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, ^{16}O, ^{17}O, ^{18}O, ^{12}C, and ^{13}C 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 vibration-rotation 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+, r_e(HO)=0.990482(7) Å and r_e(CO)=1.154468(2) Å. 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.

TABLE I: Spectroscopic parameters for the isotopic variants of HCO+. Experimental values are given in brackets.

TABLE II: Spectroscopic parameters for the isotopic variants of DCO+. Experimental values are given in brackets.

TABLE III: Spectroscopic parameters for the isotopic variants of HOC+. Experimental values are given in brackets.

TABLE IV: Spectroscopic parameters for the isotopic variants of DOC+. Experimental values are given in brackets.

The rovibrational energies computed for a vibrational Σ state v are fitted to the standard polynomial expansion in J(J+1),

$$E_v(J) = T_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \ldots$$

For a Π state, we use the expansion

$$E_v(J) = T_v + B_v [\, J(J+1) - \ell^2 \,] - D_v [\, J(J+1)-\ell^2 \,]^2 + H_v [\, J(J+1)- \ell^2 \,]^3 + \cdots$$
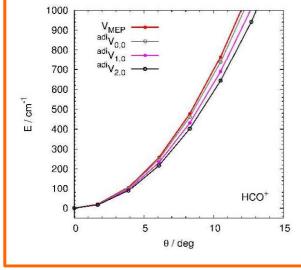$$\pm \frac{1}{2} [\, q_v J(J+1) + q_v^J J^2(J+1)^2 + q_v^{JJ} J^3(J+1)^3 + \cdots]$$

In the traditional spectroscopic approach, the rovibrational correction $\Delta B_{v1,v2,v3}$ to the equilibrium rotational constant B_e is given by
$$\Delta B_{v1,v2,v3} = B_e - B_{v1,v2,v3} = \sum_{i=1}^{3} \alpha_i (v_i + \tfrac{1}{2} d_i).$$
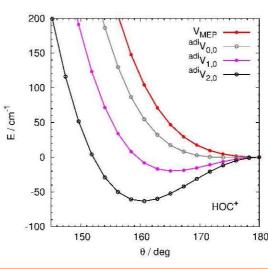This gives the correction ΔB_0 for the ground vibrational state as
$$\Delta B_0 = B_e - B_0 = \frac{1}{2}(\alpha_1 + 2\alpha_2 + \alpha_3), \quad \text{so that} \quad B_i = B_e - \Delta B_0 - \alpha_i \quad \text{for } i=1,2,3.$$
Replacing B_e with another value B_e^{est}, we obtain new estimates for 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 $^{adi}Vv_1,v_3$ for the (0,0), (1,0) and (2,0) stretching states along the Jacobi angle θ. The curves are shifted to coincide at $\theta=0^0$ for HCO+ and at $\theta=180^0$ for HOC+.

TABLE V: Equilibrium geometry of HCO+ and HOC+.[a]

HCO+	r_e(CH) / Å	r_e(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

HOC+	r_e(HO) / Å	r_e(CO) / Å
This work	0.990 482(7)	1.154 468(2)
This work, Fit 2	0.990 478	1.154 469
Botschwina et al.[16]	0.988 5	1.154 6
Martin et al.[17]	0.988 47	1.154 71

[a]Values in parentheses show one standard error to the last significant digits of the distances.

TABLE VI: Selected results for HCO+ and HOC+ from the rovibrational (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	Test 0	Test 1	Test 2
$\tilde{\nu}_1$ / cm^{-1}	3085.58	3086.20	3086.29
$\tilde{\nu}_2$ / cm^{-1}	830.72	830.88	830.91
$\tilde{\nu}_3$ / 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
$\tilde{B}_3$ / MHz	44083.53	44089.39	44098.46

	HOC+		
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
$\tilde{\nu}_3$ / cm^{-1}	1901.32	1901.34	1901.59
$\tilde{q}_2$ / MHz	517.00	516.96	517.18
$\tilde{B}_1$ / MHz	44226.43	44230.69	44240.61
$\tilde{B}_3$ / MHz	44152.40	44156.58	44166.53