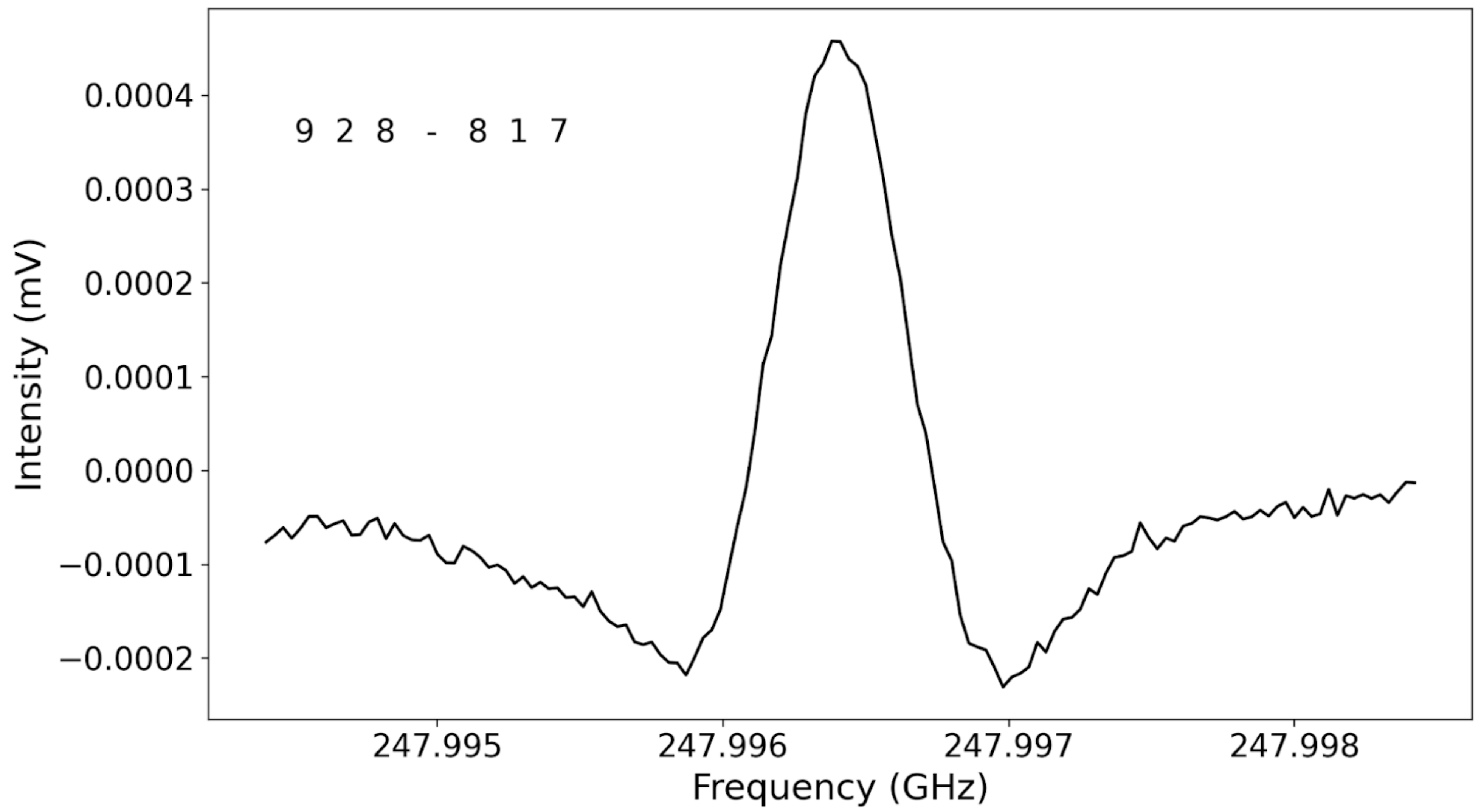


$CHD_2COH$

*Ferrer+ submitted*

# DEUTERATED ACETALDEHYDE — LAB.





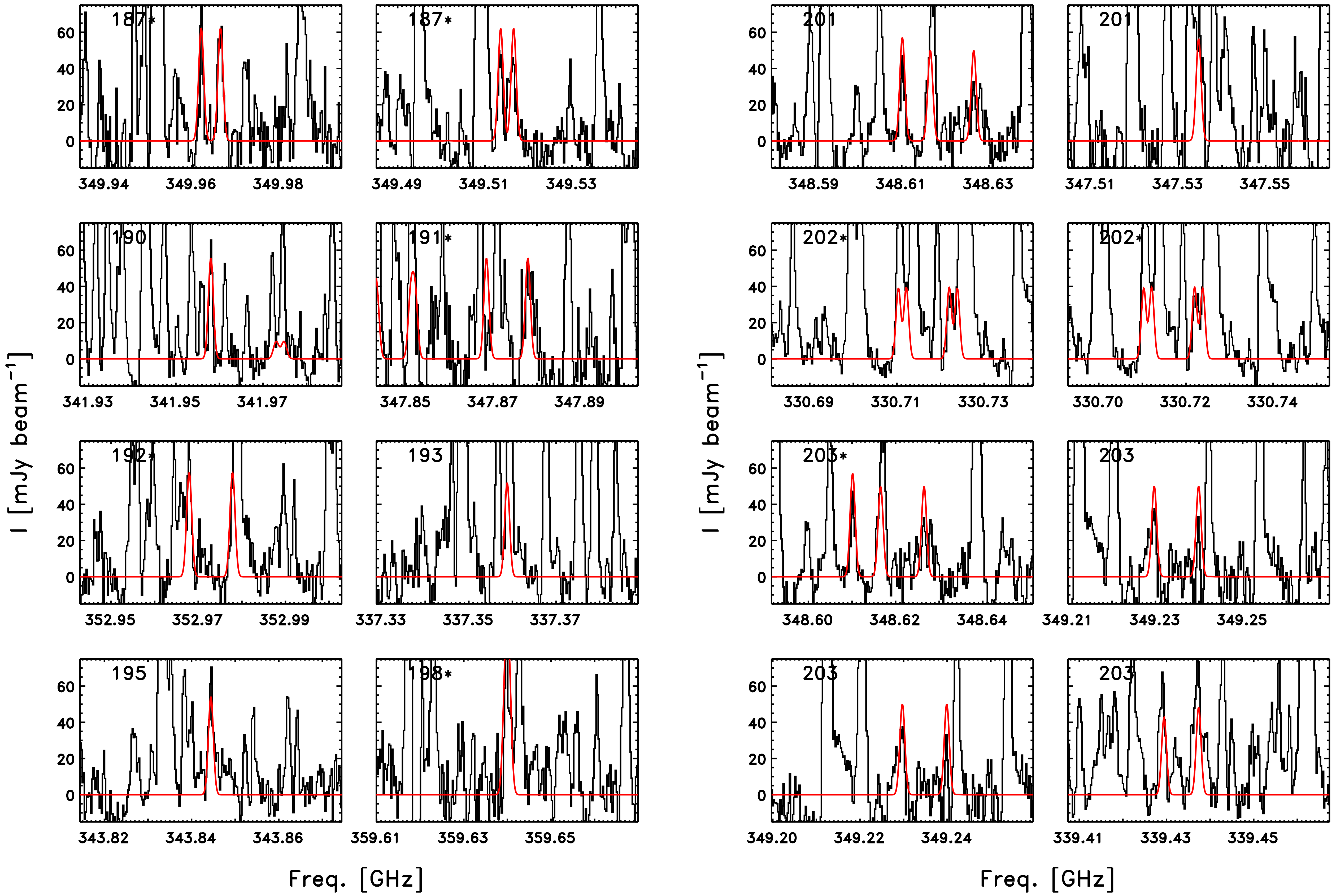
| Parameter[a] | | Value | Parameter[a] | | Value |
|---|---|---|---|---|---|
| $\theta_2$ | | 4.864(12) | $H_{KKJ}$ | $\times 10^4$ | −0.514(21) |
| $\phi_2$ | | 60.828 7(36) | $H_{JKK}$ | $\times 10^5$ | −0.112(81) |
| $\theta_{2j}$ | $\times 10^3$ | 0.293(34) | $H_J$ | $\times 10^8$ | 0.26(25) |
| $\phi_{2j}$ | $\times 10^3$ | 0.187(40) | $h_K$ | $\times 10^3$ | −0.434(63) |
| $h_2$ | | −91.824(22) | $h_{KJ}$ | $\times 10^5$ | −0.396(39) |
| $h_{2k}$ | | −0.116 7(23) | $h_J$ | $\times 10^9$ | 0.7(13) |
| $h_{2j}$ | $\times 10^2$ | 0.949(81) | | | |
| $f_2$ | $\times 10$ | 0.180 7(72) | $A^{\mathrm{Out}}$ | $\times 10^{-3}$ | 45.141 639 0(39) |
| $s_{2xz}$ | $\times 10$ | −0.194(11) | $B^{\mathrm{Out}}$ | $\times 10^{-3}$ | 9.176 200 44(90) |
| $h_{2kk}$ | $\times 10^3$ | −0.298(20) | $C^{\mathrm{Out}}$ | $\times 10^{-3}$ | 8.187 146 15(81) |
| $h_{2kj}$ | $\times 10^3$ | 0.130 7(81) | $\Delta_K$ | | 0.353 84(15) |
| $h_{2jj}$ | $\times 10^5$ | −0.277(81) | $\Delta_{KJ}$ | $\times 10$ | 0.168 73(14) |
| | | | $\Delta_J$ | $\times 10^2$ | 0.666 13(20) |
| $A^{\mathrm{In}}$ | $\times 10^{-3}$ | 47.940 411 5(57) | $\delta_K$ | $\times 10$ | −0.902 4(17) |
| $B^{\mathrm{In}}$ | $\times 10^{-3}$ | 8.778 690 6(14) | $\delta_J$ | $\times 10^3$ | 0.853 2(12) |
| $C^{\mathrm{In}}$ | $\times 10^{-3}$ | 8.175 064 5(13) | $H_{KKJ}$ | $\times 10^4$ | −0.238 0(90) |
| $\Delta_K$ | | 0.292 10(24) | $H_{JKK}$ | $\times 10^6$ | −0.31(29) |
| $\Delta_{KJ}$ | $\times 10$ | 0.778 46(42) | $H_J$ | $\times 10^8$ | 0.70(22) |
| $\Delta_J$ | $\times 10^2$ | 0.517 80(26) | $h_K$ | $\times 10^5$ | −0.3 174(13) |
| $\delta_K$ | | −0.353 56(51) | $h_{KJ}$ | $\times 10^5$ | −0.113 (21) |
| $\delta_J$ | $\times 10^3$ | 0.592 2(14) | $h_J$ | $\times 10^8$ | 0.16(12) |

[a] Parameters are in MHz except for the angles $\theta_2, \phi_2$ and **their** distortion constants which are in degrees. Uncertainties are given in parentheses in the same units as the last quoted digit.

*Ferrer+ submitted*

# DEUTERATED ACETALDEHYDE — ASTRO

- New catalogue with ~50 kHz uncertainty at 1mm (~ 300 GHz).
- 48 transitions identified in the IRAS16293-2422 protostellar system.
- $D_2/D$ ~ 0.2
- Similar to methyl formate, diethyl ether, and methanol.
- Common formation environment with enhanced deuterium fractionation.



*Ferrer+ submitted*

# TAKE HOME MESSAGES — II

- Higher spectral resolution and frequency coverage make spectroscopy more complex.
- Theory — Laboratory — Observations is key for our understanding of ISM.

- How to build your catalogue from laboratory data? Tutorial this afternoon.
- Some experimental examples on sulphur species on Thursday.