MOLECULAR STRUCTURE OF HOCO+*

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ABSTRACT

The rotational spectra of HOCO+ have been completed by the measurements of the *b*-type spectrum. The observation of the submillimeter wave spectrum of the ^{13}C isotopic form together with the previous results obtained for DOCO+ have led to the first experimental determination of the molecular structure of this tetraatomic ion.

INTRODUCTION

The recent laboratory observation of protonated carbon dioxide by submillimeter wave spectroscopy [1,2] and by infrared spectroscopy [3,4] definitively showed that the three unidentified interstellar lines observed in 1981 by Thaddeus et al. [5] and tentatively assigned to either HOCO+ or HOCN, belong to HOCO+ spectrum.

In the meantime many ab initio structure calculations have been published, especially on protonated carbon dioxide [6–9], in order to determine the best candidate for the identification of this "nonterrestrial" molecule. All these theoretical investigations have shown that the most stable isomer of HOCO+ is the O protonated form and that the O–C–O backbone of this molecule is slightly bent, by 4 to 6°, with a *trans* configuration.

If the experimental determination of the equilibrium structure of such a polyatomic molecule is to be possible, it needs a large amount of data. The substitution structure (r_s), which is generally a good approximation for the equilibrium structure (r_e), only requires a knowledge of the rotational constants of the four monoisotopic substitutions.

Nevertheless, for such a slightly bent molecule in which the heavier atoms lie close to the *a* axis, the *b* coordinates deduced from the rotational constants of the different isotopomers by using Kraitchman's equations [10] are poorly

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determined. For the isoelectronic molecules HNCO and HN_3, Yamada [11] and Winnewisser [12] have shown that a more reliable set of b coordinates for the heavier atoms can be obtained by using the center-of-mass condition, the product-of-inertia condition, and the second moment relation with the substitution moment of inertia.

In previous experiments we measured the submillimeter a-type spectra of $HOCO^+$ and $DOCO^+$. In order to determine more precisely the A rotational constants, the b-type spectra were sought and some new a-type lines were also measured in the lower frequency range.

In this work, these new results are presented together with the submillimeter spectrum of the $HO^{13}CO^+$ isotopomer. Knowledge of the rotational data for only three isotopic species is not sufficient to obtain an r_s structure of protonated carbon dioxide as precise as for HNCO or HN_3. Nevertheless, a structure based on the determination of substitution and effective coordinates is given and discussed.

EXPERIMENTAL PROCEDURE

The ions were produced in a negative glow discharge extended by a longitudinal magnetic field. This type of discharge, initially developed by De Lucia et al. [13], is particularly suitable for the search for diamagnetic molecular ions and their absorptions can be easily discriminated from those of neutral species by varying the magnetic field.

The spectra were observed by discharging mixtures of $H_2(D_2)$, $CO_2(^{13}CO_2)$ and argon. The best pressure conditions were: $P(H_2/D_2) = 8$ mtorr, $P(CO_2/^{13}CO_2) = 2$ mtorr with a total pressure of 15–20 mtorr. The $^{13}CO_2$ (99% enriched) was obtained from the Bureau des Isotopes Stables, Commissariat à l'Energie Atomique, France.

The optimum discharge current was 5 mA for a d.c. voltage of $1500-2000$ V and a magnetic field of 250 G. The cell was moderately cooled by slowly flowing liquid nitrogen through a surrounding jacket in the opposite direction to the gas flow.

The spectrometer used for the present measurements has been described elsewhere [14]. The millimeter wave power was obtained by harmonic generation from phase-locked klystrons in a Custom Microwave multiplier equipped with a Schottky-barrier diode. The submillimeter wave power was provided by a CSF carcinotron (TH 4218D) operating in the 330–406 GHz frequency range, either in free running mode or in phase-locked mode. The detection of the absorption signals was achieved with a helium-cooled InSb detector. Source modulation at 12.5 kHz was used and a phase-sensitive detection at 25 kHz provided a second derivative lineshape. A dedicated microprocessor system ensured frequency scans and data processing.

SPECTROSCOPIC RESULTS AND ANALYSIS

For a slight asymmetric prolate rotor such as protonated carbon dioxide, the rotational energy increases rapidly with K_a owing to the large value of the A constant, and, therefore, only the transitions with low K_a values belonging to a-type R branch and b-type P and R branches can be observed between 120 GHz and 405 GHz. Green et al. [15] calculated theoretical values of the a and b dipole components, i.e. $\mu_a = 2D$ and $\mu_b = 2.8D$.

Using these values, a computation of the line intensities showed that, in the same frequency range, the b-type $^rP_0$ lines and the a-type $^qR_0$ lines have the same intensities. Then, the b-type spectrum should be detectable if the frequency predictions are sufficiently accurate.

The analysis of the spectra was carried out by a least-squares procedure using the Watson's S-reduced Hamiltonian [16] in which some higher order diagonal centrifugal distortion terms were added, especially the octic term L_{KJ} and the dectic term S_{KJ}.

For the parent molecule $HOCO^+$, the a-type spectrum [2] was completed by the measurements of some millimeter transitions corresponding to $5 \leq J \leq 11$ and $K_a \leq 3$. A prediction of the b-type spectrum based on the molecular constants previously reported [2] was very inaccurate owing to the non-determination of D_K and the large uncertainty in the A constant (3 GHz). Amano and Tanaka observed both a- and b-type transitions for the ν_1 fundamental band of $HOCO^+$ [4] and predicted the frequencies of the $^rP_0$ branch from $J=2$ up to $J=30$. By carefully scanning the frequency around these predictions, 8 lines were observed for $17 \leq J \leq 29$. The differences between the observed and the predicted frequencies varied from 3 MHz for the lower J transitions up to 20 MHz for the higher J values.

The frequencies of all the new measurements are reported in Table 1.

Owing to the weakness of the lines, the comparison of their intensities was very difficult. Nevertheless it seemed that the a-type lines were roughly two times stronger than the b-type ones. This result is not in agreement with the predictions deduced from ab initio calculation of the dipole moments [5].

Though some b-type lines were measured, the strong correlation between the rotational constant A and the quartic centrifugal distortion constant D_K was not removed. This was related to the small number of observed branches. Consequently, D_K was held fixed to the value given by Amano and Tanaka [4]. In fact, Amano and Tanaka used the A-reduction Hamiltonian to analyze their data but, as the constant δ_K was not determined, we took $D_K = \Delta_K$ [16].

The molecular constants obtained by fitting 54 lines are reported in Table 2. Note that the measurements of b-type lines allowed a better determination of the A rotational constant, even if D_K cannot be independently determined.

All the constants are in good agreement with those given by Amano and Tanaka [4]. Owing to the large value of the sextic centrifugal distortion con-

TABLE 1

Observed and calculated rotational transitions of $HOCO^+$ (a- and b-type) in MHz

$J', K_a', K_c' - J'', K_a'', K_c''$	Observed[a]	Obs. − Calc.
a-*type*		
6, 0, 6 − 5, 0, 5	128295.063 (50)	0.008
7, 0, 7 − 6, 0, 6	149675.871 (60)	−0.024
7, 1, 7 − 6, 1, 6	149088.992 (60)	0.016
9, 0, 9 − 8, 0, 8	192435.181 (50)	0.029
9, 1, 9 − 9, 1, 8	191681.526 (50)	−0.014
9, 1, 8 − 8, 1, 7	193159.968 (50)	0.008
10, 0, 10 − 9, 0, 9	213813.385 (50)	0.035
10, 1, 10 − 9, 1, 9	212976.648 (50)	−0.014
10, 2, 9 − 9, 2, 8	213743.406 (60)	0.086
10, 2, 8 − 9, 2, 7	213747.449 (60)	−0.047
10, 3, 7 − 9, 3, 6	213654.543 (60)[b]	−0.106
12, 0, 12 − 11, 0, 11	256566.323 (50)	−0.011
12, 1, 12 − 11, 1, 11	255564.146 (50)	0.008
12, 1, 11 − 11, 1, 10	257534.991 (60	−0.055
12, 2, 11 − 11, 2, 10	256484.306 (50)	0.065
12, 2, 10 − 11, 2, 9	256491.405 (60)	−0.072
12, 3, 9 − 11, 3, 8	256378.492 (70)[b]	0.021
b-*type*		
28, 1, 28 − 29, 0, 29	124932.445 (80)	−0.017
27, 1, 27 − 28, 0, 28	148547.352 (80)	0.058
25, 1, 25 − 26, 0, 26	195557.025 (90)	−0.038
24, 1, 24 − 25, 0, 25	218950.762 (70)	0.081
23, 1, 23 − 24, 0, 24	242269.034 (90)	−0.241
18, 1, 18 − 19, 0, 19	357716.305 (50)	−0.003
17, 1, 17 − 18, 0, 18	380572.744 (50)	0.041
16, 1, 16 − 17, 0, 17	403350.238 (50)	−0.009

[a]The numbers in parentheses are the estimated uncertainties in units of the last digits.
[b]The K_a doublets were unresolved and the measured frequencies were fitted to the center of the doublet.

stant H_{KJ}, the introduction of the octic and dectic constants, L_{KJ} and S_{KJ} was essential to reproduce the measurements within the experimental error.

For $DOCO^+$, some new measurements were done but they concerned only a-type transitions characterized by $K_a = 0$ or 1 (Table 3). Because of the large uncertainty in the A constant and the non-determination of the D_K constant, the predictions of the b-type spectrum were estimated to be accurate only within some GHz. In order to reduce this uncertainty, an estimation of the D_K constant was obtained by using an empirical relationship between the centrifugal distortion constants $\tau'_{\alpha\alpha\alpha\alpha}$ and the corresponding rotational constants B established by Demaison [17] $\tau'^{i}_{\alpha\alpha\alpha\alpha}/\tau'^{0}_{\alpha\alpha\alpha\alpha} = (B^{i}_{\alpha}/B^{0}_{\alpha})^2$ where 0 refers to the

TABLE 2

Rotational and centrifugal distortion constants of $HOCO^+$, $DOCO^+$ and $HO^{13}CO^+$

		$HOCO^+$	$DOCO^+$	$HO^{13}CO^+$
A	(MHz)	789951.1452(1660)[a]	433713.4(1789)	789184.9642(9248)
B	(MHz)	10773.7341(16)	10163.9586(92)	10772.8593(132)
C	(MHz)	10609.4312(16)	9908.6413(92)	10608.4764(111)
D_J	(kHz)	3.4980(15)	3.0919(36)	3.4955(44)
D_{JK}	(kHz)	935.85(39)	319.89(13)	932.46(44)
D_K	(kHz)	1123.57[b]	338.[d]	1123.57[e]
d_1	(kHz)	−0.05217(73)	−0.1293(63)	−0.04677(948)
d_2	(kHz)	−0.01710(73)	−0.0777(68)	−0.01720(82)
H_{KJ}	(Hz)	3929.(95)	−364.4(41)	4208.(81)
h_2	(Hz)	0[c]	0.057(12)	0[c]
L_{KJ}	(Hz)	88.2(72)	0[c]	141.1(37)
S_{KJ}	(Hz)	−1.62(16)	0[c]	0[c]
Number of lines used in the fit		54	31	26
Standard deviation (kHz)		50.9	61.8	52.6

[a]The number in parentheses denote one standard deviation in units of the last quoted digits. [b]Fixed to the value given by Amano and Tanaka [4]. [c]Fixed. [d]See text. [e]Fixed at the value of the parent species.

TABLE 3

Observed and calculated rotational transitions of $DOCO^+$ in the millimeter wave region (in MHz)

$J', K_a', K_c' - J'', K_a'', K_c''$	Observed[a]	Obs. − Calc.
6, 0, 6 − 5, 0, 5	120429.321 (50)	0.444
6, 1, 5 − 5, 1, 4	121194.339 (50)	0.345
7, 0, 7 − 6, 0, 6	140498.006 (50)	0.530
7, 1, 6 − 6, 1, 5	141391.760 (60)	0.381
9, 0, 9 − 8, 0, 8	180631.124 (50)	0.626
11, 0, 11 − 10, 0, 10	220757.453 (50)	0.766

[a]These lines were not included in the fit. The calculated frequencies were obtained with the constants of Table 2.

parent species and i to the isotopic species. When applied to the isoelectronic species HNCO, HN_3 and HON_2^+, this formula gives agreement for D_K within 20%. The obtained value was held fixed in a least-squares fit and a new value of the rotational constant A was obtained (Table 2). Nevertheless, no lines belonging to the b-type spectrum were found. This can be explained by the weakness of these lines and by the lack of sensitivity when the carcinotron is used in free running mode. Moreover, the rotation of the principal axis of inertia induced by the deuterium atom leads to a reduction of the μ_b component for $DOCO^+$ if the total dipole moment points roughly towards the direction of H, which seems the most likely. Then, the intensity ratio of the b-type and a-type spectra should be weaker for $DOCO^+$ than for $HOCO^+$. Note that introducing the low J values, $K_a = 0,1$ lines measured in this work (Table 3) in the least-squares procedure led to the same difficulties as previously encountered with the submillimeter $K_a = 0$ lines [2]. They have been omitted in the final fit.

In order to search for the $HO^{13}CO^+$ spectrum, a first estimation of the rotational constants was achieved by scaling the constants deduced from ab initio calculation with the same factors as those obtained by comparing the ab initio constants of the parent molecule with the experimental values [18]. The prediction of the spectrum was done by using the centrifugal distortion constants of $HO^{12}CO^+$.

Because of the small amount available for this enriched isotopic species, the lines were only searched for in the submillimeter wave region with the BWO because they are more intense in this frequency range. Four ^qR a-type transitions were observed for $15 \leq J \leq 18$ and only the components with $0 \leq K_a \leq 4$ were measured. Three $^rP_0$ b-type lines equivalent to those observed for the parent species were measured. All the frequencies are reported in Table 4.

For the same reason as for $HO^{12}CO^+$, the strong correlation between the constants A and D_K was not removed. Therefore, the rotational constant A was determined by assuming D_K to be unchanged upon ^{13}C substitution. All the centrifugal distortion constants, reported in Table 2, are more or less unchanged upon isotopic substitution. The same observation applies to the rotational constants because the C atom lies very near the center of mass, as will be shown in the calculation of the atomic coordinates.

Table 5 gives some predicted frequencies of $HO^{13}CO^+$ for lower J values and for $K_a = 0$ which are of potential astrophysical interest, depending on the $^{12}C/^{13}C$ isotopic fractionation in Sagittarius B_2 where the lines of the parent species were discovered [5].

MOLECULAR STRUCTURE

For a molecule belonging to the C_s group of symmetry such as $HOCO^+$, knowledge of all the monoisotopic substitutions is essential to determine an r_s structure. In the case of $HOCO^+$, only the D and ^{13}C isotopic substitutions are

TABLE 4

Observed and calculated rotational transitions of $HO^{13}CO^+$ (in MHz)

$J', K_a', K_c' - J'', K_a'', K_c''$	Observed[a]	Obs. – Calc.
a-*type*		
16, 0, 16 – 15, 0, 15	342026.390 (50)	0.085
16, 1, 16 – 15, 1, 15	340695.680 (50)	0.010
16, 2, 15 – 15, 2, 14	341924.016 (50)	0.065
16, 2, 14 – 15, 2, 13	341941.205 (50)	0.018
16, 3, 13 – 15, 3, 12	341785.430 (50)[b]	0.015
17, 0, 17 – 16, 0, 16	363392.671 (50)	0.012
17, 1, 17 – 16, 1, 16	361980.751 (50)	−0.046
17, 1, 16 – 16, 1, 15	364773.413 (50)	−0.028
17, 2, 16 – 16, 2, 15	363285.913 (50)	−0.062
17, 2, 15 – 16, 2, 14	363306.653 (50)	−0.004
17, 3, 14 – 16, 3, 13	363139.410 (50)[b]	−0.047
17, 4, 13 – 16, 4, 12	362925.176 (60)	0.005
18, 0, 18 – 17, 0, 17	384757.122 (50)	−0.021
18, 1, 18 – 17, 1, 17	383264.391 (50)	−0.014
18, 1, 17 – 17, 1, 16	386221.043 (50)	−0.036
18, 2, 17 – 17, 2, 16	384646.440 (50)	−0.015
18, 2, 16 – 17, 2, 15	384671.047 (50)	−0.015
18, 3, 15 – 17, 3, 14	384492.103 (50)[b]	−0.024
19, 0, 19 – 18, 0, 18	406119.663 (50)	0.016
19, 1, 19 – 18, 1, 18	404546.389 (50)	−0.017
19, 2, 18 – 18, 2, 17	406005.542 (50)	0.091
19, 2, 17 – 18, 2, 16	406034.374 (50)	0.034
19, 3, 16 – 18, 3, 15	405843.394 (60)[b]	0.051
b-*type*		
18, 1, 18 – 19, 0, 19	356979.805 (70)	0.053
17, 1, 17 – 18, 0, 18	379834.942 (50)	−0.052
16, 1, 16 – 17, 0, 17	402611.365 (50)	0.025

[a]The numbers in parentheses are the estimated uncertainties in units of the last digits.
[b]The $K_a = 3$ doublets were unresolved and the measured frequencies were fitted to the center of the doublets.

known. Then, only the substitution coordinates of the C and H atoms can be evaluated.

To eliminate the most important part of the residual centrifugal distortion effects in the rotational constants, they were first transformed to the so-called Watson's determinable parameters A_0, B_0 and C_0 [16] which are given in Table 6 together with the deduced moments of inertia and the inertial defects. The relatively small values of the inertial defects Δ_0 justifies the hypothesis of a planar structure.

The H and C coordinates in the principal axis system of the parent molecule

TABLE 5

Frequency prediction for some transitions of astrophysical interest for $HO^{13}CO^+$

$J', K_a', K_c' - J'', K_a'', K_c''$	Frequency (MHz)[a]
1, 0, 1 - 0, 0, 0	21381.322 (06)
2, 0, 2 - 1, 0, 1	42762.533 (11)
3, 0, 3 - 2, 0, 2	64143.525 (17)
4, 0, 4 - 3, 0, 3	85524.186 (22)
5, 0, 5 - 4, 0, 4	106904.407 (27)
6, 0, 6 - 5, 0, 5	128284.078 (31)
7, 0, 7 - 6, 0, 6	149663.088 (34)
8, 0, 8 - 7, 0, 7	171041.328 (37)
9, 0, 9 - 8, 0, 8	192418.687 (39)
10, 0, 10 - 9, 0, 9	213795.056 (40)
11, 0, 11 - 10, 0, 10	235170.324 (40)
12, 0, 12 - 11, 0, 11	256544.381 (39)
13, 0, 13 - 12, 0, 12	277917.118 (37)
14, 0, 14 - 13, 0, 13	299288.424 (34)

[a]The numbers in parentheses denote one standard deviation in units of the last quoted digits.

were calculated by using Kraitchman's equations [10]. In order to determine the coordinates of both O atoms, two relations were used: the first moment equation, $\sum m_i \alpha_i = 0$; and the second moment equation for the parent molecule $\sum m_i \alpha_i^2 = I_\alpha$.

The corresponding coordinates can be considered as effective coordinates (r_0 structure).

The b coordinates of the O and C atoms and the a coordinate of the C atom are very small and probably include a large zero point vibration contribution. Without knowledge of the ^{18}O single isotopic substitutions, it is impossible to

TABLE 6

Watson's determinable constants and moments of inertia[a]

	$HO^{12}CO^+$	$DOCO^+$	$HO^{13}CO^+$
A_0(MHz)	789951.1521(1660)	433713.4(1789)	789184.9711(9248)
B_0(MHz)	10774.6768 (20)	10164.2841(93)	10773.7986(136)
C_0(MHz)	10610.3741(20)	9908.9673(93)	10609.4159(115)
I_a(u Å^2)	0.63975989(13)	1.165237(481)	0.64038100(75)
I_b(u Å^2)	46.9043362(87)	49.721068(45)	46.908159(59)
I_c(u Å^2)	47.6306545(90)	51.002193(48)	47.634956(52)
Δ_0(u Å^2)	0.086558	0.115886	0.086416

[a]Conversion factor $= 505379.0631$ (MHz u Å^2)

TABLE 7

Nuclear coordinates in the principal axis system of $HOCO^+$ (in Å)[a,b]

	Structure I		Structure II	
	a	b	a	b
H	−1.681991(104)	0.752520(345)	−1.681991(104)	0.752520(345)
O	−1.142923(203)	−0.055711(195)	−1.142923(203)	−0.061821(290)
C	0.062411(552)	−0.025155(18)	0.062411(552)	0.025155(18)
O	1.202081(215)	0.027168(223)	1.202081(215)	−0.004467(324)

[a]Calculated with atomic masses from ref. 19.
[b]The quoted errors are due only to errors in rotational constants.

determine a structure as precise and reliable as for the isoelectronic molecules HNCO [11] and HN_3 [12].

Moreover, the sign of the two coordinates of the C atom remains ambiguous. Two possibilities ($a_c < 0, b_c > 0$ and $a_c < 0, b_c < 0$) have been rejected since they lead to unrealistic CO bond lengths.

The two sets of coordinates are given in Table 7. The deduced bond lengths and angles are compared in Table 8 with the most recent ab initio calculations.

On the basis of the experimental data alone, it is impossible to distinguish between structure I with a *cis* conformation and a quasi-linear heavy-atom chain and structure II with a *trans* conformation and a small bend at the C atom.

Nevertheless, all the recent ab initio calculations suggest a *trans* conformer with a bent O–C–O backbone. Structure II can then be taken as the first experimental determination of the geometry of protonated carbon dioxide.

To obtain a more precise and reliable structure of this molecule it will be absolutely necessary to measure the a- and b-type spectra of both ^{18}O isotopomers.

TABLE 8

Structure of $HOCO^+$; comparison between ab initio and experimental bond lengths and angles[a]

	De Frees et al. [6]	Frisch et al. [7]	Taylor and Scarlett [8]	Yu et al. [9]	Structure I (exper.)	Structure II (exper.)
$H-O_1$	0.986	0.9874	0.986	0.972	0.9715	0.9766
O_1-C	1.237	1.2161	1.230	1.220	1.2057	1.2085
$C-O_2$	1.135	1.1298	1.120	1.111	1.1409	1.1400
$\angle O_1-C-O_2$	174.5	173.64	176.0	174.0	178.83	174.39
$\angle H-O_1-C$	118.0	119.34	118.6	119.7	122.25	119.38

[a]Distances are in Å and angles in degrees.

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