

Empirical Potential Energy Surface and Bending Angle Probability Densities for the Electronic Ground State of HCO^+

Giulia Winterhoff^a, S. C. Galleguillos Kempf^a, Per Jensen^{a,*}, P. R. Bunker^b,
~~Umpei Nagashima^c, Tsuneo Hirano^d~~

Linear molecule:

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

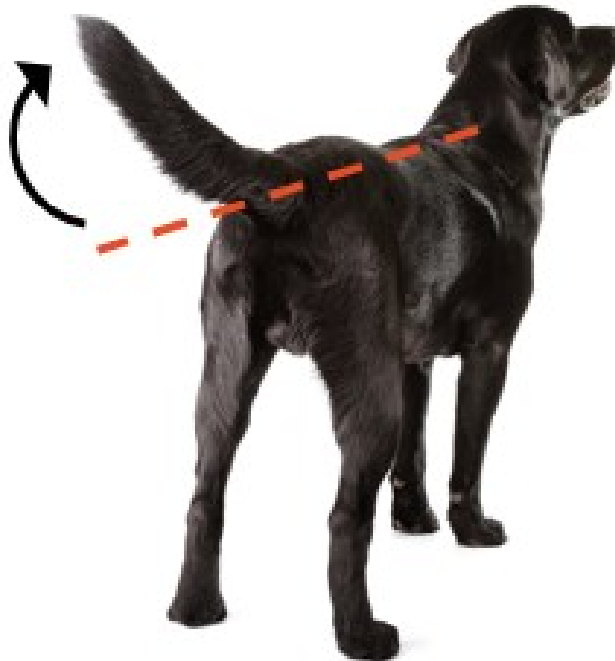
Linear molecule:

- Example of protest:

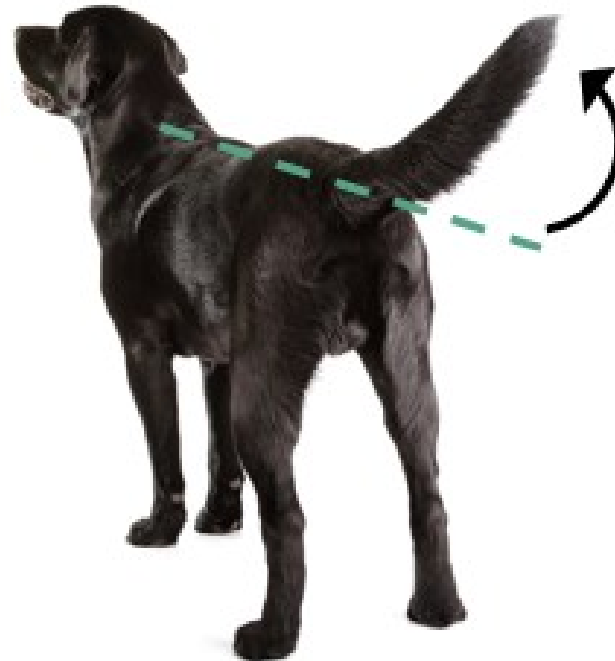
“... the bending motion is like a dog wagging its tail. Half of the time the tail is left, half of the time it is right, and on the average it is in the middle, neither left nor right.”

Renowned experimental spectroscopist,
private communication, 2017

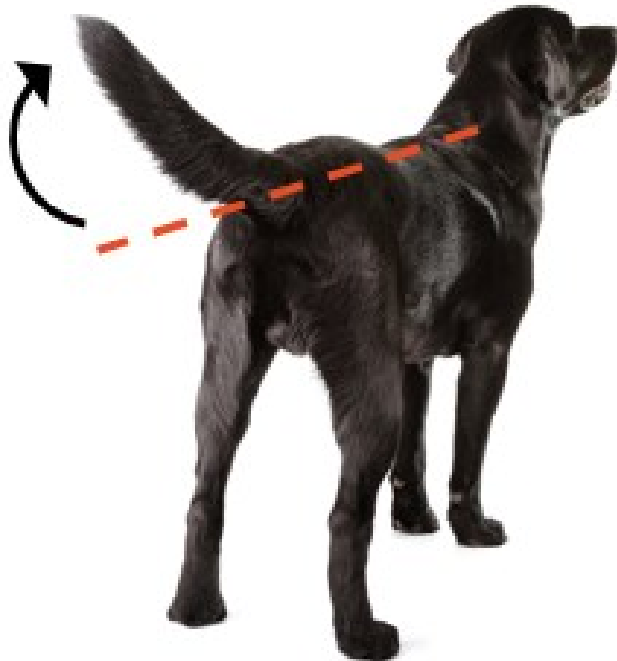
„Left-tail“



„Right-tail“

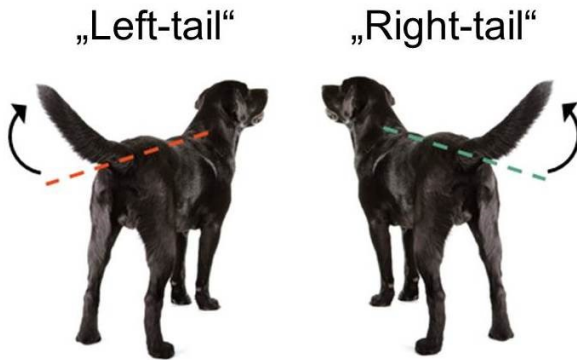


„Left-tail“

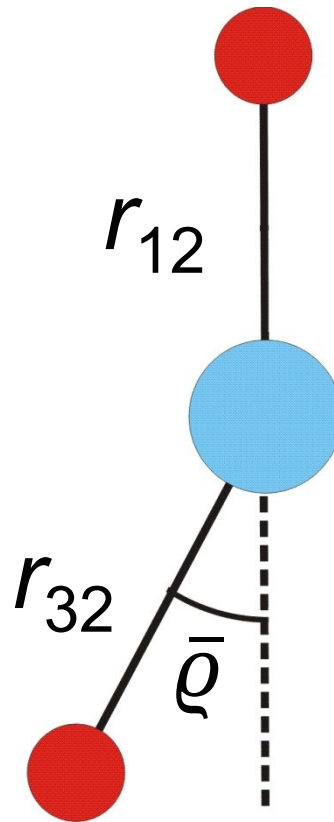


„Left-tail“

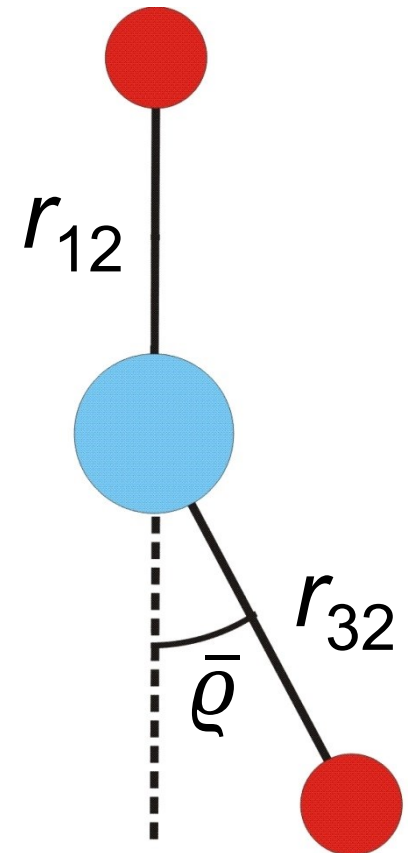




„Left-tail“



„Right-tail“



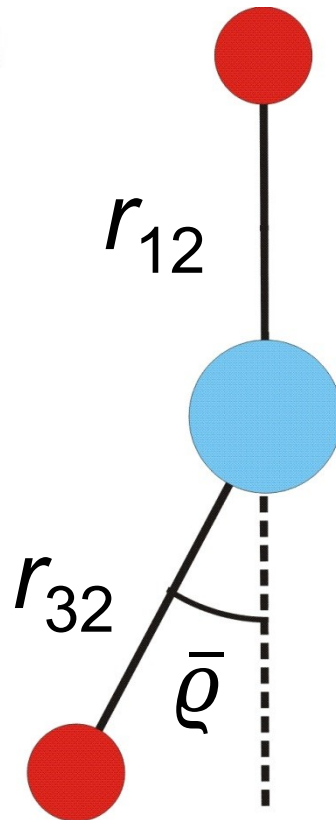
„Left-tail“



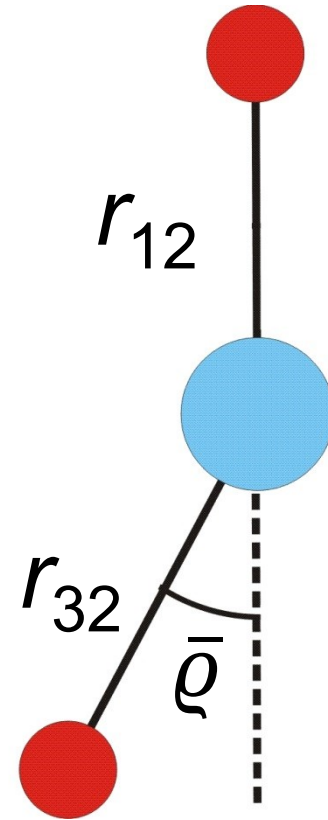
„Left-tail“



„Left-tail“



„Left-tail“



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

HCO⁺

ab initio 3D potential energy surface, calculated at RCCSD(T)/[aug-cc-pCVQZ(C,O), aug-cc-pVQZ(H)] level of theory with the MOLPRO 2010.1 suite of programs (T. Hirano and U. Nagashima, *private communication*)

Rotational structure very well reproduced by *ab initio* potential energy surface, vibrational energies somewhat off. Nuclear-motion calculations with MORBID.

Therefore:

Refinement of potential energy surface simultaneous least-squares fitting of *ab initio* data and available experimentally derived energy spacings for HCO⁺ and DCO⁺.

Bending potential curves for HCO^+

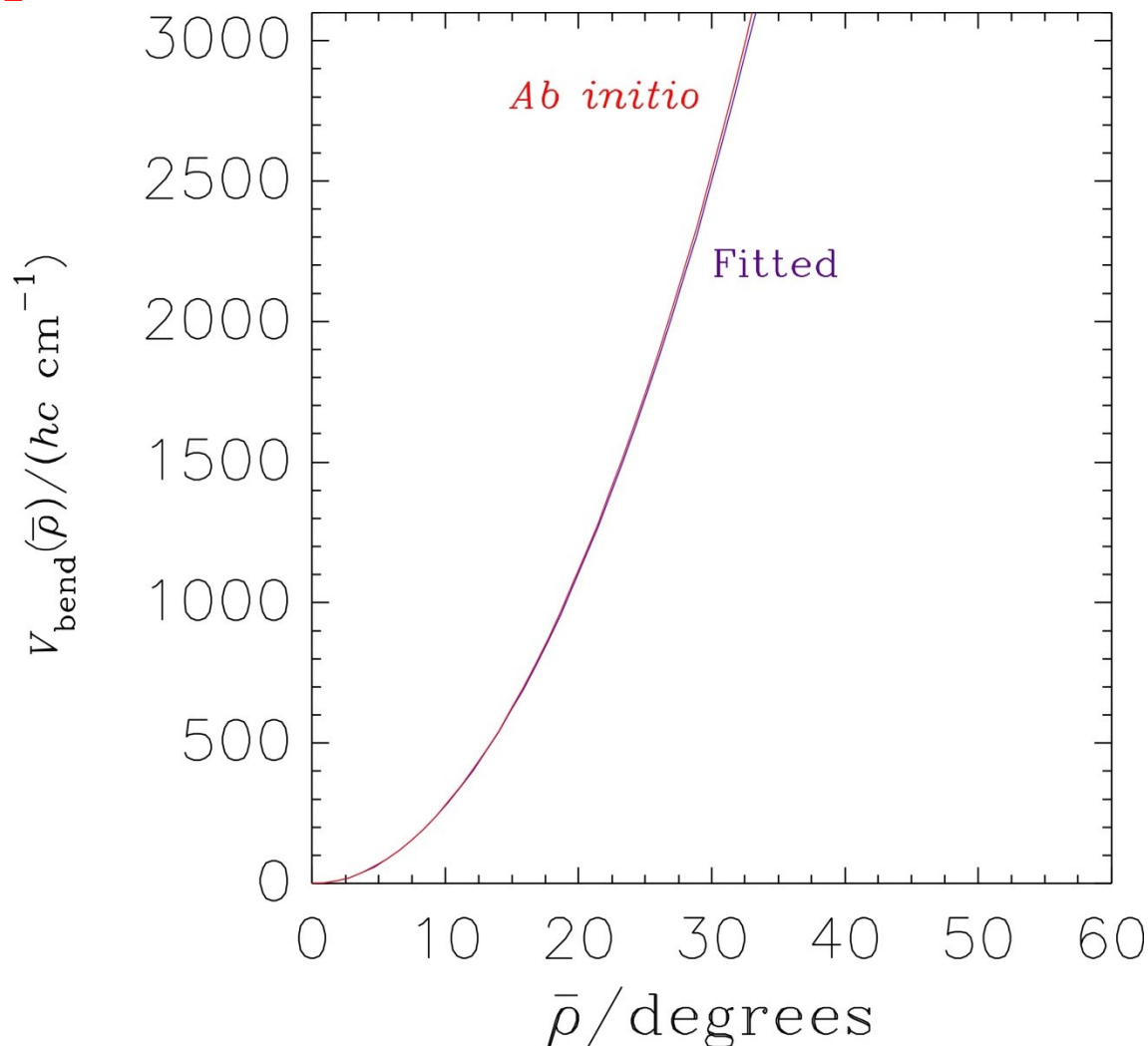


Table 2: Comparison of experimentally derived [50, 51] and calculated $J = \ell_2$ term values of HCO^+ (in cm^{-1} , measured relative to the $J = 0$ level of the vibrational ground state).

$(v_1, v_2^{\ell_2}, v_3)$		ΔE_{obs}	<i>Ab initio</i> ^a		Fitted ^b	
			ΔE_{calc}	O–C ^c	ΔE_{calc}	O–C ^c
(0,0 ⁰ ,0)		0.0	0		0	
(0,1 ¹ ,0)	<i>e</i>	831.205	822.029	9.175	824.859	6.345
	<i>f</i>	831.218	822.041	9.177	824.871	6.347
(0,2 ⁰ ,0)		1638.619	1650.709	–12.090	1645.060	–6.441
(0,2 ² ,0)	<i>e</i>	1654.367	1659.664	–5.298	1656.836	–2.469
	<i>f</i>	1654.366	1656.596	–2.229	1656.836	–2.470
(0,0 ⁰ ,1)		2183.950	2179.884	4.065	2182.640	1.310
(0,3 ¹ ,0)		2459.399	2462.389	–2.990	2453.245	6.154
(0,3 ³ ,0)		2488.427	2498.444	–10.017	2494.288	–5.862
(0,1 ¹ ,1)	<i>e</i>	3015.289	3004.677	10.612	3013.854	1.435
	<i>f</i>	3015.296	3004.689	10.607	3013.867	1.429
(1,0 ⁰ ,0)		3088.739	3068.369	20.370	3085.146	3.593
(1,1 ¹ ,0)	<i>e</i>	3895.817	3854.325	41.492	3893.084	2.733
	<i>f</i>	3895.830	3854.332	41.498	3893.094	2.736
(0,0 ⁰ ,2)		4347.786	4339.061	8.725	4345.712	2.075
(1,2 ⁰ ,0)		4679.373	4646.612	32.761	4678.338	1.035
(1,2 ² ,0)	<i>e</i>	4694.517	4649.271	45.246	4695.325	–0.808
	<i>f</i>	4694.517	4649.271	45.245	4695.325	–0.809
(1,0 ⁰ ,1)		5247.086	5218.216	28.870	5245.189	1.897
(1,1 ¹ ,1)	<i>e</i>	6054.565	6002.312	52.253	6055.484	–0.918
	<i>f</i>	6054.574	6002.314	52.260	6055.496	–0.922
(2,0 ⁰ ,0)		6078.684	6016.317	62.367	6080.982	–2.298
(1,0 ⁰ ,2)		7385.950	7352.497	33.453	7389.786	–3.836

^aCalculated by MORBID with the ‘*Ab initio*’ parameter values of Table 1.

^bCalculated by MORBID with the ‘Fitted’ parameter values of Table 1.

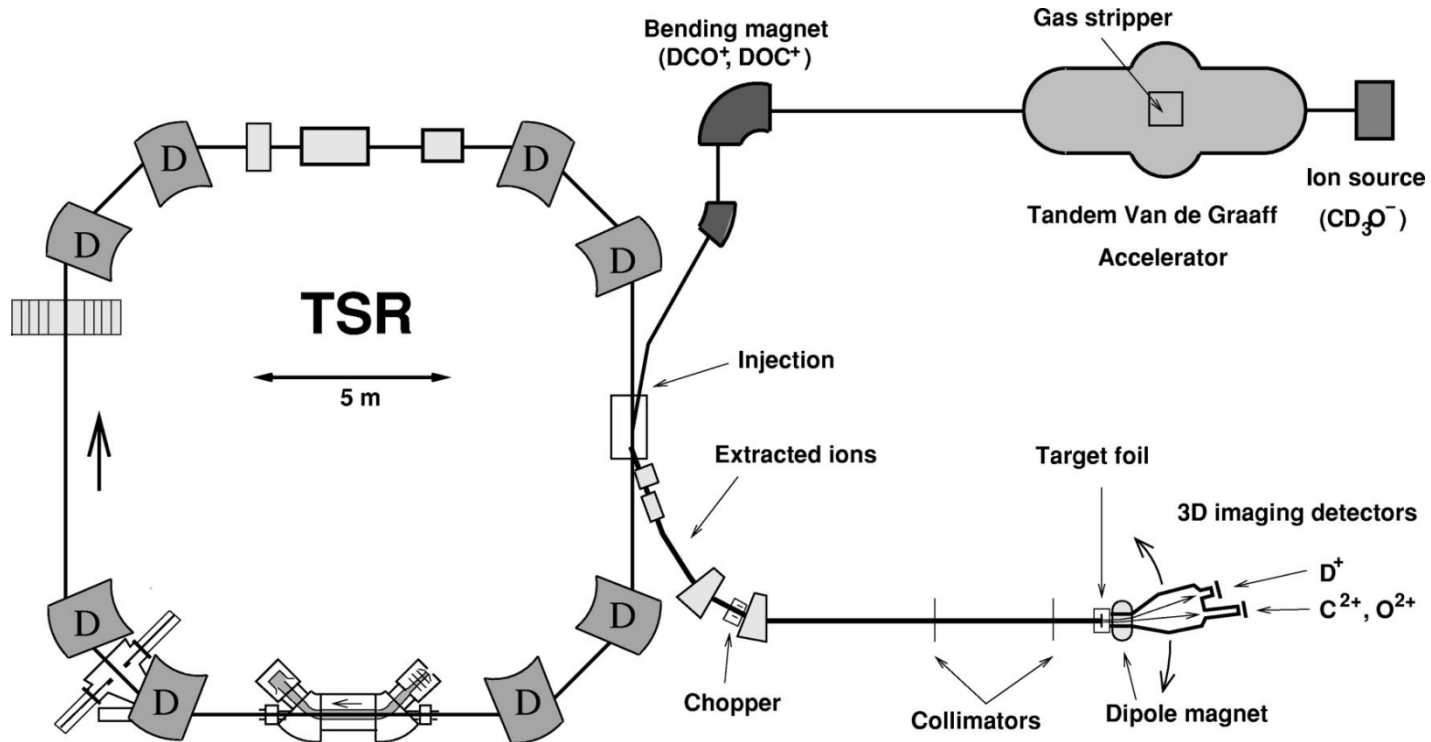
^c $\Delta E_{\text{obs}} - \Delta E_{\text{calc}}$.

Table 3: Comparison of experimentally derived [50, 51, 52, 53] and calculated B values of HCO^+ (in cm^{-1}).

	$(v_1, v_2^{\ell_2}, v_3)$	B_{obs}	<i>Ab initio</i> ^a		Fitted ^b	
			B_{calc}	$\Delta\%$ ^c	B_{calc}	$\Delta\%$ ^c
HCO^+	(0,0 ⁰ ,0)	1.48751	1.48727	0.02	1.48676	0.05
	(0,1 ¹ ,0)	<i>e</i> 1.48673	1.48439	0.16	1.48426	0.17
		<i>f</i> 1.49379	1.49029	0.23	1.49019	0.24
	(0,2 ⁰ ,0)	1.49331	1.49255	0.05	1.49286	0.03
	(0,2 ² ,0)	<i>e</i> 1.49285	1.49264	0.01	1.49022	0.18
		<i>f</i> 1.49262	1.48978	0.19	1.49006	0.17
	(0,0 ⁰ ,1)	1.47768	1.47749	0.01	1.47771	0.00
	(0,3 ¹ ,0)	1.49520	1.48521	0.67	1.48607	0.61
	(0,3 ³ ,0)	1.49560	1.49211	0.23	1.49279	0.19
	(0,1 ¹ ,1)	<i>e</i> 1.47644	1.47406	0.16	1.47459	0.13
		<i>f</i> 1.48391	1.48033	0.24	1.48090	0.20
	(1,0 ⁰ ,0)	1.47571	1.47512	0.04	1.47853	−0.19
	(1,1 ¹ ,0)	<i>e</i> 1.47562	1.47669	−0.07	1.47764	−0.14
		<i>f</i> 1.48240	1.48023	0.15	1.48277	−0.02
	(0,0 ⁰ ,2)	1.46782	1.46765	0.01	1.46855	−0.05
	(1,2 ⁰ ,0)	1.48269	1.45720	1.72	1.48813	−0.37
	(1,2 ² ,0)	<i>e</i> 1.48298	1.47509	0.53	1.49141	−0.57
		<i>f</i> 1.48276	1.47535	0.50	1.49139	−0.58
	(1,0 ⁰ ,1)	1.46651	1.46591	0.04	1.46978	−0.22
	(1,1 ¹ ,1)	<i>e</i> 1.46462	1.48361	−1.30	1.46957	−0.34
		<i>f</i> 1.47343	1.48472	−0.77	1.47556	−0.14
	(2,0 ⁰ ,0)	1.46520	1.46418	0.07	1.47035	−0.35
	(1,0 ⁰ ,2)	1.45727	1.45873	−0.10	1.47319	−1.09

Structure? Can we measure the square of ψ ?

Yes, in a Coulomb Explosion Imaging (CEI) experiment!



R. Wester, U. Hechtscher, L. Knoll, M. Lange, J. Levin, M. Scheffel, D. Schwalm, A. Wolf, A. Baer, Z. Vager, D. Zajfman, M. Mladenović, S. Schmatz, Relaxation dynamics of deuterated formyl and isoformyl cations, *J. Chem. Phys.*, **116** (2002) 7000-7011.

Bending probability density

Simulated with fitted potential energy surface

$$\begin{aligned}
 f_{J,\Gamma_{\text{rv}},m,j}(\rho) &= \int_0^\infty dr_1 \int_0^\infty dr_3 \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \\
 &\times \int_0^{2\pi} d\chi \, |\Psi_{J,\Gamma_{\text{rv}},m,j}(r_1, r_3, \rho, \theta, \phi, \chi)|^2 ; \\
 &= \sum_{K=0}^J \sum_{N_{\text{vib}}, \Gamma_{\text{vib}}} \sum_{v_2=0}^{v_2^{(\text{max})}} \sum_{v'_2=0}^{v_2^{(\text{max})}} \left(c_{N_{\text{vib}}, \Gamma_{\text{vib}}, v'_2, K}^{J, \Gamma_{\text{rv}}, m, j} \right)^* \\
 &\quad \times c_{N_{\text{vib}}, \Gamma_{\text{vib}}, v_2, K}^{J, \Gamma_{\text{rv}}, m, j} \psi_{v'_2, K}^*(\rho) \psi_{v_2, K}(\rho).
 \end{aligned}$$

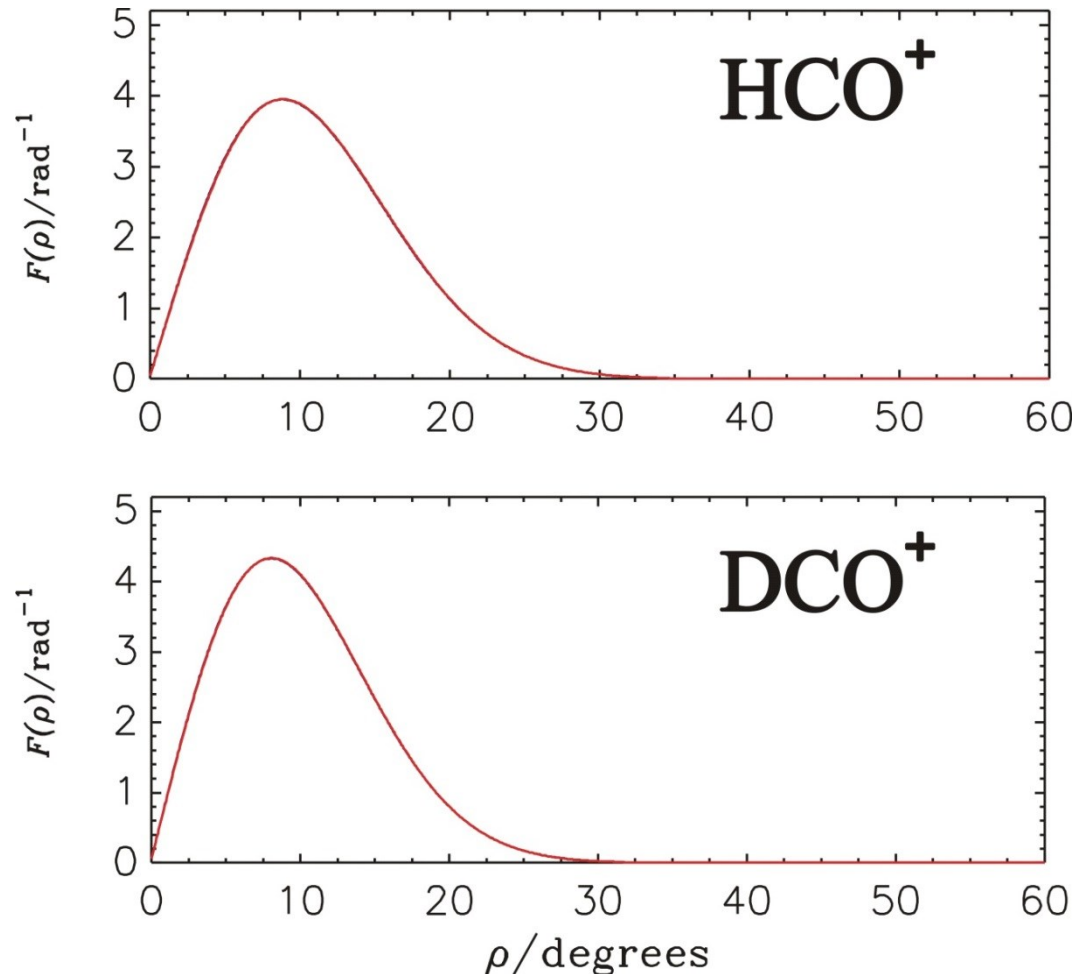
$$F(\rho) = \frac{\sum_i g_i \exp\left(-\frac{E_i}{kT}\right) f_i(\rho)}{\sum_i g_i \exp\left(-\frac{E_i}{kT}\right)}.$$

Simulated $F(\rho)$ functions

$T = 300\text{ K}$

$$dP = F(\rho) d\rho.$$

is the differential probability that the bending coordinate of a molecule in the ensemble is in the interval between ρ and $\rho + d\rho$



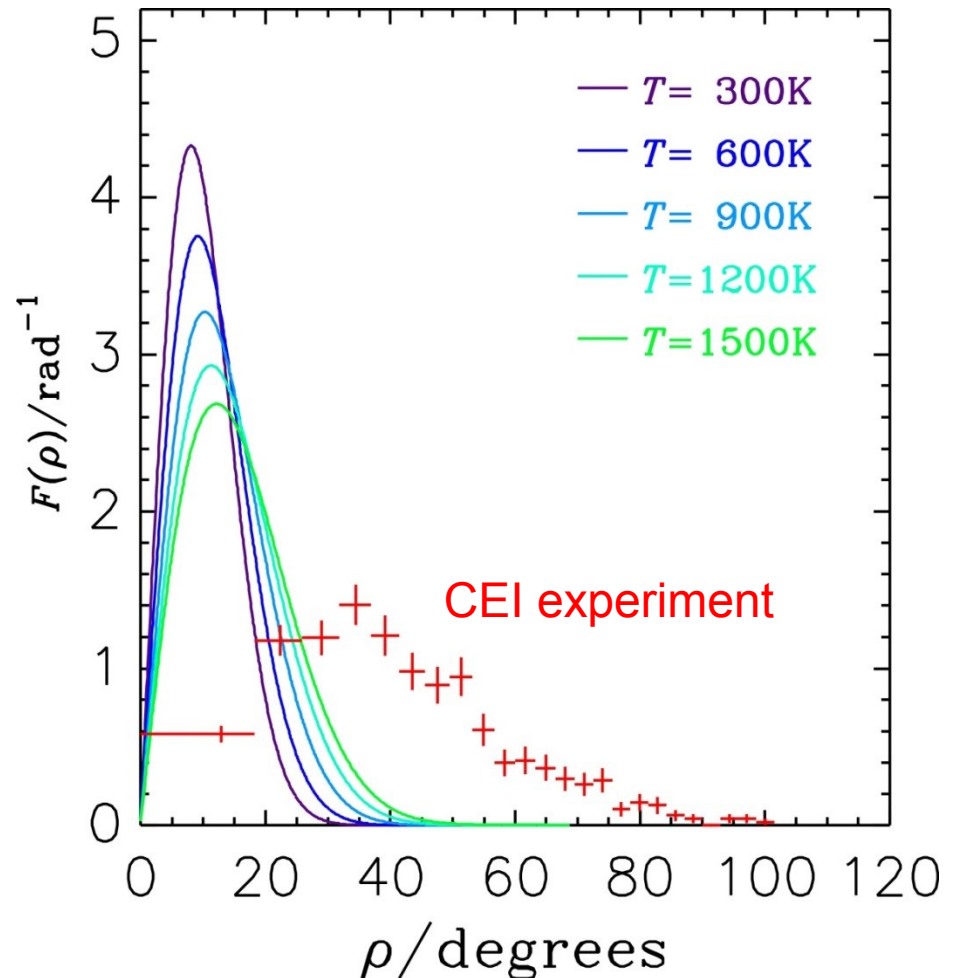
Simulated $F(\rho)$ functions for DCO^+

Increasing temperatures T

In the CEI experiment,
the ions spend 12s in
the TSR

Too short for
equilibration at 300 K.

***But the measurements
are consistent with
bent average structure
($\langle \rho \rangle > 0$)***



Calculated $\langle \rho \rangle$ values for DCO^+

Increasing temperatures T

Table 5: Average ρ -values $\langle \rho \rangle$ (Eq. (17), in degrees) as a function of temperature T for HCO^+ and DCO^+ .

T/K	HCO^+	DCO^+
300	11.0(5.8) ^a	10.1(5.2)
600	12.2(6.4)	11.6(6.1)
900	13.7(7.2)	13.2(7.0)
1200	15.2(8.0)	14.7(7.8)
1500	16.4(8.9)	15.9(8.9)

^aQuantities in parentheses are quantum mechanical uncertainties $\sqrt{\langle \rho^2 \rangle - \langle \rho \rangle^2}$ in units of degrees.



Thank you for your attention!
