

Dipole Moments of Linear Molecules: A Computational Molecular Spectroscopy Study

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Linear molecule:

- Equilibrium structure is linear by definition.
- What about the *average structure*?
 - **We say it is bent.**
 - But many spectroscopists disagree!

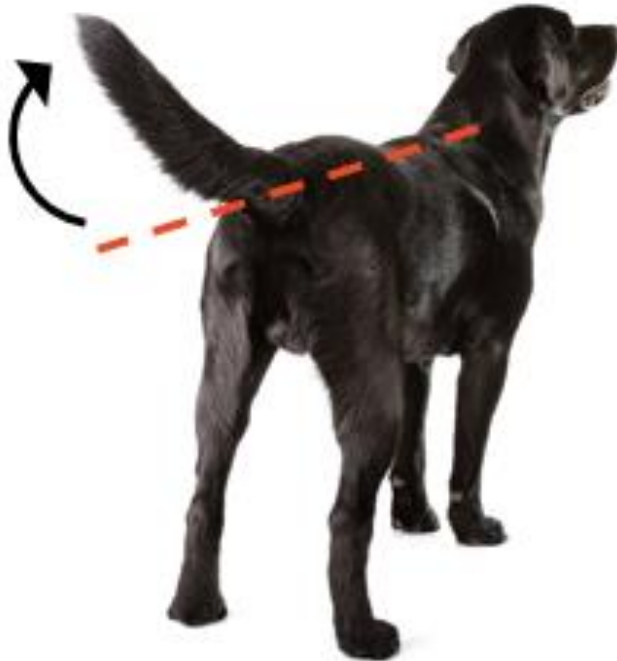
Linear molecule:

- Example of protest:

“... the bending motion is like a dog wagging its tail. Half of the time the tail is left, half of the time it is right, and on the average it is in the middle, neither left nor right.”

Renowned experimental spectroscopist,
private communication, 2017

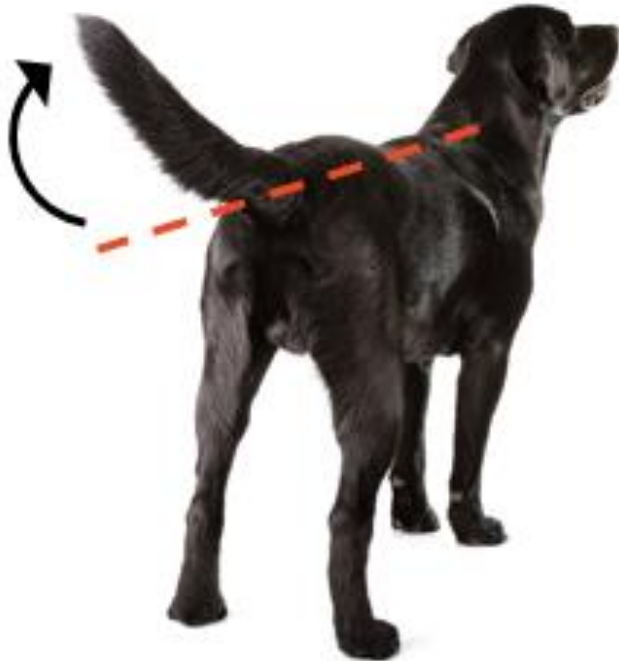
„Left-tail“



„Right-tail“

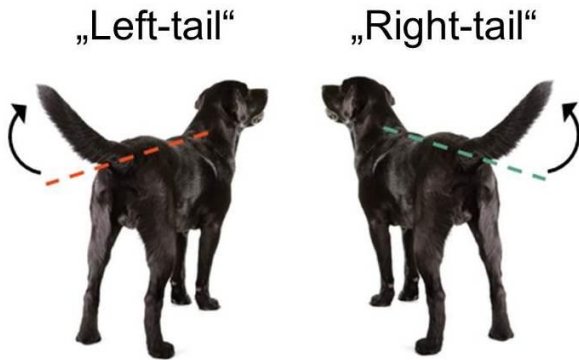


„Left-tail“

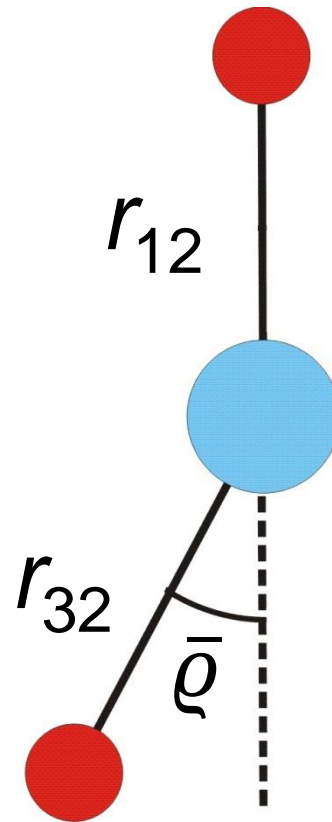


„Left-tail“

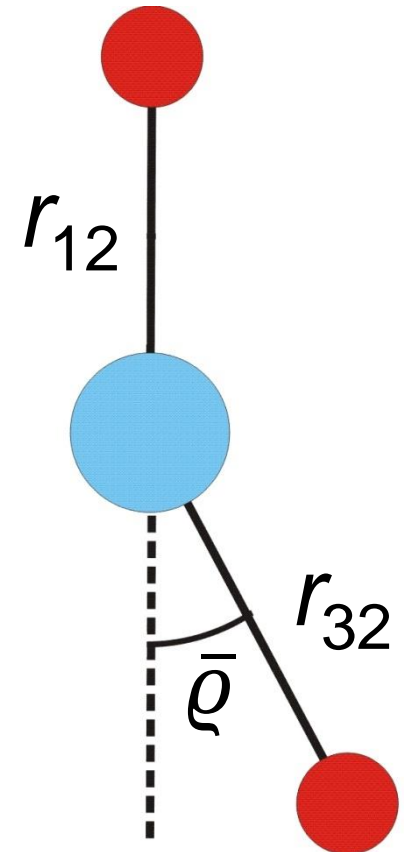




„Left-tail“



„Right-tail“



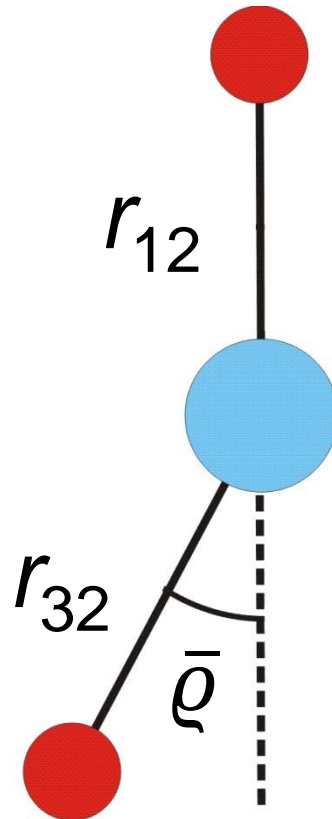
„Left-tail“



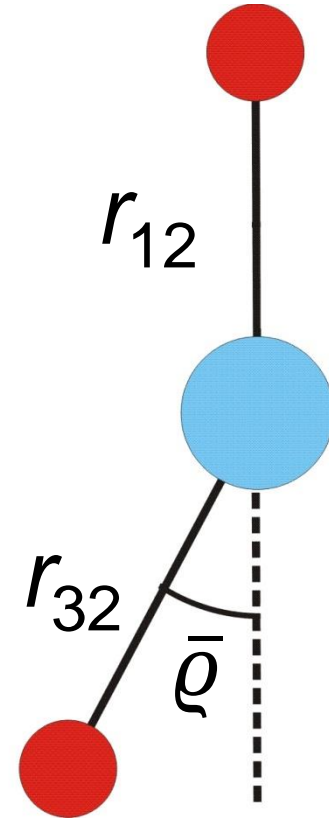
„Left-tail“



„Left-tail“



„Left-tail“



„Left-tail“
and „right-tail“
have
the same
structure!

Next question:

“If you say that CO₂ has a bent average structure, does it mean that it has a permanent dipole moment and a rotational spectrum? “

Anonymous reviewer,
private communication, 2018

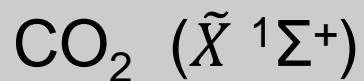
We calculate dipole moments:

Dipole moment in the **molecule-fixed principal axis system abc** .

μ_e : at equilibrium structure

$\langle \mu \rangle$: ro-vibronic average over DVR3D
wavefunction

$\langle \mu^{\text{ave}} \rangle$: calculated for the ro-vibrationally
averaged structure.



3D PES: mc-CCSD(T)/[aug-cc-pCVQZ (C, O)]

Geometry:

$r_e(\text{C-O}) = 1.1603 \text{ \AA}$, $\angle_e(\text{O-C-O}) = 180.0^\circ \rightarrow$ linear molecule ($D_{\infty h}$).

$r_0(\text{C-O}) = 1.1652 \text{ \AA}$, $\angle_0(\text{O-C-O}) = 173.3^\circ \rightarrow$ bent structure

Mulliken charge at aug-cc-CVTZ level of theory:

$$\begin{array}{ccc} \text{O} & \text{C} & \text{O} \\ \hline -0.31 e & 0.62 e & -0.31 e \end{array}$$

Accuracy of the 3D PES

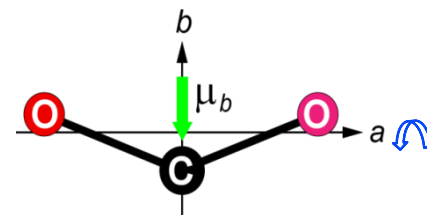
B_0 ($^{16}\text{O}^{12}\text{C}^{16}\text{O}$): 0.390218966(203) cm⁻¹ (Exp. Y.-C Guan et al)

0.39002 cm⁻¹ (DVR3D term value spacing)

Error -0.05%

Expectation values $\langle \mu \rangle^a$ for CO₂ (molecule-fixed axes)

$(v_1, v_2^{\ell_2}, v_3)$	ν/cm^{-1}	$\langle \mu_a \rangle / \text{D}$	$\langle \mu_b \rangle / \text{D}$	$\langle \mu_c \rangle^b / \text{D}$	$\langle \mu_{\text{tot}} \rangle / \text{D}$
$^{16}\text{O}^{12}\text{C}^{16}\text{O}$					
μ_e		0	0.000	0	0.0
$(0, 0^0, 0)$	0	0	-0.163	0	0.163
$(0, 1^{1e, f}, 0)$	670	0	-0.241	0	0.241
$(0, 2^0, 0)$	1288	0	-0.224	0	0.224
$(0, 2^2, 0)$	1341	0	-0.300	0	0.300
$(0, 3^{1e, f}, 0)$	1938	0	-0.286	0	0.286
$(1, 0^0, 0)$	2350	0	-0.163	0	0.163
$(2, 0^0, 0)$	4670	0	-0.163	0	0.163
$(0, 0^0, 1)$	1391	0	-0.222	0	0.222
$(0, 0^0, 2)$	2805	0	-0.294	0	0.294



Using averaged geometry

$(0, 0^0, 0)$ state	$\langle \mu_a^{\text{ave}} \rangle / \text{D}$	$\langle \mu_b^{\text{ave}} \rangle / \text{D}$	$\langle \mu_c^{\text{ave}} \rangle^c / \text{D}$	$\langle \mu_{\text{tot}}^{\text{ave}} \rangle / \text{D}$
	0	-0.164	0	0.164

a) DVR3D b) No c -axis component for triatomic molecule.

In space-fixed coordinates, $\langle \mu_b \rangle$ produces zero average (rotation about a -axis).

→ In a Stark experiment, $\langle \mu \rangle_0 = 0$.

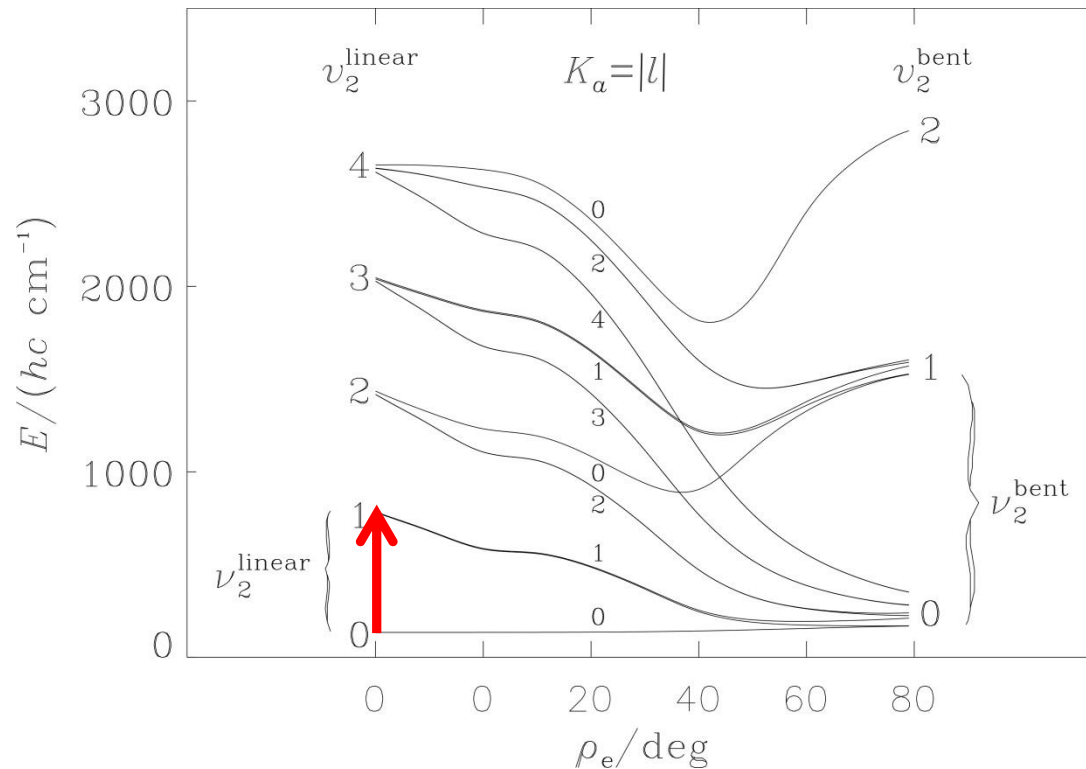
$\langle \mu_b \rangle \neq 0 \Rightarrow$ Rotational spectrum?

The b axis is the x axis ($a = z$) and $\langle \mu_b \rangle \neq 0$
produces allowed transitions with $\Delta K_a = \Delta l_2 =$
 ± 1

Where do we find such transitions for CO_2 ?

Correlation diagram linear/bent

Linear



Bent

$\Delta K_a = \Delta l_2 = \pm 1$ transitions are called the ν_2 band for CO_2

\Rightarrow No rotational transitions!

HCO⁺ ($\tilde{X}^1\Sigma^+$)

3D PES: core-valence CCSD(T)/[aV5Z (H), aCV5Z (C, O)]

Geometry:

$$r_e(\text{H-C}) = 1.0915 \text{ \AA}, r_e(\text{C-O}) = 1.1057 \text{ \AA}, \angle_e(\text{H-C-O}) = 180.0^\circ$$

→ linear molecule ($\mathbf{C}_{\infty v}$).

$$r_0(\text{H-C}) = 1.1121 \text{ \AA}, r_0(\text{C-O}) = 1.1103 \text{ \AA}, \angle_0(\text{H-C-O}) = 169.0^\circ$$

→ bent structure

Mulliken charge at aug-cc-CVTZ (RHF) level of theory:

H	C	O
0.828 e	0.206 e	-0.034 e

Accuracy of the 3D PES

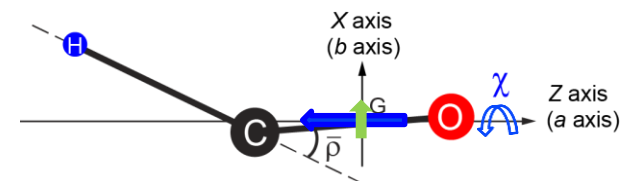
$$B_0(\text{H}^{12}\text{C}^{16}\text{O}^+): \quad 44594.42838(57) \text{ MHz} \quad (\text{Exp. C.F. Neese et al. (2013)})$$

$$\quad \quad \quad 44594.55 \text{ MHz} \quad (\text{DVR3D term value spacing})$$

Error -0.003%

Expectation values $\langle \mu \rangle^a$ of HCO⁺ (molecule-fixed coordinates)

$(v_1, v_2^{\ell_2}, v_3)$	ν/cm^{-1}	$\langle \mu_a \rangle / \text{D}$	$\langle \mu_b \rangle / \text{D}$	$\langle \mu_c \rangle^b / \text{D}$	$\langle \mu_{\text{tot}} \rangle / \text{D}$
H ¹² C ¹⁶ O ⁺					
μ_e		-3.897	0.0	0	3.897
(0,0 ⁰ ,0)	0	-3.933	0.117	0	3.935
(0,1 ^{1e,f} ,0)	832	-3.910	0.177	0	3.915
(0,2 ⁰ ,0)	1644	-3.887	0.209	0	3.895
(0,2 ² ,0)	1660	-3.887	0.255	0	3.894
(0,3 ^{1e,f} ,0)	2464	-3.865	0.249	0	3.875
(1,0 ⁰ ,0)	3088	-4.033	0.129	0	4.036
(2,0 ⁰ ,0)	6073	-4.133	0.140	0	4.136
(0,0 ⁰ ,1)	2186	-3.954	0.121	0	3.957
(0,0 ⁰ ,2)	4350	-3.976	0.125	0	3.978



Using averaged geometry

	$\langle \mu_a^{\text{ave}} \rangle / \text{D}$	$\langle \mu_b^{\text{ave}} \rangle / \text{D}$	$\langle \mu_c^{\text{ave}} \rangle^c / \text{D}$	$\langle \mu_{\text{tot}}^{\text{ave}} \rangle / \text{D}$
(0,0 ⁰ ,0) state	-3.935	0.116	0	3.937

a) DVR3D b) No c-axis component for triatomic molecule.

In space-fixed coordinates, $\langle \mu_b \rangle$ is averaged out to 0 (rotation about a-axis).

→ In a Stark experiment, $\langle \mu \rangle_0 = \langle \mu_a \rangle = 3.933 \text{ D}$. Exp. $\mu_0 = 3.921(31) \text{ D}$

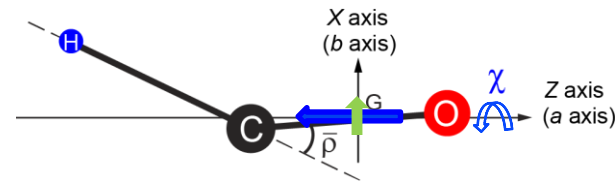
(B.J. Mount *et al.* (2012))

Summary

A linear triatomic molecule has a bent structure on ro-vibrational average. $\langle \bar{\rho} \rangle > 0$

$$\text{CO}_2 \text{ (A-B-A type)} \quad \langle \bar{\rho} \rangle_0 = 6.7^\circ$$

$$\text{HCO}^+ \text{ (A-B-C type)} \quad \langle \bar{\rho} \rangle_0 = 11.0^\circ$$



ABA symmetrical, linear triatomic molecules have $\langle \mu_b \rangle \neq 0$ but the transitions gaining intensity from this typically lie in the infrared and are called the ν_2 band, not the „rotational spectrum“

Only $\langle \mu_a \rangle$ -component is observed in Stark experiment.

→ A-B-A molecule $\langle \mu \rangle_0 = \langle \mu_a \rangle = 0$ in spite of $\langle \bar{\rho} \rangle > 0$
 A-B-C molecule $\langle \mu \rangle_0 = \langle \mu_a \rangle = \text{non-zero value.}$

For example,

$$\text{CO}_2 \quad \langle \mu \rangle_0 = \langle \mu_a \rangle = 0. \quad (\text{cf. } \langle \bar{\rho} \rangle_0 = 11.0^\circ)$$

$$\text{HCO}^+ \quad \langle \mu \rangle_0 = \langle \mu_a \rangle = 3.933 \text{ D.} \quad (\text{Exp. } \mu_0 = 3.921(31) \text{ D})$$

Comparison of three dipole moment values.

HCO⁺ case:

$\langle \mu \rangle_0$ over wavefunction	-3.933 D	} → Modest difference
$\langle \mu \rangle_0$ calc. for averaged structure	-3.935 D	
μ_e conventional practice	-3.897 D	

Exp. μ_0 3.921(31) D

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and, especially, to

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Thank you for your attention!
