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► To cite this version:

Mirjana Mladenović. Theoretical spectroscopic parameters for isotopic variants of HCO + and HOC + . Journal of Chemical Physics, American Institute of Physics, 2017, 147 (11), pp.114111. <<http://aip.scitation.org/doi/full/10.1063/1.4998467>>. <10.1063/1.4998467>. <hal-01599204>

HAL Id: hal-01599204

<https://hal-auf.archives-ouvertes.fr/hal-01599204>

Submitted on 4 Oct 2017

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# Theoretical spectroscopic parameters for isotopic variants of HCO<sup>+</sup> and HOC<sup>+</sup>

Mirjana Mladenović\*

*Université Paris-Est, Laboratoire Modélisation et Simulation Multi-Echelle (MSME),  
UMR 8208 CNRS, 5 bd Descartes, 77454 Marne la Vallée, France*

Theoretical spectroscopic parameters are derived for all isotopologues of HCO<sup>+</sup> and HOC<sup>+</sup> involving H, D, <sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O, <sup>12</sup>C, and <sup>13</sup>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,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  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<sup>+</sup>,  $r_e(\text{CH})=1.091\,98\text{ \AA}$  and  $r_e(\text{CO})=1.105\,62\text{ \AA}$ , and for the equilibrium structure of HOC<sup>+</sup>,  $r_e(\text{HO})=0.990\,48\text{ \AA}$  and  $r_e(\text{CO})=1.154\,47\text{ \AA}$ . Regarding the spectroscopic parameters, our estimates are in excellent agreement with available experimental results for the isotopic variants of both HCO<sup>+</sup> and HOC<sup>+</sup>: 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  $\ell$ -doubling constants  $q_v$  within 2 MHz. We thus expect that our results can provide useful assistance in analyzing expected observations of the rare isotopologues of HCO<sup>+</sup> and HOC<sup>+</sup> that are not yet experimentally known.

## I. INTRODUCTION

Electrons and ions play a significant role in interstellar physical chemistry and for the modelling of the composition of the interstellar medium. Knowledge about their abundances gives important information regarding the sources which heat and ionize the gas. Protonated carbon monoxide may appear as the formyl cation, HCO<sup>+</sup>, or as the isoformyl cation, COH<sup>+</sup>. The formyl cation is an abundant species in outer space, observable in many objects. In ion-molecule chemistry, HCO<sup>+</sup> is the cornerstone species with an important role in astrochemical models of chain reactions leading to the formation of organic molecules.<sup>1</sup> The formation and depletion mechanism of HOC<sup>+</sup>, as well as the abundance ratio [HCO<sup>+</sup>]/[HOC<sup>+</sup>], have attracted a lot of interest.<sup>2,3</sup> HCO<sup>+</sup> and HOC<sup>+</sup> remain the only known example of isomeric interstellar ions.<sup>4,5</sup>

During a search for HCN, Buhl and Snyder detected a new molecular line at 89.190 GHz in several interstellar media, whose carrier was named X-ogen, meaning that "it has an extraterrestrial origin".<sup>6</sup> The assignment of this transition to HCO<sup>+</sup> proposed by Klemperer<sup>7</sup> was confirmed in the laboratory by Woods and coworkers<sup>8</sup> five years later. Since then the rotational spectrum of HCO<sup>+</sup> has been extensively studied.<sup>1,9-13</sup> The recording of the pure rotational transitions in the ground vibrational state has been extended up to 1.6 THz, i.e. the transition  $J = 17 \rightarrow 16$ .<sup>13</sup> The band origins for all three vibrational fundamentals were determined by infrared laser spectroscopy, covering the stretching  $\nu_1$  mode,<sup>14,15</sup> the bending  $\nu_2$  mode,<sup>16,17</sup> and the stretching  $\nu_3$  mode.<sup>18,19</sup> The hot bands in the region of  $\nu_1$  and  $\nu_3$  are also known.<sup>20-22</sup> Some higher vibrationally excited states of HCO<sup>+</sup> were characterized experimentally.<sup>23-25</sup> Rotational transitions in the vibrationally excited state could be of astronomical interest in hot, dense environments. The stability of HCO<sup>+</sup> is apparent from the low ioniza-

tion potential of HCO of 8.27 eV known from photoelectron spectroscopy.<sup>26</sup> In outer space, HCO<sup>+</sup> has been detected in various regions, such as e.g. star-forming regions,<sup>27,28</sup> diffuse clouds,<sup>29</sup> circumstellar envelopes,<sup>30</sup> and circumstellar disks.<sup>31,32</sup>

The first spectroscopic detection of HOC<sup>+</sup> was made in 1982 by Gudeman and coworkers,<sup>33,34</sup> who observed the lowest ( $J = 0 \rightarrow 1$ ) rotational transition of HOC<sup>+</sup>, HO<sup>13</sup>C<sup>+</sup>, and H<sup>18</sup>OC<sup>+</sup> in laboratory direct-current glow discharges. Blake et al.<sup>35</sup> extended the laboratory measurements up to 350 GHz by recording the rotational transitions up to  $J = 3 \rightarrow 4$ . Woods et al.<sup>36</sup> undertook a detailed search in the interstellar medium at 14 different locations, tentatively identifying a weak emission line in Sgr B2 as the  $J = 1 \rightarrow 0$  transition of HOC<sup>+</sup>. This detection was, however, viewed with skepticism because of the high reactivity of HOC<sup>+</sup>. The observation reported by Ziurys and Apponi<sup>37</sup> towards several sources provided a final confirmation of interstellar HOC<sup>+</sup>. Since then HOC<sup>+</sup> has been observed in interstellar environments in both dense<sup>36-38</sup> and diffuse<sup>39</sup> molecular clouds, including photon-dominated regions.<sup>40</sup> Isomer ratios [HCO<sup>+</sup>/HOC<sup>+</sup>] between 300 and 6000 are reported in different interstellar regions.<sup>3,41,42</sup>

High-resolution infrared spectroscopy has provided information on the excited vibrational states of HOC<sup>+</sup>.<sup>41</sup> The infrared absorption of the  $\nu_1$  band was detected by Nakanaga and Amano in a hollow-cathode discharge in a mixture of CO and H<sub>2</sub>.<sup>43</sup> Amano<sup>44</sup> suggested that the  $\nu_2$  frequency of HOC<sup>+</sup> is likely lower than 300 cm<sup>-1</sup> from the observation of the  $\nu_1 + \nu_2 - \nu_2$  combination band, suggesting that  $\nu_2$  is a large-amplitude motion. The pure rotational transitions in the  $\nu_2$  excited state of HOC<sup>+</sup> were investigated a few years later by Amano and Maeda.<sup>45</sup> No experimental information is available for the stretching  $\nu_3$  mode.

Several isotopologues of HCO<sup>+</sup> and HOC<sup>+</sup> were observed in the laboratory and in outer space,<sup>1,9,33,46-50</sup>

but not all of them. The situation with the rare isotopes is expected to change with the increasing sensitivity of receivers and large collecting areas. The Northern Extended Millimeter Array (NOEMA) radiotelescope will double the number of antennas (to twelve) by 2019, which will improve its spatial resolution and sensitivity, such that NOEMA will soon become the most advanced facility for millimeter radio astronomy in the Northern Hemisphere.<sup>51</sup> To fully exploit advanced facilities (such as Herschel, ALMA, SOFIA), spectroscopic studies over larger energy ranges are needed already now, in particular for molecular systems of astrophysical/astrochemical relevance, such as  $\text{HCO}^+$ .

In astrochemical models, isotope fractionation reactions were introduced to describe the enrichment of heavy isotopes in dark interstellar clouds.<sup>52,53</sup> These enrichment processes are also important in geochemistry.<sup>54</sup> The isotope fractionation reaction of  $\text{HCO}^+/\text{HOC}^+$  with CO was a subject of our recent studies,<sup>55,56</sup> which provide new exothermicities and rate coefficients relevant for temperatures of dark interstellar cloud environments for all the isotopologues involving  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ , H, and D. These results were obtained with the help of the global three-dimensional potential energy surface (PES) previously developed for the isomerizing system  $\text{HCO}^+/\text{HOC}^+$  at the CCSD(T)/cc-pVQZ level of theory.<sup>57</sup> The localized  $\text{HCO}^+$  and  $\text{HOC}^+$  energy levels below the ground-state adiabatic isomerization barrier for  $J = 0 - 2$  and all bound vibrational levels for  $J = 0$  (in total 6042 bound states up to the first classical dissociation limit  $\text{H}^+ + \text{CO}$  at  $51\,621\text{ cm}^{-1}$ ) were studied for the CCSD(T)/cc-pVQZ PES in our original work.<sup>57</sup> A simple empirical model, developed there to simulate energy level pattern of isomerizing linear triatomic molecules, is useful for chemical models at high temperatures. To our knowledge, the CCSD(T)/cc-pVQZ potential energy surface remains the only available functional representation designed for both  $\text{HCO}^+$  and  $\text{HOC}^+$ , based on higher-energy *ab initio* points, too. Its accuracy was documented previously.<sup>57</sup>

In the present work, we revisit the CCSD(T)/cc-pVQZ PES with the purpose of providing a spectroscopic characterization of the isotopologues of  $\text{HCO}^+$  and  $\text{HOC}^+$  by theoretical means. Quantum mechanical calculations of the rovibrational energies are performed by means of the DVR+DGB method (Section II). The computed energies are used to derive the parameters of the effective spectroscopic Hamiltonian (Section III A). Using the experimental ground-state rotational constants  $B_0$  in combination with our theoretical rotation-vibration corrections (obtained beyond a perturbational approach), we additionally determine a new estimate for the equilibrium structure of both  $\text{HCO}^+$  and  $\text{HOC}^+$  (Section III B). Least-squares procedures for the linear and nonlinear fitting are used.<sup>58</sup>

Nominal abundances of carbon isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  are 98.90(3) and 1.10(3)%, nominal abundances of oxygen isotopes  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$  are 99.762(15), 0.038(3),

and 0.200(12)%; and, finally, nominal abundances of H and D are 99.985(1) and 0.015(1)%, as given by Mills and coworkers.<sup>59</sup> In the present work, the mass numbers are stated for each of the elements in the chemical formulas only in Tables I-IV. In the rest of the text, we provide the isotope information in chemical formulas only if the isotope is not the most abundant.

## II. THEORETICAL ASPECTS

In the calculations of the rovibrational energies of  $\text{HCO}^+/\text{HOC}^+$ , we have employed orthogonal (Jacobi) internal coordinates  $(r, R, \theta)$  in the body-fixed formulation, where  $r$  is the CO bond length,  $R$  the distance from the proton to the center of mass of the C-O subunit, and  $\theta$  the angle between the Jacobi vectors  $\mathbf{r}$  and  $\mathbf{R}$ . The two-vector embedded body-fixed reference frame is chosen such that the body-fixed  $z$ -axis is aligned with the bond-distance vector  $\mathbf{r}$ .<sup>60</sup> The nuclear dynamics calculations were carried out by means of the discrete variable representation (DVR) for the angular coordinate in conjunction with real two-dimensional distributed Gaussian basis (DGB) functions for the radial degrees of freedom. Using a sequential diagonalization and basis-set truncation, the computational strategy leads to a very compact final rovibrational basis of relatively modest size. This approach is termed DVR+DGB and involves no dynamical approximation.<sup>57,61</sup>

We use the global three-dimensional potential energy surface developed for  $\text{HCO}^+/\text{HOC}^+$  in its electronic ground state ( $^1\Sigma^+$ ) at the CCSD(T)/cc-pVQZ level of theory by Mladenović and Schmatz.<sup>57</sup> This is an isomerizing system with a bare barrier to isomerization at  $26838\text{ cm}^{-1}$  (3.33 eV) relative to the global  $\text{HCO}^+$  minimum. The isoformyl molecular ion,  $\text{HOC}^+$ , is  $13876\text{ cm}^{-1}$  (1.72 eV) higher in energy than  $\text{HCO}^+$ . On this PES, the equilibrium distances of  $\text{HCO}^+$  are  $r_e(\text{CH})=1.0935\text{ \AA}$  and  $r_e(\text{CO})=1.1086\text{ \AA}$ . For  $\text{HOC}^+$ , we have  $r_e(\text{HO})=0.9904\text{ \AA}$  and  $r_e(\text{CO})=1.1579\text{ \AA}$ .

For  $\text{HCO}^+/\text{HOC}^+$  and  $\text{DCO}^+/\text{DOC}^+$ , we consider all the isotopic variants of  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ . The rovibrational calculations were carried out for the total rotational angular momentum  $J$  as high as  $J = 15$  in both parities for each of the species (in total 24 species). Additional calculations were performed also for  $J = 30$  for the purpose of verifying the derived spectroscopic constants.

## III. RESULTS

The vibrational states of  $\text{HCO}^+$  and  $\text{HOC}^+$  are labelled by  $(v_1, v_2^\ell, v_3)$ , where  $v_1, v_3$  are quantum numbers for the stretching  $\nu_1, \nu_3$  vibrations and  $v_2$  for the doubly degenerate bending  $\nu_2$  vibration. The vibrational angular momentum quantum number is  $\ell$ . The total rotational quantum number  $J$  and parity  $p$  are strictly con-

served. The energy of the state  $(\nu_1, \nu_2^\ell, \nu_3)$  is denoted by  $E_{\nu_1, \nu_2^\ell, \nu_3}$  or  $E_{\nu_1, \nu_2, \nu_3}$ .

### A. Spectroscopic parameters

We follow common practice of experiment. The rovibrational energies computed for a vibrational  $\Sigma$  state  $\nu$  are fitted to the standard polynomial expansion in  $J(J+1)$ ,

$$E_\nu(J) = T_\nu + B_\nu J(J+1) - D_\nu J^2(J+1)^2 + H_\nu J^3(J+1)^3 + \dots \quad (1)$$

For a  $\Pi$  state, we use the expansion

$$E_\nu(J) = T_\nu + B_\nu [J(J+1) - \ell^2] - D_\nu [J(J+1) - \ell^2]^2 + H_\nu [J(J+1) - \ell^2]^3 + \dots \pm \frac{1}{2} [q_\nu J(J+1) + q_\nu^J J^2(J+1)^2 + q_\nu^{JJ} J^3(J+1)^3 + \dots] \quad (2)$$

In Eqs. (1) and (2),  $T_\nu$  is the term energy and  $B_\nu$  the effective rotational constant. The centrifugal distortion contribution is expressed in terms of the quartic centrifugal distortion constant  $D_\nu$  and the higher order constants, such as  $H_\nu$  (sextic),  $L_\nu$  (octic), and so on. The rotational dependence of the  $\ell$ -type doubling contribution is described by a polynomial in  $J(J+1)$ , with  $q_\nu$  being the  $\ell$ -type doubling constant. The parameters  $q_\nu^J, q_\nu^{JJ}$ , and so on are the centrifugal distortion corrections. Lattanzi et al.<sup>1</sup> also used the expansions of Eqs. (1) and (2) in their analysis of laboratory data on  $\text{HCO}^+$ ,  $\text{DCO}^+$ ,  $\text{H}^{13}\text{CO}^+$ , and  $\text{D}^{13}\text{CO}^+$ .

The spectroscopic parameters obtained in the fit for the vibrational ground state and the excited  $\nu_1, \nu_2$  and  $\nu_3$  states are summarized in Tables I and II for the isotopic variants of  $\text{HCO}^+$  and in Tables III and IV for the isotopic variants of  $\text{HOC}^+$ . Available experimental data are also given there. We use  $X_0, X_1, X_2, X_3$  to denote the value of the parameter  $X$  in the vibrational states  $(0, 0^0, 0)$ ,  $(1, 0^0, 0)$ ,  $(0, 1^1, 0)$ , and  $(0, 0^0, 1)$ , respectively. The  $\Pi$  state  $(0, 1^1, 0)$  is accessible for  $J \geq 1$  only. It has two components of different parities, denoted by  $(0, 1^{1e}, 0)$  and  $(0, 1^{1f}, 0)$  in the convention of Brown et al.<sup>66</sup> for the labeling of parity doublet levels in linear molecules. In Eq. (2), the plus sign is used for the level  $(0, 1^{1f}, 0)$ . The effective spectroscopic parameters of Eq. (2) reported for  $(0, 1^1, 0)$  in Tables I-IV are computed by means of the two-step procedure employing

$$\frac{E_2^f(J) + E_2^e(J)}{2} = T_2 + B_2 [J(J+1) - \ell^2] - D_2 [J(J+1) - \ell^2]^2 + \dots \quad (3)$$

and

$$E_2^f(J) - E_2^e(J) = q_2 J(J+1) + q_2^J J^2(J+1)^2 + q_2^{JJ} J^3(J+1)^3 + \dots, \quad (4)$$

where  $E_2^f(J)$  and  $E_2^e(J)$  are the energies of  $(0, 1^{1f}, 0)$  and  $(0, 1^{1e}, 0)$ , respectively. In regular spectroscopic situations,  $E_2^f(J) > E_2^e(J)$  holds.

In the fitting procedure, higher-order rotational Hamiltonians were also considered since we use high  $J$  values. The sixth-order spectroscopic Hamiltonian was found satisfactory to describe the rotational excitation in the vibrational states of  $\text{HCO}^+$  in Table I and  $\text{DCO}^+$  in Table II, except for the  $\nu_1$  state of  $\text{DCO}^+$ . To fit centrifugal distortion effects in  $\nu_1$  of  $\text{DCO}^+$ , terms higher than  $L_1$  were necessary. In the case of  $\text{HOC}^+$ , terms up to  $L_\nu$  are used for the ground vibrational state,  $\nu_1$ , and  $\nu_2$  and up to  $K_\nu$  for  $\nu_3$  in Table III. The terms up to  $K_\nu$  are used for all four states of  $\text{DOC}^+$  in Table IV. The fit standard deviations  $\sigma$  in Tables I-IV are approximately 10 Hz. The maximum deviation is 22 Hz in Table I, 40 Hz in Table II, 37 Hz in Table III, and 13 Hz in Table IV. The fitted rotational energies are up to approximately  $350 \text{ cm}^{-1}$  (about 10 THz) for  $J = 15$ .

Combining microwave data coming from different experimental groups, Lattanzi et al.<sup>1</sup> derived the spectroscopic parameters for the ground vibrational state of  $\text{HCO}^+$ , which include a large, negative sextic centrifugal distortion constant,  $H_0 = -0.341(156)$  Hz. This finding for  $H_0$  led Tinti et al.<sup>12</sup> to reinvestigate the rotational transitions of  $\text{HCO}^+$ , reporting  $H_0 = 0.083(36)$  Hz with an uncertainty of 43%. Cazzoli et al.<sup>13</sup> recorded the rotational transitions in the frequency range 1-1.6 THz and derived  $H_0 = 0.0774(58)$  Hz with an uncertainty of 7.5% in their Fit 2. Including the octic centrifugal distortion constant (Fit 1), they found  $H_0 = 0.137(46)$  Hz and  $L_0 = -0.118(91)$  mHz, so that  $H_0$  with an uncertainty of 34% became less accurate. Since Cazzoli et al.<sup>13</sup> suggested that Fit 2 is more reliable than Fit 1, we quote their values from Fit 2 in Table I. These authors also reported the equilibrium sextic centrifugal distortion constant  $H_e = 0.060$  Hz, obtained by the vibrational second-order perturbational approach at the CCSD(T)/aug-cc-pCV5Z level of theory.

The sextic centrifugal distortion constant  $H_0$  for the ground vibrational state of  $\text{HCO}^+$  in Table I is explicitly  $H_0 = 0.0711171(59)$  Hz, where the uncertainty in the last digits quoted in parentheses is one standard deviation. To test the quality of our  $H_0$ , we included  $J = 20$  and  $J = 30$  transitions in the fitting procedure, yielding  $H_0 = 0.07071(1)$  Hz with  $\sigma_0 = 506$  Hz for the sixth-order rotational representation and  $H_0 = 0.0712989(4)$  Hz,  $L_0 = -0.0004022(3)$  mHz, and  $\sigma_0 = 1.41$  Hz for the eighth-order rotational representation. The latter  $H_0$  value and  $H_0$  from Table I differ by 0.00018 Hz (0.25%). The difference between our  $H_0$  and the result of Cazzoli et al.<sup>13</sup> is 0.006 Hz (less than 10%).

Individual standard deviations of the fitting param-

TABLE I: Spectroscopic parameters for the isotopic variants of  $\text{HCO}^+$ . Experimental values are given in brackets.

Parameter	$\text{H}^{12}\text{C}^{16}\text{O}^+$	$\text{H}^{12}\text{C}^{17}\text{O}^+$	$\text{H}^{12}\text{C}^{18}\text{O}^+$	$\text{H}^{13}\text{C}^{16}\text{O}^+$	$\text{H}^{13}\text{C}^{17}\text{O}^+$	$\text{H}^{13}\text{C}^{18}\text{O}^+$
$B_0$ / MHz	44376.28	43315.62	42372.29	43164.34	42087.62	41129.91
$D_0$ / kHz	81.95 [82.83] <sup>a</sup>	78.10 [79.08] <sup>b</sup>	74.76	77.59 [78.41] <sup>c</sup>	73.80	70.51
$H_0$ / Hz	0.071 [0.077] <sup>a</sup>	0.065	0.061	0.063	0.058	0.053
$\sigma_0$ / Hz	8.45	9.03	7.64	8.52	7.63	6.67
$\Delta B_0$ / MHz	243.73	235.44	228.15	234.10	225.80	218.50
$B_0^{\text{est}}$ / MHz	44594.42 [44594.43] <sup>a</sup>	43528.77 [43528.93] <sup>b</sup>	42580.99 [42581.21] <sup>d</sup>	43377.18 [43377.30] <sup>c</sup>	42295.37	41333.14 [41333.59] <sup>e</sup>
$T_2$ / $\text{cm}^{-1}$	829.25 [828.23] <sup>c</sup>	828.21	827.29	821.80	820.75	819.82
$B_2$ / MHz	44456.45	43393.39	42447.94	43235.29	42156.31	41196.62
$D_2$ / kHz	83.57 [84.49 <sup>c</sup> , 84.44 <sup>g</sup> ]	79.62	76.19	79.01	75.13	71.76
$H_2$ / Hz	0.084	0.077	0.071	0.074	0.067	0.062
$\sigma_2$ / Hz	11.45	10.43	8.69	9.37	8.69	7.58
$q_2$ / MHz	209.85 [211.76 <sup>f</sup> , 211.78 <sup>g</sup> ]	200.21	191.82	200.36	190.75	182.40
$q_2^J$ / kHz	-1.79 [-1.73 <sup>f</sup> , -1.83 <sup>g</sup> ]	-1.67	-1.56	-1.65	-1.53	-1.42
$q_2^{JJ}$ / Hz	0.024	0.021	0.019	0.020	0.018	0.016
$\sigma_q$ / Hz	9.14	7.36	6.62	11.55	7.07	8.66
$\alpha_2$ / MHz	-80.17	-77.77	-75.66	-70.95	-68.69	-66.70
$B_2^{\text{est}}$ / MHz	44674.59 [44677.15 <sup>c,f</sup> , 44676.97 <sup>g</sup> ]	43606.54	42656.65 [42659.16] <sup>e</sup>	43448.13 [43450.52] <sup>e</sup>	42364.07	41399.84 [41402.39] <sup>e</sup>
$T_3$ / $\text{cm}^{-1}$	2179.09 [2183.95] <sup>c</sup>	2152.31	2128.19	2145.35	2117.55	2092.51
$B_3$ / MHz	44083.69	43032.70	42097.95	42880.92	41814.02	40865.01
$D_3$ / kHz	82.04 [82.90] <sup>g</sup>	78.18	74.83	77.69	73.89	70.59
$H_3$ / Hz	0.070	0.065	0.060	0.062	0.057	0.053
$\sigma_3$ / Hz	7.51	7.09	6.05	7.07	6.23	5.65
$\alpha_3$ / MHz	292.59	282.91	274.34	283.42	273.60	264.90
$B_3^{\text{est}}$ / MHz	44301.83 [44299.87] <sup>c,g</sup>	43245.85	42306.65 [42305.02] <sup>e</sup>	43093.76 [43091.85] <sup>e</sup>	42021.77	41068.24
$T_1$ / $\text{cm}^{-1}$	3085.58 [3088.74] <sup>c</sup>	3083.08	3080.96	3062.99	3060.86	3059.05
$B_1$ / MHz	44023.87	42972.11	42037.62	42836.68	41769.75	40821.17
$D_1$ / kHz	81.22 [82.09 <sup>f</sup> , 82.06 <sup>g</sup> ]	77.42	74.11	76.98	73.20	69.93
$H_1$ / Hz	0.068	0.065	0.061	0.062	0.058	0.054
$\sigma_1$ / Hz	14.70	13.02	10.42	9.29	9.19	9.37
$\alpha_1$ / MHz	352.41	343.51	334.67	327.66	317.87	308.74
$B_1^{\text{est}}$ / MHz	44242.01 [44240.53] <sup>f,g</sup>	43185.26	42246.32 [42244.86] <sup>e</sup>	43049.52 [43048.16] <sup>e</sup>	41977.50	41024.39

<sup>a</sup> Fit 2 of Cazzoli et al.<sup>13</sup><sup>b</sup> Dore et al.<sup>49</sup><sup>c</sup> Lattanzi et al.<sup>1</sup><sup>d</sup> Bogey et al.<sup>9</sup><sup>e</sup> taken from Puzzarini et al.<sup>62</sup><sup>f</sup> Neese et al.<sup>21</sup><sup>g</sup> Hirao et al.<sup>63</sup>

TABLE II: Spectroscopic parameters for the isotopic variants of  $\text{DCO}^+$ . Experimental values are given in brackets.

Parameter	$\text{D}^{12}\text{C}^{16}\text{O}^+$	$\text{D}^{12}\text{C}^{17}\text{O}^+$	$\text{D}^{12}\text{C}^{18}\text{O}^+$	$\text{D}^{13}\text{C}^{16}\text{O}^+$	$\text{D}^{13}\text{C}^{17}\text{O}^+$	$\text{D}^{13}\text{C}^{18}\text{O}^+$
$B_0$ / MHz	35851.81	35006.52	34252.67	35201.11	34339.34	33570.60
$D_0$ / kHz	55.21 [55.80] <sup>a, b</sup>	52.49	50.13	52.85	50.16	47.83
$H_0$ / Hz	0.050 [0.052 <sup>a</sup> , 0.054 <sup>b</sup> ]	0.046	0.043	0.046	0.043	0.040
$\sigma_0$ / Hz	6.56	6.16	5.62	5.74	5.05	3.81
$\Delta B_0$ / MHz	173.53	167.61	162.40	168.75	162.78	157.52
$B_0^{\text{est}}$ / MHz	36019.81 [36019.77] <sup>a, b</sup>	35170.82	34413.66	35366.70	34501.13	33729.00
$T_2$ / $\text{cm}^{-1}$	666.30 [666±3] <sup>c</sup>	664.98	663.81	656.85	655.51	654.33
$B_2$ / MHz	35946.99	35099.19	34343.11	35288.40	34424.21	33653.32
$D_2$ / kHz	56.82 [57.52 <sup>a</sup> , 57.41 <sup>d</sup> ]	54.00	51.56	54.30	51.52	49.11
$H_2$ / Hz	0.063	0.058	0.054	0.058	0.053	0.049
$\sigma_2$ / Hz	12.29	9.29	9.25	8.60	8.83	10.38
$q_2$ / MHz	169.56 [171.02 <sup>a</sup> , 170.99 <sup>d</sup> ]	161.98	155.36	165.76	158.07	151.35
$q_2^J$ / kHz	-1.32 [-1.84 <sup>a</sup> , -1.29 <sup>d</sup> ]	-1.23	-1.15	-1.25	-1.16	-1.08
$q_2^{JJ}$ / Hz	0.023	0.021	0.019	0.020	0.018	0.016
$\sigma_q$ / Hz	5.05	7.90	4.07	6.73	5.28	11.54
$\alpha_2$ / MHz	-95.18	-92.68	-90.45	-87.29	-84.87	-82.72
$B_2^{\text{est}}$ / MHz	36115.00 [36116.79 <sup>a</sup> , 36116.67 <sup>d</sup> ]	35263.50	34504.10	35453.99	34586.00	33811.72
$T_3$ / $\text{cm}^{-1}$	1900.81 [1904.06] <sup>a</sup>	1885.26	1870.75	1893.85	1877.24	1861.73
$B_3$ / MHz	35646.33	34809.36	34062.72	35003.43	34149.75	33388.01
$D_3$ / kHz	55.18 [55.58] <sup>a</sup>	52.45	50.09	52.81	50.12	47.78
$H_3$ / Hz	0.049	0.045	0.043	0.044	0.042	0.039
$\sigma_3$ / Hz	2.44	3.07	3.23	3.29	1.42	3.84
$\alpha_3$ / MHz	205.48	197.16	189.94	197.69	189.59	182.59
$B_3^{\text{est}}$ / MHz	35814.34 [35813.35] <sup>a, d</sup>	34973.67	34223.71	35169.01	34311.54	33546.41
$T_1$ / $\text{cm}^{-1}$	2580.46 [2584.56] <sup>a</sup>	2566.34	2554.23	2529.47	2515.77	2504.09
$B_1$ / MHz	35626.92	34766.94	34001.31	34835.62	33975.49	33199.35
$D_1$ / kHz	46.05 [46.36] <sup>a</sup>	41.38	40.52	40.28	32.04	14.39
$H_1$ / Hz	-2.441	-1.051	0.040	-4.010	-7.542	-21.207
$L_1$ / mHz	0.326	-0.234	-0.199	1.566	3.765	15.944
$K_1$ / $\mu\text{Hz}$	0.037	0.081	0.004	-0.697	-1.974	-11.878
$M_1$ / nHz				0.300	0.797	5.932
$\sigma_1$ / Hz	3.92	6.83	3.17	9.76	16.40	30.07
$\alpha_1$ / MHz	224.89	239.58	251.36	365.50	363.85	371.25
$B_1^{\text{est}}$ / MHz	35794.93 [35792.33] <sup>a, d</sup>	34931.25	34162.30	35001.20	34137.28	33357.74

<sup>a</sup> Lattanzi et al.<sup>1</sup><sup>b</sup> Caselli and Dore.<sup>50</sup><sup>c</sup> Foltynowicz et al.<sup>64</sup><sup>d</sup> Hirao et al.<sup>65</sup>

eters in Tables I-IV are not listed for brevity. For a given model, the vast majority of the parameters are found to be statistically well-defined, with an uncertainty of less than 1%. All the parameters for the isotopic variants of HCO<sup>+</sup> in Table I have an uncertainty of less than 0.1%. Uncertainties of three parameters in Table II, five in Table III, and three in Table IV are larger than 5%. In Table II, for instance, these are  $K_1(\text{DC}^{18}\text{O}^+) = 0.0041(7)$   $\mu\text{Hz}$ ,  $M_1(\text{D}^{13}\text{CO}^+) = 0.300(40)$  nHz, and  $M_1(\text{D}^{13}\text{C}^{17}\text{O}^+) = 0.797(67)$  nHz.

For all the systems in Tables I-IV, we additionally calculated the rovibrational energies for  $J = 30$  in both parities and compared them with the predictions from the term formulas. We found an agreement better than 1 MHz for all 24 systems in the vibrational ground state, as well as for HCO<sup>+</sup> and DCO<sup>+</sup> in the excited  $\nu_2$  and  $\nu_3$  states. For the HOC<sup>+</sup> and DOC<sup>+</sup> forms in the excited  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  states, the agreement is within 17 and 7 MHz, respectively. The rotational excitation in the  $\nu_1$  state of the D<sup>12</sup>CO<sup>+</sup> forms is predicted better than 10 MHz. For D<sup>13</sup>C<sup>16</sup>O<sup>+</sup>, D<sup>13</sup>C<sup>17</sup>O<sup>+</sup>, and D<sup>13</sup>C<sup>18</sup>O<sup>+</sup> in the excited  $\nu_1$  state, the agreement is within 40, 75, and 625 MHz. The less satisfactory performance in the latter three cases is an indication of more complex internal dynamics. The  $J = 30$  rotational energies correspond to approximately 1400 cm<sup>-1</sup> (about 40 THz).

## B. Equilibrium structure

The rotational constants  $B_0, B_1, B_2, B_3$  in Tables I-IV are approximately 200 MHz smaller than the experimental values. These discrepancies arise primarily from the equilibrium distances, found to be slightly too long (approximately 0.2-0.3 %) for the CCSD(T)/cc-pVQZ potential energy surface.<sup>57</sup>

In the traditional spectroscopic approach,<sup>67</sup> the rovibrational correction  $S_{v_1, v_2, v_3}$  to the equilibrium rotational constant  $B_e$  is given by

$$S_{v_1, v_2, v_3} = B_e - B_{v_1, v_2, v_3} = \sum_{i=1}^3 \alpha_i \left( v_i + \frac{d_i}{2} \right), \quad (5)$$

where  $\alpha_i$  is a vibration-rotation interaction constant for the  $i$ th vibrational mode with the degree of degeneracy  $d_i$ , in fact

$$\begin{aligned} \alpha_1 &= B_{0,0,0} - B_{1,0,0}, & \alpha_2 &= B_{0,0,0} - B_{0,1,0}, & \text{and} \\ \alpha_3 &= B_{0,0,0} - B_{0,0,1}. \end{aligned} \quad (6)$$

For the ground vibrational state, this gives

$$S_0 = \frac{1}{2} (\alpha_1 + 2\alpha_2 + \alpha_3), \quad (7)$$

so that

$$B_i = B_e - S_0 - \alpha_i \quad \text{for } i = 1, 2, 3. \quad (8)$$

From our calculations, on the other hand, we have

$$\Delta B_0 = B_e^{th} - B_0^{th}, \quad (9)$$

where  $B_e^{th}$  and  $B_0^{th}$  are theoretical values of the rotational constant at equilibrium and in the ground vibrational state, respectively. Thus

$$B_i^{th} = B_e^{th} - \Delta B_0 - \alpha_i^{th} \quad \text{for } i = 1, 2, 3, \quad (10)$$

where  $\alpha_i^{th} = B_0^{th} - B_i^{th}$ . The equilibrium rotational constant  $B_e^{th}$  provides the major contribution to  $B_i^{th}$  in Eq. (10). Replacing  $B_e^{th}$  with another value  $B_e^{est}$ , we obtain new estimates for the ground state rotational constant,  $B_0^{est}$ , and for the rotational constant in the excited  $i$ th vibrational mode,  $B_i^{est}$ , as follows

$$B_0^{est} = B_e^{est} - \Delta B_0 \quad \text{and} \quad B_i^{est} = B_e^{est} - \Delta B_0 - \alpha_i^{th}, \quad (11)$$

respectively. Hereby we assume that  $\Delta B_0$  and  $\alpha_i^{th}$  are unchanged with respect to Eqs. (9) and (10), in fact that the coupling between the overall rotation and vibrations is well described by the computational approach employed. To obtain good estimates  $B_i^{est}$  in Eq. (11), we need a best possible estimate  $B_e^{est}$ . In Tables I-IV, the theoretical values  $B_i^{th}$  and  $\alpha_i^{th}$  are shown without the superscript.

The experimental ground state rotational constants  $B_0^{exp}$  are available for HCO<sup>+</sup>, HC<sup>17</sup>O<sup>+</sup>, HC<sup>18</sup>O<sup>+</sup>, H<sup>13</sup>CO<sup>+</sup>, and H<sup>13</sup>C<sup>18</sup>O<sup>+</sup> (Table I), as well as for DCO<sup>+</sup>, DC<sup>18</sup>O<sup>+</sup>, and D<sup>13</sup>CO<sup>+</sup> (Table II). Combining the experimental  $B_0^{exp}$  values with our vibration-rotation corrections  $\Delta B_0$ , so that

$$B_e^{est} = B_0^{exp} + \Delta B_0, \quad (12)$$

we determined from eight  $B_e^{est}$  values the equilibrium distances  $r_e(\text{CH})$  and  $r_e(\text{CO})$  of HCO<sup>+</sup> by means of a non-linear least-squares technique (the Levenberg-Marquardt algorithm). The calculated distances  $r_e(\text{CH})$  and  $r_e(\text{CO})$  are listed in Table V, along with the values recommended by Botschwina et al.,<sup>68</sup> Puzzarini et al.,<sup>62</sup> and Dore et al.<sup>69</sup> The equilibrium distances due to Puzzarini et al.<sup>62</sup> are quoted there with the uncertainty of one standard deviation, as given also in Ref. 69. Dore et al.<sup>69</sup> derived the equilibrium structure of HCO<sup>+</sup> from the millimeter wave spectroscopy data for the four species HCO<sup>+</sup>, DCO<sup>+</sup>, H<sup>13</sup>CO<sup>+</sup>, and HC<sup>18</sup>O<sup>+</sup>. In our Fit 4, we employ the data from Tables I and II only for these four systems. Our results in Table V agree nicely with the experimental values of Dore and coworkers,<sup>69</sup> with our  $r_e(\text{CH})$  distance being shorter by  $6 \times 10^{-5}$  Å and  $r_e(\text{CO})$  longer by  $3.5 \times 10^{-5}$  Å. The agreement of the corresponding  $B_e$  constants is within 1.6 MHz. Table V provides also the equilibrium structure computed by Czako et al.<sup>70</sup> at the all electron CCSD(T)/aug-cc-pCVQZ level of theory. Compared to the results of Dore et al.<sup>69</sup> and found here, the theoretical  $r_e(\text{CH})$  and  $r_e(\text{CO})$  values of Czako et al.<sup>70</sup> are both longer,  $r_e(\text{CH})$  by  $5 \times 10^{-4}$  Å and  $r_e(\text{CO})$  by  $1 \times 10^{-3}$  Å, whereas  $B_e$  is smaller by 74 MHz.

The equilibrium structure of HOC<sup>+</sup> was a subject of controversy. From the observation of the isotopic variants H<sup>18</sup>OC<sup>+</sup> and HO<sup>13</sup>C<sup>+</sup>, Gudeman and Woods<sup>33</sup> derived a

TABLE III: Spectroscopic parameters for the isotopic variants of  $\text{HOC}^+$ . Experimental values are given in brackets.

Parameter	$\text{H}^{16}\text{O}^{12}\text{C}^+$	$\text{H}^{17}\text{O}^{12}\text{C}^+$	$\text{H}^{18}\text{O}^{12}\text{C}^+$	$\text{H}^{16}\text{O}^{13}\text{C}^+$	$\text{H}^{17}\text{O}^{13}\text{C}^+$	$\text{H}^{18}\text{O}^{13}\text{C}^+$
$B_0$ / MHz	44510.75	43757.35	43078.22	42652.08	41884.71	41192.97
$D_0$ / kHz	113.76	109.59	105.96	104.17	100.14	96.64
	[114.57] <sup>a</sup>					
$H_0$ / Hz	0.760	0.658	0.579	0.620	0.526	0.458
	[2.12] <sup>a</sup>					
$L_0$ / mHz	-0.046	-0.038	-0.032	-0.035	-0.028	-0.023
$\sigma_0$ / Hz	4.30	3.66	2.99	2.76	3.18	2.36
$\Delta B_0$ / MHz	42.57	54.65	65.13	44.20	55.75	65.71
$B_0^{\text{est}}$ / MHz	44743.93	43987.56	43305.74	42876.39	42105.94	41411.39
	[44743.91] <sup>a</sup>		[43305.99] <sup>b</sup>	[42876.56] <sup>b</sup>		
$T_2$ / $\text{cm}^{-1}$	243.60	242.26	241.08	243.22	241.89	240.71
$B_2$ / MHz	44705.05	43933.78	43239.03	42831.80	42047.22	41340.39
$D_2$ / kHz	116.15	111.68	107.78	106.30	102.04	98.31
	[117.23] <sup>a</sup>					
$H_2$ / Hz	0.284	0.226	0.177	0.229	0.186	0.147
$L_2$ / mHz	0.028	0.027	0.026	0.018	0.019	0.018
$\sigma_2$ / Hz	8.38	7.84	6.77	3.57	4.61	6.12
$q_2$ / MHz	517.07	502.44	489.34	475.81	461.30	448.38
	[518.77] <sup>a</sup>					
$q_2^J$ / kHz	-20.66	-19.07	-17.72	-17.84	-16.35	-15.12
	[-20.48] <sup>a</sup>					
$q_2^{JJ}$ / Hz	1.484	1.326	1.204	1.196	1.054	0.949
$q_2^{JJJ}$ / mHz	-0.150	-0.132	-0.118	-0.105	-0.095	-0.087
$q_2^{JJJJ}$ / $\mu\text{Hz}$	0.016	0.015	0.012	0.008	0.008	0.012
$\sigma_q$ / Hz	2.40	1.17	1.60	1.92	1.62	3.57
$\alpha_2$ / MHz	-194.30	-176.43	-160.80	-179.72	-162.51	-147.42
$B_2^{\text{est}}$ / MHz	44938.23	44163.99	43466.54	43056.12	42268.46	41558.81
	[44939.79] <sup>a</sup>					
$T_3$ / $\text{cm}^{-1}$	1901.32	1880.68	1862.01	1858.64	1837.41	1818.20
$B_3$ / MHz	44152.59	43406.90	42734.72	42314.73	41555.11	40870.41
$D_3$ / kHz	115.39	111.06	107.30	105.45	101.30	97.72
$H_3$ / Hz	1.066	0.859	0.725	0.715	0.612	0.528
$L_3$ / mHz	-0.251	-0.142	-0.091	-0.057	-0.047	-0.037
$K_3$ / $\mu\text{Hz}$	0.119	0.054	0.026	0.007	0.005	0.005
$\sigma_3$ / Hz	8.36	4.19	3.43	7.06	5.64	3.01
$\alpha_3$ / MHz	358.16	350.45	343.50	337.35	329.60	322.56
$B_3^{\text{est}}$ / MHz	44385.77	43637.11	42962.23	42539.05	41776.34	41088.83
$T_1$ / $\text{cm}^{-1}$	3276.54	3269.21	3262.83	3276.14	3268.78	3262.43
	[3268.03] <sup>c</sup>					
$B_1$ / MHz	44226.48	43487.88	42821.85	42385.97	41632.26	40953.21
$D_1$ / kHz	115.01	110.57	106.81	105.58	100.93	97.28
	[116.4] <sup>c</sup>					
$H_1$ / Hz	1.045	0.893	0.820	0.863	0.713	0.628
$L_1$ / mHz	-0.067	-0.055	-0.058	-0.013	-0.040	-0.035
$\sigma_1$ / Hz	14.12	5.05	12.65	23.52	10.85	3.64
$\alpha_1$ / MHz	284.27	269.47	256.37	266.11	252.45	239.76
$B_1^{\text{est}}$ / MHz	44459.65	43718.10	43049.36	42610.28	41853.49	41171.63
	[44457.10] <sup>c</sup>					

<sup>a</sup> Amano and Maeda.<sup>45</sup><sup>b</sup> calculated from the transition  $J = 0 \rightarrow 1$  observed by Gudeman and Woods.<sup>33,34</sup><sup>c</sup> Nakanaga and Amano.<sup>43</sup>

preliminary substituted  $r_s$  structure of  $\text{HOC}^+$ , with the substitution bond lengths equal to  $r_s(\text{CO}) = 1.1595 \text{ \AA}$  and  $r_s(\text{OH}) = 0.9342 \text{ \AA}$ . Compared to available theoretical values,<sup>72</sup>  $r_e(\text{CO}) = 1.1536 \text{ \AA}$  and  $r_e(\text{OH}) = 0.9892 \text{ \AA}$ ,

the result for  $r_s(\text{OH})$  appeared to be too short. This discrepancy has been ascribed to a very low-frequency bending mode. Gudeman and Woods<sup>33</sup> also suspected that the bending potential of  $\text{HOC}^+$  may possibly be



TABLE IV: Spectroscopic parameters for the isotopic variants of  $\text{DOC}^+$ . Experimental values are given in brackets.

Parameter	$\text{D}^{16}\text{O}^{12}\text{C}^+$	$\text{D}^{17}\text{O}^{12}\text{C}^+$	$\text{D}^{18}\text{O}^{12}\text{C}^+$	$\text{D}^{16}\text{O}^{13}\text{C}^+$	$\text{D}^{17}\text{O}^{13}\text{C}^+$	$\text{D}^{18}\text{O}^{13}\text{C}^+$
$B_0$ / MHz	38013.93	37570.59	37166.05	36472.02	36012.45	35593.01
$D_0$ / kHz	93.59	90.40	87.60	85.27	82.21	79.52
	[93.86] <sup>a</sup>					
$H_0$ / Hz	2.305	2.100	1.925	1.896	1.716	1.564
	[2.15] <sup>a</sup>					
$L_0$ / mHz	-0.245	-0.217	-0.193	-0.188	-0.165	-0.147
$K_0$ / $\mu\text{Hz}$	0.026	0.022	0.018	0.018	0.016	0.014
$\sigma_0$ / Hz	0.88	0.90	1.13	1.08	1.35	1.00
$\Delta B_0$ / MHz	-146.99	-132.31	-119.25	-137.33	-123.03	-110.33
$B_0^{\text{sst}}$ / MHz	38193.18	37748.78	37343.26	36645.09	36184.37	35763.86
	[38193.20] <sup>a</sup>					
$T_2$ / $\text{cm}^{-1}$	176.57	174.88	173.37	176.06	174.36	172.86
$B_2$ / MHz	38338.54	37877.02	37456.30	36777.25	36299.86	35864.58
$D_2$ / kHz	100.63	96.79	93.44	91.51	87.85	84.65
$H_2$ / Hz	1.734	1.543	1.382	1.429	1.261	1.119
$L_2$ / mHz	-0.049	-0.036	-0.027	-0.039	-0.029	-0.017
$K_2$ / $\mu\text{Hz}$	-0.012	-0.011	-0.010	-0.007	-0.006	-0.009
$\sigma_2$ / Hz	1.02	1.22	0.70	0.99	1.40	0.53
$q_2$ / MHz	512.16	505.01	498.38	473.08	465.62	458.72
$q_2^J$ / kHz	-31.90	-30.35	-28.95	-27.86	-26.40	-25.09
$q_2^{JJ}$ / Hz	3.024	2.813	2.631	2.481	2.297	2.140
$q_2^{JJJ}$ / mHz	-0.378	-0.346	-0.318	-0.288	-0.263	-0.246
$q_2^{JJJJ}$ / $\mu\text{Hz}$	0.056	0.048	0.043	0.039	0.034	0.034
$\sigma_q$ / Hz	1.74	1.42	1.61	1.72	1.84	1.48
$\alpha_2$ / MHz	-324.61	-306.43	-290.25	-305.23	-287.42	-271.57
$B_2^{\text{sst}}$ / MHz	38517.78	38055.22	37633.51	36950.33	36471.78	36035.43
$T_3$ / $\text{cm}^{-1}$	1839.77	1826.19	1813.48	1800.12	1785.61	1772.06
$B_3$ / MHz	37753.34	37314.77	36914.28	36225.78	35770.95	35355.57
$D_3$ / kHz	94.01	91.10	88.50	85.72	82.88	80.36
$H_3$ / Hz	2.352	2.180	2.029	1.941	1.787	1.652
$L_3$ / mHz	-0.250	-0.228	-0.207	-0.189	-0.173	-0.156
$K_3$ / $\mu\text{Hz}$	0.023	0.024	0.020	0.011	0.015	0.013
$\sigma_3$ / Hz	5.76	3.21	1.64	8.91	2.72	3.74
$\alpha_3$ / MHz	260.59	255.83	251.77	246.23	241.50	237.45
$B_3^{\text{sst}}$ / MHz	37932.58	37492.96	37091.50	36398.86	35942.87	35526.41
$T_1$ / $\text{cm}^{-1}$	2482.93	2467.11	2453.43	2478.97	2463.55	2450.23
$B_1$ / MHz	37718.13	37285.03	36890.03	36191.94	35742.86	35333.10
$D_1$ / kHz	99.88	95.84	92.34	90.66	86.84	83.54
$H_1$ / Hz	3.434	3.061	2.758	2.801	2.486	2.229
$L_1$ / mHz	-0.425	-0.367	-0.316	-0.327	-0.280	-0.244
$K_1$ / $\mu\text{Hz}$	0.058	0.046	0.036	0.037	0.032	0.027
$\sigma_1$ / Hz	3.84	4.73	4.28	7.21	5.20	3.41
$\alpha_1$ / MHz	295.80	285.56	276.02	280.08	269.59	259.92
$B_1^{\text{sst}}$ / MHz	37897.37	37463.23	37067.24	36365.02	35914.78	35503.94

<sup>a</sup> Amano and Maeda.<sup>45</sup>

quasilinear. The calculations of Kraemer and Bunker<sup>73</sup> showed that  $\text{HOC}^+$  is not quasilinear, but linear with a very shallow bending potential.

To derive the equilibrium structure of  $\text{HOC}^+$ , we employ the ground-state rotational constants for  $\text{HOC}^+$  and  $\text{DOC}^+$  due to Amano and Maeda.<sup>45</sup> From the  $J = 0 \rightarrow 1$  transition, observed for  $\text{HO}^{13}\text{C}^+$  and  $\text{H}^{18}\text{OC}^+$  by Gudeman and Woods,<sup>33,34</sup> we derive the rotational constant

$B_0$  from

$$\Delta E_0^1 = 2B_0 - 4D_0, \quad (13)$$

where  $\Delta E_0^1$  stands for the lowest transition. For  $D_0$ , we employ our result from Table III. The values obtained with the help of Eq. (13) are listed in Table III as experimental  $B_0$  results for  $\text{HO}^{13}\text{C}^+$  and  $\text{H}^{18}\text{OC}^+$ . The computed equilibrium distances  $r_e(\text{HO})$  and  $r_e(\text{CO})$  are provided in Table V. In Fit 2, we use only the experimental  $B_0$  values reported by Amano and Maeda.<sup>45</sup>

TABLE V: Equilibrium distances (in Å) and equilibrium rotational constants (in MHz) of  $\text{HCO}^+$  and  $\text{HOC}^+$ .<sup>a</sup>

$\text{HCO}^+$	$r_e(\text{CH})$	$r_e(\text{CO})$	$B_e(\text{HCO}^+)$
This work	1.091 981(7)	1.105 615(2)	44 838.2
This work, Fit 4	1.091 989(1)	1.105 6137(3)	44 838.2
Dore et al. <sup>69</sup>	1.092 04	1.105 58	44 839.8
Puzzarini et al. <sup>62</sup>	1.091 9(3)	1.105 5(1)	44 847.1
Botschwina et al. <sup>68</sup>	1.091 9	1.105 8	44 826.7
Czakó et al. <sup>70</sup>	1.092 5	1.106 6	44 764.4
$\text{HOC}^+$	$r_e(\text{HO})$	$r_e(\text{CO})$	$B_e(\text{HOC}^+)$
This work	0.990 482(7)	1.154 468(2)	44 786.5
This work, Fit 2	0.990 478	1.154 469	44 786.5
Botschwina et al. <sup>68</sup>	0.988 5	1.154 6	44 800.3
Martin et al. <sup>71</sup>	0.988 17	1.154 71	44 796.6

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

The best estimate of Martin et al.<sup>71</sup> and the values recommended by Botschwina et al.<sup>68</sup> are also shown. Our finding agrees with the results from Refs. 68,71 within 0.002 Å and 0.0001-0.0002 Å for  $r_e(\text{HO})$  and  $r_e(\text{CO})$ , respectively.

The equilibrium structures of Table V for  $\text{HCO}^+$  and  $\text{HOC}^+$  are used to compute the best estimates  $B_e^{\text{est}}$  of the equilibrium rotational constants. Having derived  $B_e^{\text{est}}$ , the best estimates  $B_i^{\text{est}}$  of the effective rotational constant for the  $i$ th fundamental vibration are calculated using Eq. (11). The values of  $B_i^{\text{est}}$  are given in Tables I-IV, where we also list the theoretical vibration-rotation constants  $\alpha_1, \alpha_2, \alpha_3$ . As seen, our  $B_2^{\text{est}}$  values are smaller and  $B_1^{\text{est}}, B_3^{\text{est}}$  larger by at most 3 MHz than the experimental results.

Additional note is needed regarding the procedure we use to derive the equilibrium structure of  $\text{HCO}^+$  and  $\text{HOC}^+$ . We compute the equilibrium distances by nonlinear least-squares fittings of  $B_e^{\text{est}}$ , computed from the experimental  $B_0^{\text{exp}}$  and theoretical  $\Delta B_0 = B_e^{\text{th}} - B_0^{\text{th}}$  values. Each of the input data was associated with a standard deviation  $\sigma_{e_{\text{exp}}}$ . Experimental standard deviations  $\sigma_e$  for  $B_0^{\text{exp}}$  are known from the literature,<sup>1,9,13,33,34,45,49,50,62</sup> varying from 0.00016 MHz to 0.060 MHz. For standard deviations  $\sigma_\Delta$  of  $\Delta B_0$ , we used standard deviations of our  $B_0$  values, which are in order of  $10^{-7}$  MHz and thus much smaller than  $\sigma_e$ . Herewith the description of our mathematical model is completed. The equilibrium distances shown in Table V should be viewed as the least-squares solutions to this well-postulated mathematical problem. The standard deviations in order of  $10^{-6}$  Å in Table V are a mathematical (quantitative) measure of the accuracy of  $r_e$  with respect to the model used. The accuracy of our

model is defined by the accuracy of the experimental data coming from different sources and the accuracy of the CCSD(T)/cc-pVQZ potential energy surface. The PES does not include effects beyond the Born-Oppenheimer approximation or relativistic corrections. This deficiency, however, poses no major problem since we use the PES only to determine  $\Delta B_0$ . We expect small change of excluded electronic-structure contributions over the coordinate range relevant in our calculations. Good agreement of our results with known experimental data in Tables I-III supports this statement. To exemplify the changes of the equilibrium rotational constant with the equilibrium distances reported so far, we provide also the corresponding  $B_e$  values in Table V.

#### IV. FINAL REMARKS

In the present work, we employed a pure ab initio potential energy surface in combination with the exact kinetic energy operator and an efficient numerical approach to calculate the rovibrational energies of  $\text{HCO}^+$  and  $\text{HOC}^+$  for  $J = 0 - 15$ . Fitting them to appropriate spectroscopic formulae, we derived the theoretical spectroscopic parameters, including higher-order centrifugal distortion constants. Since the fit standard deviations are approximately 10 Hz ( $3 \cdot 10^{-10} \text{ cm}^{-1}$ ), the spectroscopic parameters provide a compact representation of the calculated rovibrational energies and allow for a quick comparison with experiment. This type of analysis was carried out for each of the isotopologues of  $\text{HCO}^+$  and  $\text{HOC}^+$  involving H, D, <sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O, <sup>12</sup>C, and <sup>13</sup>C. As such, these results form a consistent set of data. Combining the experimental  $B_0$  rotational constants with our vibration-rotation corrections  $\Delta B_0$  for the ground vibrational state, we additionally derived the equilibrium structures of  $\text{HCO}^+$  and  $\text{HOC}^+$ .

In experimental approaches, the vibration-rotation interaction constants  $\alpha_1, \alpha_2, \alpha_3$  are used to determine the vibration-rotation correction  $S_0$  of Eq. (7) in the ground vibrational state. For small-amplitude vibrations (rigid molecular systems),  $S_0 \approx \Delta B_0$  holds. In other cases, the use of  $S_0$  may lead to the equilibrium structure inconsistency problem. This was reported by Dore et al.<sup>69,74</sup> for the case of the formyl cation. These authors invoked the vibration-rotation Coriolis interaction to deperturb the state (1,0,0) involved in their description in the Coriolis coupling with (0,1<sup>1</sup>,1), most strongly exhibited in  $\text{DCO}^+$ . Inclusion of additional terms into the effective spectroscopic Hamiltonian is a standard procedure for improving the spectroscopic model, effectively based on the harmonic-oscillator-rigid-rotor description as a zero-order picture. We only note that the Coriolis coupling term in our calculations plays an ordinary (usual) role in the overall internal dynamics of the formyl cation at lower energies.<sup>57</sup>

From the experimental  $B_i^{\text{exp}}$  values listed in Table II for  $\text{DCO}^+$ , one finds using the expression of Eq. (6)

that the experimental vibration-rotation interaction constants are  $\alpha_1^{exp} = 227.44$  MHz,  $\alpha_2^{exp} = -96.9$  MHz, and  $\alpha_3^{exp} = 206.42$  MHz. They agree with our  $\alpha_i$  results within 2.6 MHz. From  $\alpha_i^{exp}$  and  $\alpha_i$ , we calculate  $S_0^{exp} = 120.03$  MHz and  $S_0 = 120.01$  MHz according to Eq. (7). These  $S_0$  values are smaller by 53.5 MHz than  $\Delta B_0(\text{DCO}^+) = 173.53$  MHz in Table II. For the other species involved in our fitting procedure, the difference  $\Delta B_0 - S_0$  amounts to 32.2 and -25.5 MHz for  $\text{DC}^{18}\text{O}^+$  and  $\text{D}^{13}\text{CO}^+$ , respectively, whereas it varies from -1.6 to 1.5 MHz for the hydrogen-containing forms. This is clear evidence for somewhat different internal dynamics in the  $\text{HCO}^+$  and  $\text{DCO}^+$  isotopologues.

To extract information about the equilibrium structure from the experimental rotational  $B_0$  constants, we actually need the quantity  $\Delta B_0$ . This information as such is not accessible to experiment in an easy fashion. In perturbational approaches,  $B_0$  is computed as the vibrationally averaged rotational constant by using some (rigid-rotor) formula for the rotational constant or as  $B_e - S_0$ . Due to this inherent problem, the perturbatively computed  $\Delta B_0$  values are at best of a semi-quantitative nature. We are thus left with the variational method as the only approach capable of providing well-founded  $\Delta B_0$  values that may assist experiment in the evaluation of the equilibrium structure. This is the line of reasoning followed in the present work. As we go further away from rigid molecular systems, this reasoning becomes even more important. In the case of larger systems, where the full-dimensional variational calculation is currently out of reach, we may use a reduced-dimensionality description of the internal motion to obtain variationally computed  $\Delta B_0$  values. In the reduced-dimensionality description, one combines as accurate as possible representations for those degrees of freedom dominating the internal dynamics with a simpler (even harmonic) picture for the other (kinetically inactive) modes. Descriptions of this type are successfully used for weakly bound complexes.

The rovibrational calculations presented in this work were carried out using the atomic masses (given by Mills et al.<sup>59</sup>). This is common practice in quantum mechanical considerations of the internal molecular motion. In the framework of the Born-Oppenheimer approximation, the nuclear motion should, strictly speaking, involve the nuclear masses. To investigate the influence of the atomic versus nuclear masses on the rovibrational states of  $\text{HCO}^+/\text{HOC}^+$ , we performed two test calculations. These results are summarized in Table VI. In Test 1 we replaced  $m(\text{H})$  with the proton mass and in Test 2 we used the nuclear masses of H, C, and O. The reference computation with the atomic masses is denoted as Test 0. The test calculations were carried out for  $J = 0$  and  $J = 1$  only. The properties, we compare in Table VI,

TABLE VI: Selected results for  $\text{HCO}^+$  and  $\text{HOC}^+$  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 <sup>+</sup>			
Property	Test 0	Test 1	Test 2
$\tilde{\nu}_1 / \text{cm}^{-1}$	3085.58	3086.20	3086.29
$\tilde{\nu}_2 / \text{cm}^{-1}$	830.72	830.88	830.91
$\tilde{\nu}_3 / \text{cm}^{-1}$	2179.09	2179.20	2179.44
$\tilde{q}_2 / \text{MHz}$	209.85	209.86	209.94
$\tilde{B}_0 / \text{MHz}$	44376.11	44382.06	44391.21
$\tilde{B}_1 / \text{MHz}$	44023.71	44029.62	44038.64
$\tilde{B}_3 / \text{MHz}$	44083.53	44089.39	44098.46
HOC <sup>+</sup>			
Property	Test 0	Test 1	Test 2
$\tilde{\nu}_1 / \text{cm}^{-1}$	3276.54	3277.30	3277.34
$\tilde{\nu}_2 / \text{cm}^{-1}$	245.07	245.14	245.15
$\tilde{\nu}_3 / \text{cm}^{-1}$	1901.32	1901.34	1901.59
$\tilde{q}_2 / \text{MHz}$	517.00	516.96	517.18
$\tilde{B}_0 / \text{MHz}$	44510.53	44514.78	44524.84
$\tilde{B}_1 / \text{MHz}$	44226.43	44230.69	44240.61
$\tilde{B}_3 / \text{MHz}$	44152.40	44156.58	44166.53

are

$$\begin{aligned}
 \tilde{\nu}_i &= E_i(J=0) - E_0(J=0) \quad \text{for } i = 1, 3, \\
 \tilde{\nu}_2 &= E_2^e(J=1) - E_0(J=0), \\
 \tilde{q}_2 &= \frac{1}{2} \left[ E_2^f(J=1) - E_2^e(J=1) \right], \quad \text{and} \\
 \tilde{B}_i &= \frac{1}{2} \left[ E_i^e(J=1) - E_i(J=0) \right] \quad \text{for } i = 0, 1, 3.
 \end{aligned} \tag{14}$$

The substitution of the atomic masses with the nuclear masses affects the wavenumbers of the  $\nu_1, \nu_2, \nu_3$  vibrations by 0.8, 0.08, and 0.27  $\text{cm}^{-1}$ , respectively. The  $\ell$ -type doubling constant  $\tilde{q}_2$  is changed by 0.09 MHz. The rotational constants  $\tilde{B}_0, \tilde{B}_1$ , and  $\tilde{B}_3$  are increased by 15 MHz.

To quantify the degree of quasilinearity of molecular vibrations, Yamada and Winnemisser<sup>75</sup> introduced the quasilinearity parameter  $\gamma_0$ . In the nomenclature of linear molecules,  $\gamma_0$  is defined by

$$\gamma_0 = 1 - 4 \frac{E_{0,1^1,0} - E_0}{E_{0,2^0,0} - E_0}, \tag{15}$$

yielding  $\gamma_0 = -1$  for a typical linear molecule and  $\gamma = 1$  for a typical bent molecule. Molecules falling between the two limiting cases are commonly called quasilinear. Our results give  $\gamma_0 = -1$  for  $\text{HCO}^+$ , as expected for a degenerate bending mode in well-behaved linear

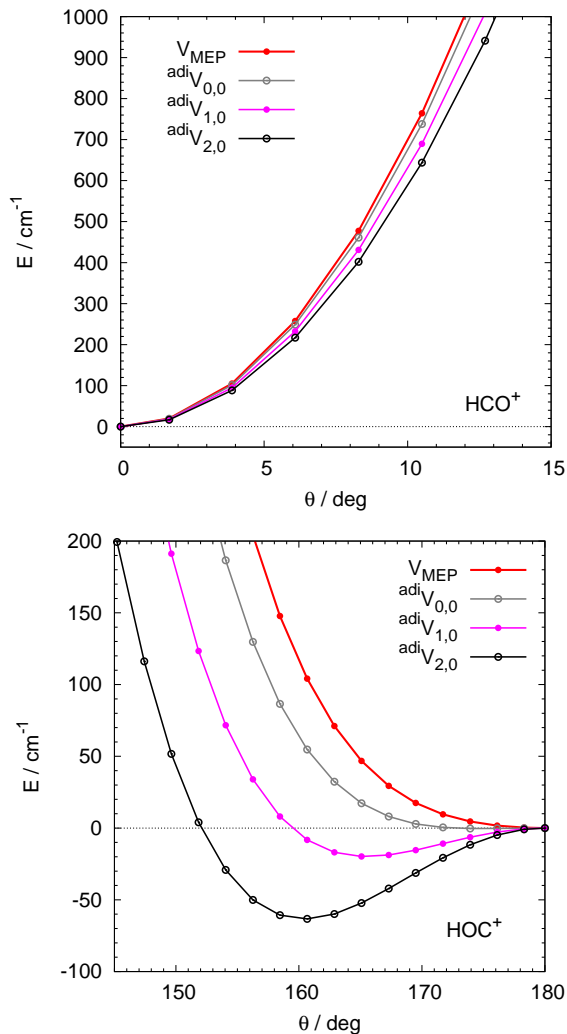


FIG. 1: Minimum energy path  $V_{\text{MEP}}$  and effective bending potential  $\text{adi}V_{v_1,v_3}$  for the (0,0), (1,0) and (2,0) stretching states along the Jacobi angle  $\theta$ . The curves are shifted to coincide at  $\theta = 0^\circ$  for  $\text{HCO}^+$  and at  $\theta = 180^\circ$  for  $\text{HOC}^+$ .

molecules. For  $\text{HOC}^+$ , we find  $\gamma_0 = -0.75$ , such that the two-dimensional bending  $\nu_2$  vibration of  $\text{HOC}^+$  is a quasilinear mode. For comparison purposes, we note that  $\gamma_0 = -0.65$  for the  $\nu_5$  vibration of fulminic acid,  $\text{HCNO}$ ,<sup>75,76</sup> and  $\gamma_0 = -0.12$  for the  $\nu_5$  mode of cyanocarbene,  $\text{HCCN}$ .<sup>77</sup>

To illustrate the internal molecular dynamics in  $\text{HCO}^+$  and  $\text{HOC}^+$ , Figure 1 compares the minimum energy path  $V_{\text{MEP}}$  along the Jacobi angle  $\theta$  with the effective bending potentials  $\text{adi}V_{v_1,0}$  for the excited  $\nu_1$  stretching vibration. The effective bending potentials  $\text{adi}V_{v_1,v_3}$  are computed by an adiabatic projection scheme designed for the DVR+DGB approach in the spirit of the method previously developed for tetratomic molecules.<sup>78</sup> The profile  $\text{adi}V_{v_1,v_3}$  differs from  $V_{\text{MEP}}$  by the angle-dependent energy of the stretching state  $(v_1, v_3)$ , such that  $\text{adi}V_{v_1,v_3}$  provides a more useful rationalization of the bending vibration. We see that  $\text{HCO}^+$  in Fig. 1 becomes less rigid upon excitation of  $\nu_1$ , resulting in a lower effective  $\nu_2$  bending frequency. For  $\text{HOC}^+$ , a wide flat region around  $180^\circ$  is seen on the minimum energy path and on the effective ground-state profile  $\text{adi}V_{0,0}$ , where  $V_{\text{MEP}}(\theta = 160^\circ)$  and  $\text{adi}V_{0,0}(\theta = 160^\circ)$  are approximately 150 and 50  $\text{cm}^{-1}$  higher in energy than the corresponding linear arrangements. The excitation of the stretching  $\nu_1$  vibration increases the floppyness of  $\text{HOC}^+$  since a wider angular region is accessible to  $\nu_2$ . In addition,  $\text{HOC}^+$  becomes effectively bent when the  $\nu_1$  vibration is excited. The barrier to linearity is 20 and 60  $\text{cm}^{-1}$  for  $v_1 = 1$  and  $v_1 = 2$ , respectively. Bending of a linear molecule upon stretching was previously observed in the case of  $\text{C}_3$ .<sup>79</sup>

The profiles in Fig. 1 manifest the coupling between the  $\nu_1$  and  $\nu_2$  vibrational modes. The other effects, such as the radial coupling, the centrifugal distortion effects, or the Coriolis coupling and their influence of the rovibrational structure of  $\text{HCO}^+$  and  $\text{HOC}^+$  will be addressed in more detail in a future publication.

Our final remark concerns the comparison between experiment and theory. To properly address this issue, in addition to electronic-structure single-point computations, full-dimensional rovibrational calculations in conjunction with a potential energy surface are also required.<sup>80,81</sup> This is especially important in the case of non-rigid and quasilinear molecular systems with strong potential energy couplings between the vibrational modes and strong kinetic-energy (vibration-rotation) couplings.

## Acknowledgments

The author thanks Evelyne Roueff, Mila Lewerenz, and Marius Lewerenz for critical reading of the manuscript.

\* Corresponding author; Electronic address: Mirjana.Mladenovic@u-pem.fr

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