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▶ To cite this version:

Mirjana Mladenović. Theoretical spectroscopic parameters for the low-lying states of isotopic variants of HCO+ and HOC+. The 25th Colloquium on High-Resolution Molecular Spectroscopy HRMS 2017, Aug 2017, Helsinki, Finland. hal-01599206

HAL Id: hal-01599206 https://auf.hal.science/hal-01599206

Submitted on 1 Oct 2017

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Theoretical spectroscopic parameters for the low-lying states of isotopic variants of HCO⁺ and HOC⁺

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The theoretical spectroscopic parameters are derived for all isotopologues of HCO+ and HOC+ involving H, D, ¹⁶O, ¹⁷O, ¹⁸O, ¹²C, and ¹³C by means of a two-step procedure. Full-dimensional rovibrational calculations are first carried out to obtain numerically exact rovibrational energies for J=0-15 in both parities. Effective spectroscopic constants for the vibrational ground state, v_1 , v_2 , and v_3 are determined by fitting the calculated rovibrational energies to appropriate spectroscopic Hamiltonians. Combining our vibrationrotation corrections with the available experimental ground-state rotational constants, we also derive the new estimate for the equilibrium structure of HCO+, re(CH)=1.091981(7) Å and re(CO)=1.105615(2) Å, and for the equilibrium structure of HOC+, re(HO)=0.990482(7) A and re (CO)=1.154468(2) A. Regarding the spectroscopic parameters, our estimates are in exelent agreement with available experimental results for both HCO⁺ and HOC⁺: the agreement for the rotational constants B_v is within 3 MHz, for the quartic centrifugal distortion constants D_v within 1 kHz, and for the effective *l*-doubling constants q_v within 2 MHz. We thus expect that our results can provide useful assistance in analyzing expected observations of the rare forms of HCO⁺ and HOC⁺ that are not yet experimentally known.



The rovibrational energies computed for a vibrational Σ state v are fitted to the standard polynomial expansion in J(J+1), $E_v(J) = T_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \dots$ For a Π state, we use the expansion

In the traditional spectoscopic approach, the rovibrational correction $\Delta B_{v1,v2,v3}$ to the equilibrium rotational constant B_e is given by $\Delta B_{v1,v2,v3} = B_e - B_{v1,v2,v3} = \sum_{i=1}^{3} \alpha_i (v_i + \frac{1}{2} d_i)$.

This gives the correction ΔB_0 for the ground vibrational state as

 $\Delta B_0 = B_e - B_0 = \frac{1}{2}(\alpha_1 + 2\alpha_2 + \alpha_3),$ so that $B_i = B_e - \Delta B_0 - \alpha_i$ for i=1,2,3.

Replacing B_e with another value B_e^{est} , we obtain new estimates for the ground state rotational constant, $B_0^{est} = B_e^{est} - \Delta B_0$, and for the rotational constant in the excited *i*-th vibrational state, $B_i^{est} = B_e^{est} - \Delta B_0 - \alpha_i$.



Minimum energy path V_{MEP} and effective bending potential ^{adi}Vv₁v₃ for the (0,0), (1,0) and (2,0) stretching states along the Jacobi angle θ . The curves are shifted to coincide at $\theta=0^{\circ}$ for HCO+ and at $\theta=180^{\circ}$ for HOC+.

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BLE V: Equilibrium	a geometry of 1	ICO ⁺ and IIO
HCO ⁺	$r_{c}(\mathrm{CH})$ / Å	$r_e(\text{CO})$ / Å
This work	1.091 981(7)	1,105 615(2)
Dore et al. ¹⁵	1.092.04	1.105 58
Puzzarini et al. ⁵	1.091 97	1,105 46
Botschwina et al. ¹⁶	1.091.9	1,105.8
нос+	<i>т</i> ∗(HO) / Å	$r_{\rm e}({\rm CO})$ / Å
This work	0.990482(7)	1.154468(2)
This work, Fit 2	0.990478	1.154469
Botschwina et al. ¹⁶	0.988.5	1.154.6
Martin et al. ¹⁷	0.98817	1.154 71

Values in parentheses show one standard error to the last signif-ant digits of the distances.

TABLE VI: Selected results for HCO⁺ and HOC⁺ from the rowbrational (J = 0, 1) DVR-DGB calculations employing the atomic masses (Test 0), the proton mass in combination with the atomic masses for carbon and oxygen (Test 1), and the nuclear masses (Test 2).

	HCO^+			
Property	'l'est 0	Test 1	Test 2	
$\tilde{\nu}_1$ / cm ⁻¹	3085.58	3086.20	3086.29	
$\tilde{\nu}_2 \ / \ \mathrm{cm}^{-1}$	830.72	830.88	830.91	
$\tilde{\nu}_3 / \mathrm{cm}^{-1}$	2179.09	2179.20	2179.44	
\tilde{q}_2 / MHz	209.85	209.86	209.94	
\tilde{B}_1 / MHz	44023.71	44029.62	44038.64	
\widetilde{B}_3 / MHz	44083.53	44089.39	44098.46	
		$IIOC^+$		
Property	Test 0	Test 1	Test 2	
$\tilde{\nu}_1$ / cm ⁻¹	3276.54	3277.30	3277.34	
$\tilde{\nu}_2$ / cm ⁻¹	245.07	245.14	245.15	
$\tilde{\nu}_3 / \mathrm{cm}^{-1}$	1901.32	1901.34	1901.59	
\tilde{q}_2 / MHz	517.00	516.96	517.18	
B. / MHz	44226.43	44230.69	44240.61	