C_3 – linear or bent at equilibrium?

- Very Long Ago (before 1984): C_3 generally believed to be linear.

  G. O. Sørensen, in: Topics in Current Chemistry, Vol. 82 (M. J. S. Dewar et al., eds.), Springer-Verlag, Heidelberg, 1979.

- 1984: *ab initio* calculation, CI-SD with TZP basis set: Barrier to linearity 21 cm^{-1}, $\angle(C\text{-}C\text{-}C)_e = 162°$

  W. P. Kraemer, P. R. Bunker, M. Yoshimine, *J. Mol. Spectrosc.* **107**, 191 (1984)

For comparison: C_3O_2 is believed to be bent

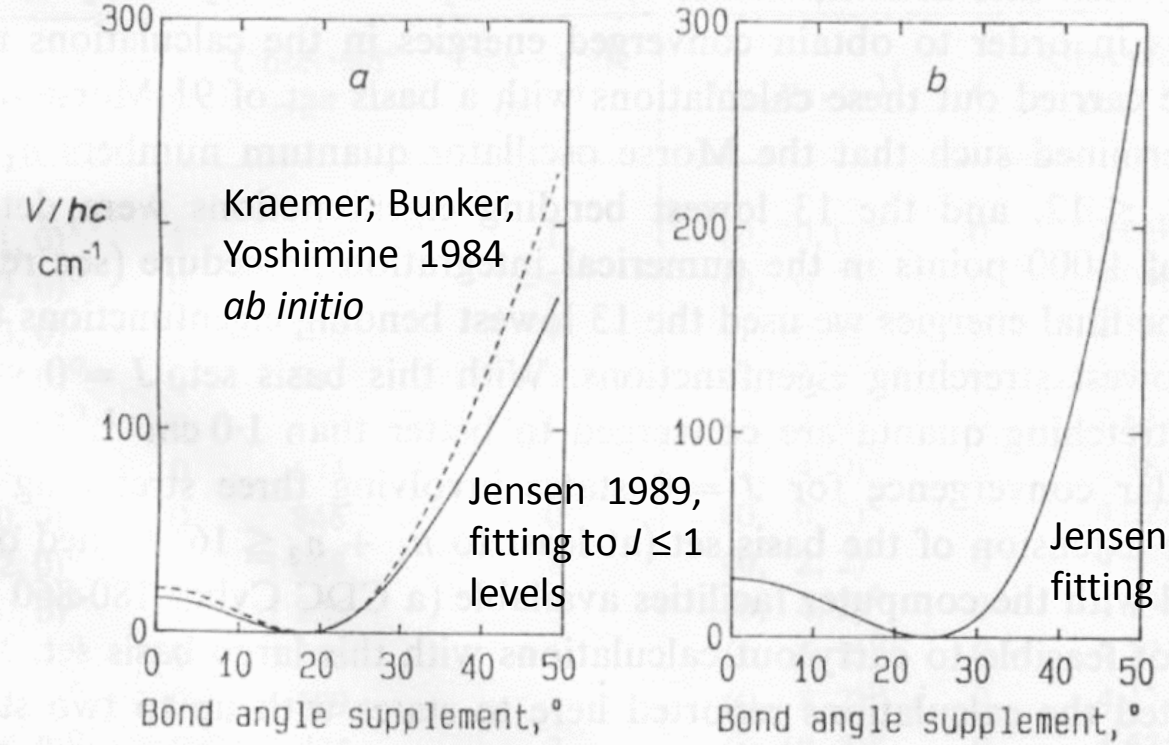
- 1981: ab initio calculation produces barrier to linearity for CCC bend

  R. L. Lozes, J. R. Sabin, J. Oddershede, *J. Mol. Spectrosc.* **86**, 357 (1981)

- 1986: Analysis of experimental spectra (semirigid bender) produces barrier to linearity of 28 cm^{-1} for the CCC chain.

  P. Jensen, J.W.C. Johns, *J. Mol. Spectrosc.* **118**, 248 (1986)

C_3 C_3 chain in C_3O_2



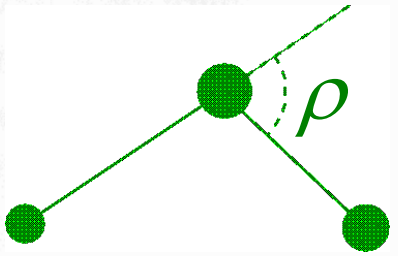


FIG. 1

Comparison of bending potential function for C_3 and for the CCC chain in C_3O_2. *a* Bending potential function for C_3 determined in the present work (solid curve), and the function computed *ab initio* by Kraemer *et al.*[2] (dashed curve); *b* the bending potential energy for the CCC chain in C_3O_2 determined by Jensen and Johns[5]

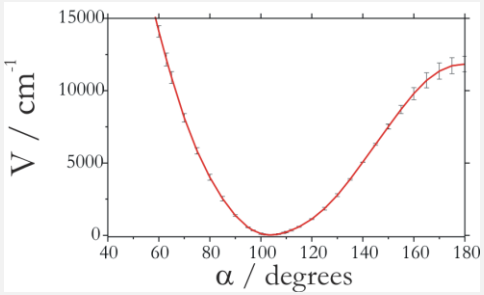
P. Jensen, *Collection of Czechoslovak Chemical Communications* **54**, 1209-1218 (1989).

2. W. P. Kraemer, P. R. Bunker, M. Yoshimine, *J. Mol. Spectrosc.* **107**, 191 (1984), *ab initio*

5. P. Jensen, J.W.C. Johns, *J. Mol. Spectrosc.* **118**, 248 (1986)

The general scheme of things

(at least in this lecture….)

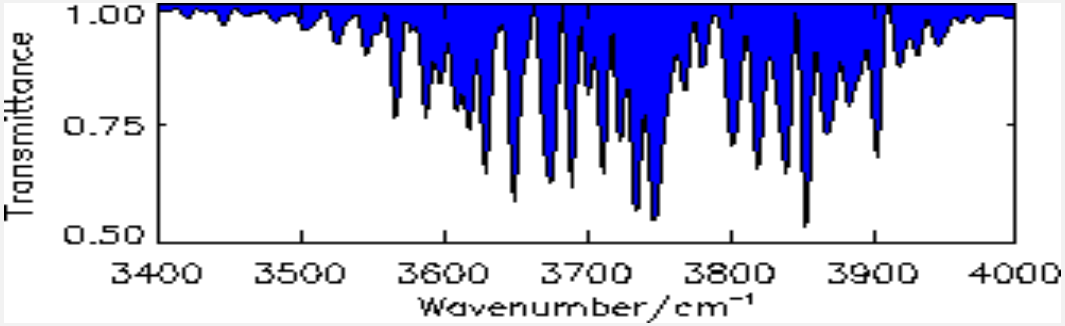


Potential energy surface
Dipole moment surface …

in general obtained from *ab initio* calculations

M
O
R
B
I
D

Simulated rotation-vibration spectra



Nuclear-motion program:

MORBID (Morse Oscillator Rigid Bender Internal Dynamics)

treats triatomic molecule in isolated electronic state

P. Jensen, *J. Mol. Spectrosc.* **128**, 478 (1988)

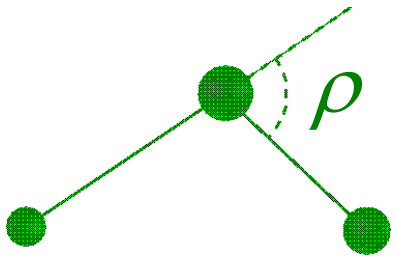
So is C_3 linear or bent at equilibrium?

New *ab initio* potential energy surface:

CASSCF, (13*s*8*p*6*d*4*f*) basis contracted to [5*s*4*p*2*d*1*f*], outermost *s* and *p* functions uncontracted. CASSCF active space included 12 electrons in 12 orbitals derived from the carbon 2*s* and 2*p* valence space (114000 configurations)

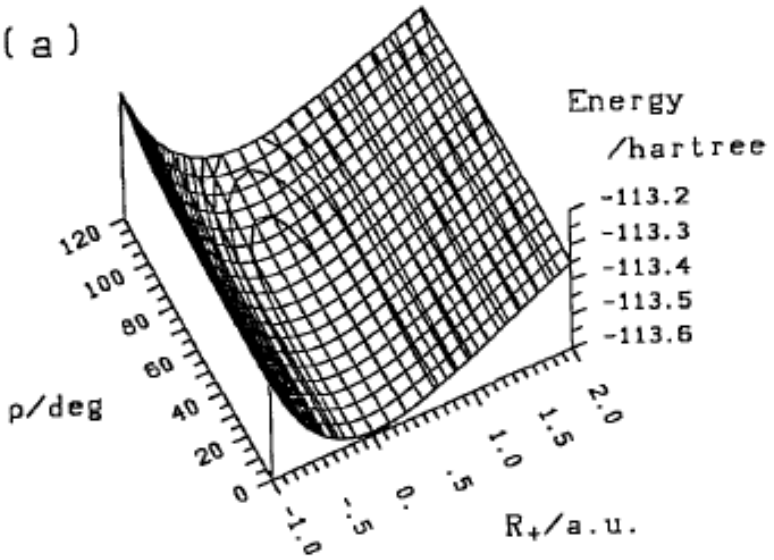
P. Jensen, C. M. Rohlfing, J. Almlöf, *J. Chem. Phys.* **97**, 3399 (1992)

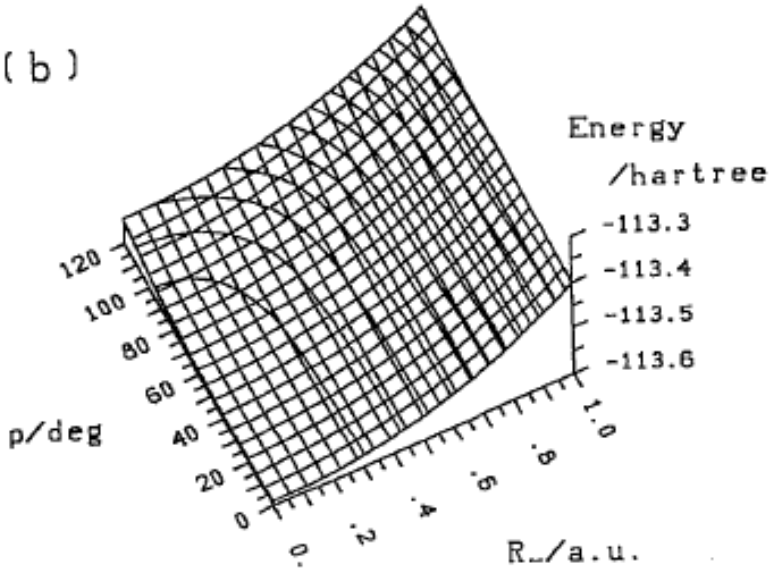
Barrier to linearity $H = 0$ cm^{-1}



$$R_+ = \Delta r_1 + \Delta r_3$$
$$= r_1 + r_3 - 2r_e$$

$$R_- = \Delta r_1 - \Delta r_3$$
$$= r_1 - r_3$$



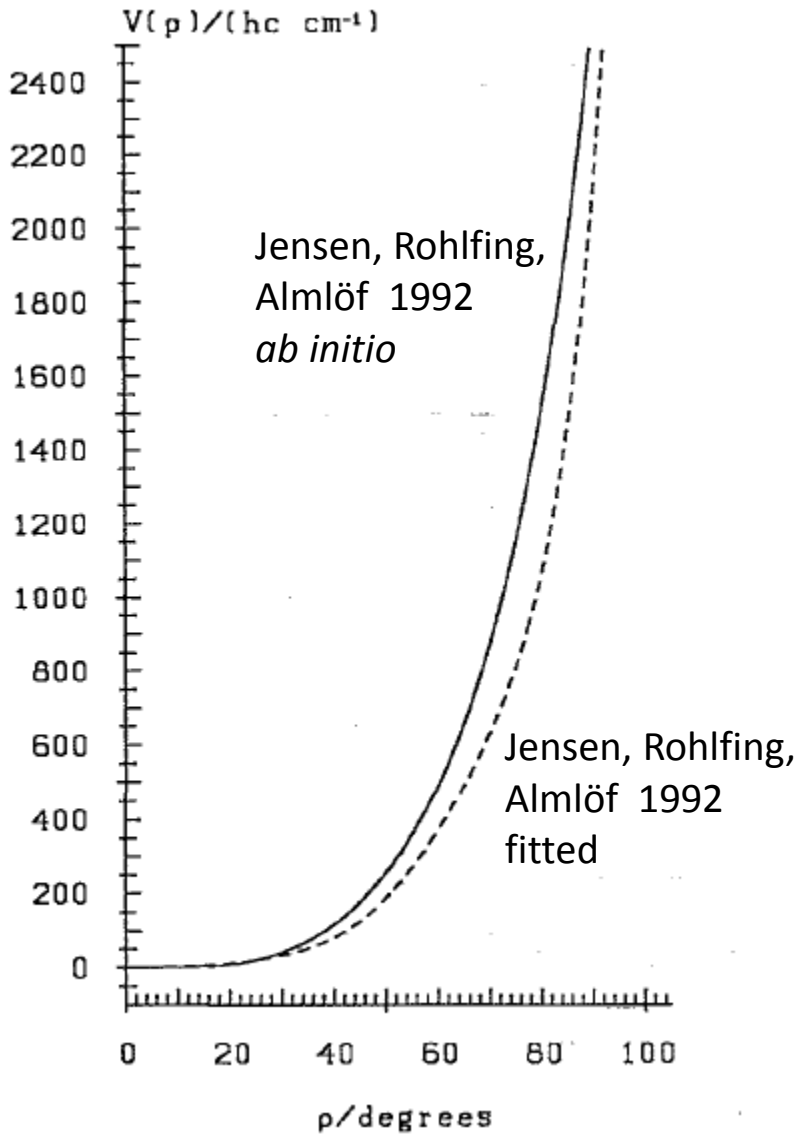


New fitted potential energy surface:

Input: Experimentally derived term value spacings below 5000 cm^{-1} involving $J \leq 2$

Standard deviation 8.2 cm^{-1}

P. Jensen, C. M. Rohlfing, J. Almlöf, *J. Chem. Phys.* **97**, 3399 (1992)



MORBID calculations of the fundamental term values:

Potential energy	Barrier *H*	ν_1	ν_2	ν_3
ab initio, Kraemer, Bunker, Yoshimine 1983	21 cm^{-1}	1278 cm^{-1}	68 cm^{-1}	2113 cm^{-1}
Fitting, Jensen 1989	16.5 cm^{-1}	1220 cm^{-1}	63 cm^{-1}	2037 cm^{-1}
ab initio, Jensen, Rohlfing, Almlöf 1992	0 cm^{-1}	1191.9 cm^{-1}	70.2 cm^{-1}	2007.3 cm^{-1}
Fitting, Jensen, Rohlfing, Almlöf 1992	0 cm^{-1}	1223.4 cm^{-1}	62.7 cm^{-1}	2039.9 cm^{-1}
Experiment		1226.6 cm^{-1}	63.416529 cm^{-1}	2040.0192 cm^{-1}

F. J. Northrup, T. J. Sears, *J. Op. Soc. Am. B* **7**, 1924 (1990)

C. A. Schmuttenmaer, R. C. Cohen, N. Pugliano, J. R. Heath, A. L. Cooksy, K. L. Busarow, R. J. Saykally, *Science* **249**, 897 (1990)

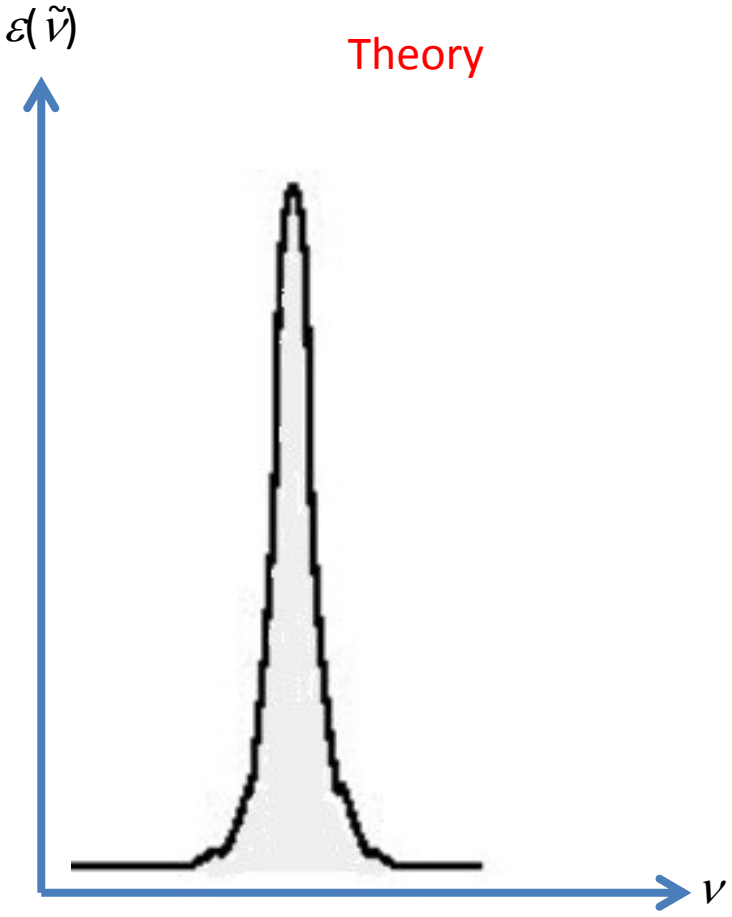
K. Kawaguchi, K. Matsumura, H. Kanamori, E. Hirota, *J. Chem. Phys.* **91**, 1953 (1989)

Energy spacings $E(v_1, v_2^{0e}, v_3 = 0; J = 2) - E(v_1, v_2^{2e}, v_3 = 0; J = 2)$ for $\tilde{X}\,^1\Sigma_g^+$ $^{12}C_3$ (in cm^{-1}).

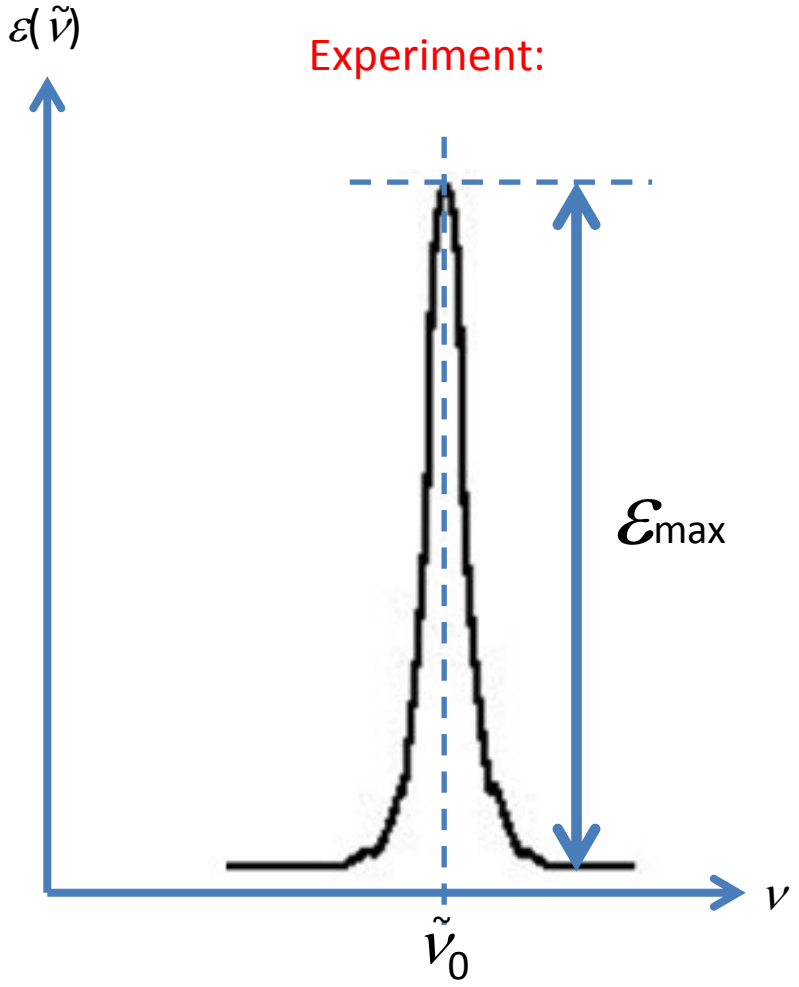
v_2	Obs.[a]	H=16.5 cm^{-1}	H=0 cm^{-1}
States with $v_1 = 0$			
2	1.56	5.71	2.73
4	1.25	3.96	1.65
6	1.05	3.88	0.94
8	0.86	3.43	0.75
10	0.73	3.05	0.93
12	0.68	2.71	1.20
14	0.61	3.14	2.12
16	0.55	3.05	2.40
States with $v_1 = 1$			
2	− 2.26	2.74	− 3.77
4	− 1.74	0.11	− 1.85
6	− 1.23	6.34[d]	0.65[d]
8	− 0.97	0.17	− 2.27

Conclusion: Barrier H = 0 cm^{-1}

Line shape functions (LSF):



Theory



Experiment:

$$I(\mathrm{f} \leftarrow \mathrm{i}) = \int_{\text{Line}} \varepsilon(\tilde{\nu})\, \mathrm{d}\tilde{\nu} = \frac{8\pi^3 N_A \tilde{\nu}_{\mathrm{if}}}{(4\pi\varepsilon_0)3hc} \frac{\mathrm{e}^{-E_\mathrm{i}/kT}}{Q} [1 - \exp(-hc\tilde{\nu}_{\mathrm{if}}/kT)] S(\mathrm{f} \leftarrow \mathrm{i})$$

$$S(\mathrm{f} \leftarrow \mathrm{i}) = g_{\mathrm{ns}} \sum_{m_\mathrm{f}, m_\mathrm{i}} \sum_{A=X,Y,Z} |\langle \Phi_{\mathrm{rv}}^{(\mathrm{f})} \Phi_{\mathrm{elec}}^{(\mathrm{f})} | \mu_A | \Phi_{\mathrm{elec}}^{(\mathrm{i})} \Phi_{\mathrm{rv}}^{(\mathrm{i})} \rangle|^2$$

$\varepsilon(\tilde{\nu}_0 + \Delta\tilde{\nu}) = I(f \leftarrow \mathrm{i}) \times \mathrm{LSF}(\Delta\tilde{\nu})$

$\varepsilon_{max} = I(f \leftarrow \mathrm{i}) \times \mathrm{LSF}(0)$

Intensities

- 1984: *ab initio* calculation, $\varepsilon_{max}(\nu_3) \approx 20\text{-}30 \times \varepsilon_{max}(\nu_2)$

  W. P. Kraemer, P. R. Bunker, M. Yoshimine, *J. Mol. Spectrosc.* **107**, 191 (1984)

- 1990: Experimental observation: $\varepsilon_{max}(\nu_3) \approx \varepsilon_{max}(\nu_2)$

  C. A. Schmuttenmaer, R. C. Cohen, N. Pugliano, J. R. Heath, A. L. Cooksy, K. L. Busarow, R. J. Saykally, *Science* **249**, 897 (1990)

Intensities

- 1992: *ab initio* calculation of the dipole moment function + experimental information (J. R. Heath) T_{rot} = 10 K, T_{vib} = 50 K, Gaussian LS functions with FWHH = 6 MHz for ν_2 and 90 MHz for ν_3

P. Jensen, C. M. Rohlfing, J. Almlöf, *J. Chem. Phys.* **97**, 3399 (1992)

- $\varepsilon_{max}(\nu_3) \approx 2\varepsilon_{max}(\nu_2)$

Considered to be within the error limits of the experimental determination (J.R. Heath)

What now?

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Herschel/HIFI: first science highlights

Astronomy & Astrophysics
Special feature

LETTER TO THE EDITOR

Excitation and abundance of C_3 in star forming cores

Herschel/HIFI⋆ observations of the sight-lines to W31C and W49N⋆⋆

B. Mookerjea[1], T. Giesen[2], J. Stutzki[2], J. Cernicharo[3], J. R. Goicoechea[3], M. De Luca[4], T. A. Bell[5], H. Gupta[6], M. Gerin[4], C. M. Persson[7], P. Sonnentrucker[9], Z. Makai[2], J. Black[7], F. Boulanger[10], A. Coutens[13], E. Dartois[10], P. Encrenaz[4], E. Falgarone[4], T. Geballe[14], B. Godard[4], P. F. Goldsmith[6], C. Gry[11], P. Hennebelle[4], E. Herbst[8], P. Hily-Blant[12], C. Joblin[13], M. Kaźmierczak[17], R. Kołos[16], J. Krełowski[17], D. C. Lis[5], J. Martin-Pintado[3], K. M. Menten[15], R. Monje[5], J. C. Pearson[6], M. Perault[4], T. G. Phillips[5], R. Plume[18], M. Salez[4], S. Schlemmer[2], M. Schmidt[19], D. Teyssier[20], C. Vastel[13], S. Yu[4], P. Dieleman[23], R. Güsten[15], C. E. Honingh[2], P. Morris[21], P. Roelfsema[23], R. Schieder[2], A. G. G. M. Tielens[22], and J. Zmuidzinas[5]

(Affiliations are available on page 5 of the online edition)

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ABSTRACT

We present spectrally resolved observations of triatomic carbon (C_3) in several ro-vibrational transitions between the vibrational ground state and the low-energy ν_2 bending mode at frequencies between 1654–1897 GHz along the sight-lines to the submillimeter continuum sources W31C and W49N, using *Herschel*'s HIFI instrument. We detect C_3 in absorption arising from the warm envelope surrounding the hot core, as indicated by the velocity peak position and shape of the line profile. The sensitivity does not allow to detect C_3 absorption due to diffuse foreground clouds. From the column densities of the rotational levels in the vibrational ground state probed by the absorption we derive a rotation temperature ($T_{\rm rot}$) of ~50–70 K, which is a good measure of the kinetic temperature of the absorbing gas, as radiative transitions within the vibrational ground state are forbidden. It is also in good agreement with the dust temperatures for W31C and W49N. Applying the partition function correction based on the derived $T_{\rm rot}$, we get column densities $N(C_3) \sim 7–9 \times 10^{14}$ cm^{-2} and abundance $x(C_3) \sim 10^{-8}$ with respect to H_2. For W31C, using a radiative transfer model including far-infrared pumping by the dust continuum and a temperature gradient within the source along the line of sight we find that a model with $x(C_3) = 10^{-8}$, $T_{\rm kin} = 30–50$ K, $N(C_3) = 1.5 \times 10^{15}$ cm^{-2} fits the observations reasonably well and provides parameters in very good agreement with the simple excitation analysis.

Key words. ISM: lines and bands – ISM: molecules – radiative transfer – ISM: individual objects: W49N – ISM: individual objects: W31C

This paper uses *ab initio* intensity data from P. Jensen, C. M. Rohlfing, J. Almlöf, *J. Chem. Phys.* **97**, 3399 (1992)

But these data are 20 years old – maybe update and probable improvement are due!