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

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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, ν₁, ν₂, and ν₃ 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⁺ , r^e (CH)=1.091981(7)** Å **and r^e (CO)=1.105615(2)** Å**, and for the equilibrium structure of HOC⁺ , re (HO)=0.990482(7)** Α **and r^e (CO)=1.154468(2)** Α**. 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). $E_v(J) = T_v + B_v J(J+1) - D_v J^2 (J+1)^2 + H_v J^3 (J+1)^3 + ...$ For a Π state, we use the expansion

$$
E_{\nu}(J) = T_{\nu} + B_{\nu} [J(J+1) - \ell^2] - D_{\nu} [J(J+1) - \ell^2]^2 + H_{\nu} [J(J+1) - \ell^2]^3 +
$$

$$
\pm \frac{1}{2} [q_{\nu} J(J+1) + q_{\nu} J^2 (J+1)^2 + q_{\nu} J^3 (J+1)^3 +]
$$

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

ΔB₀ = B_e- B₀ = $\frac{1}{2}$ (α₁+2α₂+ α₃), so that $B_i = B_a - \Delta B_0 - \alpha_i$ for i=1,2,3.

Replacing B_e with another value B_e^{est}, we obtain new estimates for the ground state rotational constant, B₀^{est} = B_e^{est} - AB₀, and for the rotational constant in the excited *i*-th vibrational state, $B_i^{\text{est}} = B_i^{\text{est}} - \Delta B_0 - \alpha_i$.

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 $HCO⁺$

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Dore et al.¹⁵

Programmi at al.

Botschwina et a

This work, Fit 2

Botschwina et al.'
Martin et al.'
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TABLE V: Equilibrium geometry of HCO" and HOC

 $r_c{\rm (CH)}$ / Å

 $1.091981(7)$

 $1.001.07$

1.0919

 $r_e(HO)/$

0.990 478

 0.9885

0.988.17

 $\,$ "Values in parentheses show one standard error to the last significant digits of the distances.

 $0.990(482(7))$

 r (CO) / λ

 $1.105615(2)$

 $1.105.58$

 $1.105.46$

1.1058

 r_e (CO) / Å

1.154.468(2)

1.154 469

1.1546

1.154.71

arne la Valle