SUBMILLIMETER-WAVE SPECTROSCOPY OF NITROGEN CONTAINING MOLECULES OF ASTROPHYSIC INTEREST

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Almost 30 nitrile molecules, which contain the cyano group (C≡N), have been detected in the (ISM) so far.

Except these two species, no molecules with two nitrogen detected.

Nitrogen chemistry is difficult and widely unknown.
Ethyl-isocyanide (CH$_3$CH$_2$NC): The few isocyananides detected in the ISM are always isomers of the corresponding : HNC, CH$_3$NC, HCCNC

Di-cyanomethane (malonitrile-NC-CH$_2$-CN) and isocyanomethane: Following the first microwave study of a bis-isocyananide derivative diisocyanomethane (Motiyenko et al., A&A 2012, 544 A82)

Hydroxyacetoniitrile (HOCH$_2$CN): Compete with aminomethanol (NH$_2$CH$_2$OH), a glycine precursor, through the Strecker synthesis (Danger G. et al., ApJ 756, 11, 2012)

Acetyl isocyanate (CH$_3$CONCO)
- Isocyanic acid, HNCO, was among the very early molecules to be detected in space
Solid state sources spectrometer: 150 - 990 GHz

- Very compact
- Power: 50 µW - 5mW
- Broad band: Assignment easier with series, like in IR
- Full coverage with high resolution in 5 days
Ethyl-iscocyanide (CH$_3$CH$_2$NC)

- Isocyanides molecules are poorly studied mainly due to difficulties in synthesis and kinetic instability of many of them.

- Ethyl-iscocyanide (CH$_3$CH$_2$NC) is isomer of one of the most abundant Complex Organic Molecules. The study was limited to MW domain up to 40 GHz. (Kruger et al., Z. Naturforsch. 1992, A47, 1067), making the prediction inaccurate in the millimeter-submillimeter wave domain.
Ethyl-isocyanide: results

Relatively stable compound: the range 150-990 GHz was recorded.
Despite this new job, no detection in ORION...
dicyanomethane (malonitrile) and isocyanomethane

- No MW study about the cyano-isocyanomethane (CNCH$_2$CN).
- We decided also to reinvestigate the most stable isomer malonitrile for two reasons:
  - Study is limited to 240 GHz (Burie et al. 1982, J. Phys. 43, 1319)
  - Spin statistic we put in evidence in the diisocyanomethane study was not took into account.
Isocyanomethane: spectra

- The sample is unstable, it can explode on heating (if $t^\circ > -10^\circ$C). A flow was used, the optimal temperature of evaporation was found to be close to $-25^\circ$C.

- The dipole moment: $\mu_a = 0.2$ D, $\mu_b = 3.7$ D, $\mu_c = 0$

- Spectra is mainly Q branch series

- 110-180 GHz range

- 5-10 GHz windows located in the Q-branches regions from 200 to 640 GHz

- Malonitrile which is a stable and commercial sample: 150-660 GHz
Dicyanomethane (Malonitrile) : results

- As for di-isocyanomethane, spin statistic have an influence on the intensity of the lines
- This should be take into account in case of ISM detection

Motiyenko et al., A&A 2012, 544 A82
Hydroxyacetonitrile


- 3-hydroxy propionitrile \((\text{HOCH}_2\text{CH}_2\text{CN})\) recently investigate in the millimeter save domain (Braakman et al, 2010, JMS, 262, 100). In this paper: « Hydroxyacetonitrile \((\text{HOCH}_2\text{CN})\) would have been another natural target » (not commercial, high vapor pressure)

- Compete with aminomethanol \((\text{NH}_2\text{CH}_2\text{OH})\), a glycine precursor, through the Strecker synthesis (Danger G. et al., ApJ 756, 11, 2012)

- Its photochemistry leads to the formation of formylcyanide \((\text{CHO\text{CN}})\), ketenimine \((\text{CH}_2\text{CNH})\), formaldehyde \((\text{CH}_2\text{O})\), hydrogen cyanide \((\text{HCN})\), carbon monoxyde \((\text{CO})\) (Danger G. et al. A&A 549, A93, 2012)
Previous study

- IR work in solid Argon at 14-17 K (not the torsional motion) (Mielke et al, *J. Phys. Chem.* 1989, 93, 558-564)

  - 56 lines for both sub-states up to $J = 8$ and $K_a = 3$
  - the standard deviation of the fit is nearly 500kHz, but a good starting point for our analysis
  - Derived Energy difference between the torsional substates (no $\mu_c$ lines): 110 700 MHz same order of magnitude as our value!
  - Torsional equilibrium angles found from potential function analysis was 56° angles: *ab initio* value determined is 60°
Internal rotation of the hydroxyl group

« Relaxed » PES at the B3LYP/6-311++G(3df,2pd) level
Internal rotation of the hydroxyl group

- Tunneling between the two equivalent gauche configurations split each rotational levels.

\[
\Delta E = 112.7 \text{ GHz} = 3.76 \text{ cm}^{-1}
\]

\[v_t = 1\]

\[214 \text{ cm}^{-1}\]

\[g. s.\]
Analysis

- We used the same method as for Ethanetellurol (R. A. Motiyenko et al., JPC A, 114, 2794, 2010). Analysis was done considering coriolis interactions between the two substates. The Picket RAS formalism was used (H. M. Pickett, J. Chem. Phys., 56, 1715, 1972):

\[
H_{\text{RAS}} = \sum_{\nu=0}^{1} |\nu\rangle (E^\nu + H_R^\nu) \langle \nu | + \left[ |0\rangle \langle 1| + |1\rangle \langle 0| \right] H_I,
\]

- \( H_I \): Coriolis interaction terms \( F_{bc}, F_{ac} \)
- \( H_R \): Watson S-reduction in the \( I^r \) representation Hamiltoniann.
- The rotational dependence of the energy difference has been expressed as (D. Christen and H. S. P. Müller, Phys. Chem. Chem. Phys., 5, 3600, 2003):

\[
H_{\Delta} = E^* + E_J^* J^2 + E_K^* J_z^2 + E_2^* \left( J_+^2 + J_-^2 \right) + D_{ac}^* \left( J_a J_c + J_c J_a \right) + E_{JJ}^* J^4 + E_{JJ}^* J_z^2 \]
\[
H_{\Delta} = E_{KK}^* J_+^4 + E_{KK}^* J_-^4 + E_{2J}^* J^2 \left( J_+^2 + J_-^2 \right) + E_4^* \left( J_+^4 + J_-^4 \right) + \ldots
\]
Analysis

- First prediction from MW measurements with two separate states.
- Even for the $K_a=0$ lines, difficult to assign unambiguously the + substates lines in the low frequency range (up to 300 GHz)
- Surprisingly: at high frequency (from 400 to 650 GHz) for both substates the $K_a=0$ lines and $K_a=1$, $K_c=J$ are not so perturbed. This permits to fix rotational constants and distortional terms.
• Second step: global fit
  • Coriolis term was adjusted « by hand » with keeping $\Delta E$ constant
  • Assigning $\Delta V=\pm 1$ lines
Acetyl isocyanate

- cis and trans isomerism:
  - most molecules with a conjugated double-bond structure seem to prefer the trans conformations (acrolein and derivatives of butadiene...).
  - Even the more analogous vinyl isocyanate prefer the trans configuration (C. Kirby, H.W. Kroto JMS. 70 (1978) 216.)
  - However, for vinyl azide it has been shown by relative intensity measurements of microwave spectra that the cis form is the more stable
  - the cis form is the more stable conformer in the gas, but the trans form is the stable form in the solid (K.A. Krutules, et al., J. Mol. Struct. 293 (1993) 23.)

- Isocyanate functional group (-NCO) is highly reactive and many chemicals containing isocyanate groups were used for the synthezises of polyurethanes.
Previous studies

- MW spectra up to 40 GHz (B.M. Landsberg et al. J.C.S. Faraday, 76, 1208, 1980):
  - $J_{max}=23$ and $K_{a,max}=3$
  - Dipole moment (Stark measurements): $\mu_a=0.954\,\text{D}$ $\mu_b=1.48\,\text{D}$
  - 1st order internal rotation parameters determined

- MW spectra of CD$_3$C(O)NCO and $^{13}$CH$_3$C(O)NCO (Y. Uchida et al. J. Mol. Spectrosc. 256, 163, 2009)
  - Ab initio calculations
  - Molecular structure

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<tr>
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<th>$V_3$ in cm$^{-1}$</th>
<th>$\rho$</th>
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<tbody>
<tr>
<td>HCOOCH$_3$</td>
<td>373</td>
<td>0.08</td>
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<tr>
<td>CH$_3$(ONCO)</td>
<td>356</td>
<td>0.06</td>
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Similar case to methyl formate, should not be too difficult....
CH₃ internal Rotation

Methyl group is C₃ᵥ symmetry: 

\[ V(\alpha) = \frac{V_3^3}{2} (1 - \cos 3\alpha) + \frac{V_6^6}{2} (1 - \cos 6\alpha) + \ldots \]

- Due to tunnel effect, the transitions are split into two components: A and E
- The code used in these studies is « RAM36-code » from V. Ilyushin (Karkhov-Ukraine). The former name comes from the Toluene study (V. Ilyushin et al. J. Mol. Spectrosc 259, 26, 2010)
Experimental details

- The synthesis is well known: Acetyl isocyanate was prepared by the reaction of acetyl chloride with silver cyanate (Rodd’s Chemistry of Carbon Compounds (Elsevier, Amsterdam, 2nd edn, 1965), vol. I, part C, p. 360)

- The compound is relatively stable, could be stored in the fridge (-20°C) for months, but the spectra obtained have poor signal to noise ratio. We thought it was reactive with metal, it was recorded 3 times
  - Mai 2013: static mode in the inox cell
  - December 2013: flow mode in the inox cell
  - Mars 2014: flow mode with the pyrex cell
175-180 GHz spectra

Mai 2013: static mode in the inox cell

December 2013: flow mode in the inox cell

Mars 2014: flow mode with the pyrex cell

Not noise but huge number of lines!
Vibrational energy levels up to 250 cm\(^{-1}\)  
(from B3LYP/6-311G++(3df,2pd) anharm force field)

- 9 energy levels below 250 cm\(^{-1}\): floppy!
- In particular 3 levels at 83, 102 ans 117 cm\(^{-1}\), spectra difficult to assign
  - Dense spectra: relative intensity to g.s. are from 67 to 57%
  - Levels are interacting together and with g.s.
- In fact this « floppy » behaviour is logic if we are considering the very floppy case HNCO!
Assignement

- The most intense line don’t have great signal to noise ratio
- Intensity decrease fastly with $K_a$, close to prolate limit case
Conclusions

- These works will help potential detection with the ALMA powerfull facility.
- In case of detection: this could improve the knowledge about the ratio cyano/isocyano in the ISM and help the understanding of the unknown nitrogen chemistry.
- Hydroxyacetonitrile: Spectroscopy of one target molecule for exobiology is done up to 0.5 THz.
- Acethyl isocyanate:
  - Assignment is still in progress for higher $K_a$ values and up to 450 GHz.
  - Treatment of the bending and torsional modes could be possible in the near future: V.V. Illyushin, I. Kleiner and J. Hougen are coding the interactions...
Collaborations

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Aknowledgements

- Action sur Projets de l'INSU : "Physique et Chimie du Milieu Interstellaire"

- Centre National d'Etudes Spatiales (CNES)

- Ukrainian-French CNRS-PICS 6051

- ANR-13-BS05-0008-02 IMOLABS

And many thanks for your attention