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SiCCO and CCCO: accurate equilibrium structures and spectroscopic constants

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Abstract

Cubic force fields have been calculated for SiCCO and CCCO by means of the coupled cluster variant CCSD(T) and Dunning's cc-pVQZ basis set. There from, a variety of spectroscopic constants (harmonic vibrational wavenumbers, vibration–rotation coupling constants, l-type doubling constants and equilibrium quartic centrifugal distortion constants) has been computed. Accurate equilibrium structures are established for both molecules and precise predictions are made for the ground-state rotational constants of less abundant isotopomers of SiCCO.

Keywords: Linear SiCCO and CCCO; Equilibrium structures; Rotational constants; Vibration–rotation coupling constants; Electric dipole moment

1. Introduction

Very recently, the linear tetra-atomic molecule SiCCO could be generated in a supersonic expansion by means of a DC electric discharge of silane, acetylene and carbon monoxide highly diluted in neon [1]. The spectroscopic identification was carried out by Fourier transform microwave spectroscopy in the 5–26 GHz frequency range. A total of four rotational lines, corresponding to the $J' \leftarrow J''$ transitions $1 \leftarrow 0$, $2 \leftarrow 1$, $3 \leftarrow 2$ and $4 \leftarrow 3$, was observed. From the line positions, precise values of the ground-state rotational and quartic centrifugal distortion constant could be determined.

Prior to the detection of the first member of the SiC_nO series with $n>1$, four carbon chains of type SiC_nS were characterized in a joint theoretical/experimental investigation [2]. Since C_3O, C_3S and various species of type SiC_n are well-known interstellar species (see Ref. [1]), both SiCCO and SiCCS (and also the higher members of the corresponding series) are of substantial interest to radioastronomers.

The present paper aims at a more extensive characterization of SiCCO than was possible by experiment so far. For this purpose, high-level ab initio calculations have been carried out. In particular, an accurate equilibrium structure has been established through combination of theoretical and experimental data and various spectroscopic constants have been calculated. Rather precise predictions for the ground-state rotational and centrifugal distortion constants of less abundant isotopomers of SiCCO will be reported which should be of help to microwave spectroscopists in their search for rotational transitions of these species. Furthermore, calculated vibration–rotation and l-type doubling constants should facilitate the analysis of rotational spectra in excited vibrational states.

2. Details and results of calculations

The coupled cluster variant CCSD(T) [3] in conjunction with Dunning's cc-pVQZ basis sets [4,5] was employed to calculated complete cubic force fields for SiCCO and CCCO. These are given in the form

$$V - V_e = \sum_{ijklm} C_{ijklm} \Delta R_1^i \; \Delta R_2^j \; \Delta R_3^k \alpha_4^l \beta_5^m. \qquad (1)$$

The coefficients C_{ijklm} correspond to the quadratic and cubic force constants, ΔR_i $(i=1–3)$ are stretching

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coordinates and the angles α and β describe SiCC (CCC) and CCO bending out from the linear nuclear configuration, respectively. They are defined to have the same sign for a *cis*-like distortion of the nuclear framework. The underlying CCSD(T) energies were calculated with the MOLPRO suite of programs [6–8], valence electrons being correlated in the calculations. The CCSD(T) total energies at equilibrium (V_e) were obtained to be -440.229695 (SiCCO) and $-189.134233\ E_h$ (CCCO). The numerical values of the coefficients C_{ijklm} were obtained by appropriate least-squares fitting, making use of a self-written program. The fits are based on 50 CCSD(T) energies per molecule, each having a numerical accuracy of ca. $10^{-12}\ E_h$. Small distortions from equilibrium not exceeding $0.02a_0$ and 2° were employed in the selection of the points. The stretch-only part of the cubic force field, the bend-only part and the stretch-bend part were handled separately. Results are listed in Table 1 which also quotes the calculated equilibrium bond lengths in the legend.

The central CC equilibrium bond length (R_{2e}) in the two molecules differs by only 0.0034 Å while a somewhat larger difference of 0.0127 Å is obtained for the CO equilibrium distance. Likewise, the corresponding diagonal CC stretching force constants (coefficients C_{02000} and C_{03000}) are almost identical. The CO equilibrium bond length calculated for SiCCO is very close to the value of 1.1627 Å as obtained for CO_2 from analogous CCSD(T) calculations [9].

Table 1
CCSD(T)/cc-pVQZ cubic force fields for SiCCO and CCCO

i	*j*	*k*	*l*	*m*	SiCCO[a]	CCCO[a]
2	0	0	0	0	0.1945465	0.3612792
3	0	0	0	0	−0.1681083	−0.3803337
0	2	0	0	0	0.3270141	0.3278629
0	3	0	0	0	−0.3460026	−0.3425382
0	0	2	0	0	0.5002040	0.5419962
0	0	3	0	0	−0.6203489	−0.6737585
1	1	0	0	0	0.0087620	0.0108486
0	1	1	0	0	0.0717924	0.0632892
1	0	1	0	0	−0.0260397	−0.0387271
2	1	0	0	0	−0.0105288	−0.0129373
1	2	0	0	0	−0.0084107	−0.0141583
0	2	1	0	0	−0.0304397	−0.0274126
0	1	2	0	0	−0.0447928	−0.0411942
2	0	1	0	0	0.0078052	0.0122766
1	0	2	0	0	0.0018372	0.0049643
1	1	1	0	0	0.0099255	0.0155340
0	0	0	2	0	0.0078141	0.0057005
0	0	0	0	2	0.0763797	0.0732464
0	0	0	1	1	0.0038557	0.0033915
1	0	0	2	0	−0.0144247	−0.0176540
1	0	0	0	2	−0.0058324	−0.0034157
1	0	0	1	1	0.0187322	0.0189113
0	1	0	2	0	−0.0158648	−0.0198924
0	1	0	0	2	−0.0571543	−0.0537245
0	1	0	1	1	0.0034054	0.0048098
0	0	1	2	0	0.0003467	0.0059419
0	0	1	0	2	−0.0557412	−0.0550710
0	0	1	1	1	−0.0004689	−0.0010169

Valence electrons correlated. Equilibrium bond lengths: (1) SiCCO: $R_{1e}(SiC_{(1)}) = 1.6720$ Å, $R_{2e}(C_{(1)}C_{(2)}) = 1.2981$ Å and $R_{3e}(C_{(2)}O) = 1.1635$ Å. (2) CCCO: $R_{1e}(C_{(1)}C_{(2)}) = 1.2763$ Å, $R_{2e}(C_{(2)}C_{(3)}) = 1.3015$ Å and $R_{3e}(C_{(3)}O) = 1.1508$ Å.

[a] For the definition of the coefficients (C_{ijklmn}, quoted in atomic units) see Eq. (1).

Table 2
Harmonic vibrational wavenumbers (ω_r), vibration–rotation coupling constants (α_r), l-type doubling constants (q_t^e and q_t^J) and quartic centrifugal distortion constants (D_e^J) for SiCCO and CCCO

	SiCCO	CCCO	
	CCSD(T)[a]	CCSD(T)[a]	CEPA-1 [10,11][b]
ω_1 (cm^{-1})	2192.3	2299.5	2263.3
ω_2 (cm^{-1})	1539.0	1933.7	1944.3
ω_3 (cm^{-1})	656.4	945.8	953.1
ω_4 (cm^{-1})	600.8	589.5	605.9 (596)
ω_5 (cm^{-1})	107.6	119.4	138.0 (124)
α_1 (MHz)	12.747	28.400 (27.6)[c]	29.3
α_2 (MHz)	10.702	19.085	19.1
α_3 (MHz)	4.129	8.556	8.7
α_4 (MHz)	−2.987	−7.835	−7.3 (−7.4)
α_5 (MHz)	−16.333	−37.197 (−37.7)[c]	−31.2 (−34.9)
ΔB_0 (MHz)[d]	−5.531	−17.012	−9.9 (−13.7)
q_4^e (MHz)	1.043	3.385	3.4 (3.4)
q_5^e (MHz)	4.286	12.888 (13.5)[c]	11.3 (12.5)
q_4^J (Hz)	−0.083	−1.507	−1.2 (−1.3)
q_5^J (Hz)	−21.99	−136.2	−87.0 (−119)
D_e^J (Hz)	176.8 (235)[e]	532.7 (778)[e]	529

[a] CCSD(T)/cc-pVQZ; valence electrons correlated.

[b] Values in parentheses make use of CEPA-1 quadratic bending force constants as obtained with the larger basis set of 132 contracted Gaussian-type orbitals [10].

[c] Experimental values [13,15].

[d] Calculated as $\Delta B_0 = B_e - B_0 \approx 1/2 \sum_r \alpha_r d_r$, where d_r is a degeneracy factor (1 for stretching and 2 for bending vibrations).

[e] Experimental ground-state values [1,15].

As is obvious from the values of the quadratic force constant C_{00020} quoted in Table 1, the CCC bending potential of CCCO is more shallow than the SiCC bending potential. As a consequence, CCCO may be considered to be a more flexible species than SiCCO (see below).

CCSD(T)/cc-pVQZ spectroscopic constants for SiCCO and CCCO are listed in Table 2. Those for the latter molecule may be compared with the author's previous results [10,11] as obtained within the coupled electron pair approximation (CEPA) [12]. Throughout, agreement between the two sets of theoretical spectroscopic constants is quite good, considering also the fact that the earlier data were obtained 14 years ago. Comparison with precise gas-phase experimental values [13] is possible for the vibration–rotation coupling constants α_1 and α_5 and the l-type doubling constant q_5. Agreement between the present theoretical and the available experimental values is very good. The calculated equilibrium quartic centrifugal constants for SiCCO and CCCO, termed D_e^J, may be compared with the corresponding experimental ground-state values D_0^J [1,15]. As emphasized repeatedly by the author, the ratio D_0^J/D_e^J provides a rather good indicator for the degree of