The rotational spectrum of cyclohexyl formate, chemically prepared within a supersonic expansion

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ABSTRACT

The pulsed supersonic jet expansion microwave spectra of the parent and of the CD=O monodeuterated species of cyclohexylformate have been measured in the 6.5–18 GHz range. The samples have been obtained by direct esterification of HCOOH (or DCOOH) with cyclohexyl alcohol during a supersonic expansion in a microwave cavity. Most of the observed transitions are split into two component lines, due to the tunnelling motion connecting two equivalent *gauche* forms. The tunnelling barrier has been determined to be B_2 = 267 (10) cm^{-1}. Structural information has been obtained from the 6 available rotational constants.

1. Introduction

Many efforts have recently been dedicated to the investigation of the rotational spectra of esters [1–13], due either to their astrochemical interest or to their complex and intriguing internal dynamics.

The rotational features of methylformate [14], methylacetate and ethylformate [15] have been indeed observed in the interstellar space. In order to enable astronomical observations of the heavier homologues, the measurements of the rotational spectra of several esters have been systematically extended, including less abundant isotopologues, to the millimeter-wave region [16–18].

Also, from a physical chemistry point of view, esters are quite interesting, due to their internal dynamics, mainly related to the low barrier to internal rotation of one (or more) methyl groups. In addition, esters with aliphatic chains can generate complex conformational equilibria.

Recently, we went through the investigation of some relatively heavy esters almost accidently: when trying to record the rotational spectra of complexes between carboxylic acids and primary or secondary alcohols, we discovered that the partner molecules were reacting, thereby forming the ester [19–21]. This was the case as well when mixing formic acid and cyclohexanol at a low (few %) concentrations in a rare gas (carrier): only strong lines of the ester, $HCOOC_6H_{11}$ (CHF) were observed. We report below the analysis of the rotational spectrum of CHF.

2. Experimental

The rotational spectra were measured in a pulsed jet Fourier transform microwave (FTMW) spectrometer [22] with a COBRA (Coaxial Oriented Beam and Resonator Axes) configuration [23] in the frequency range 6–18 GHz which has been described previously [24]. The rotational spectrum of CHF was observed as a reaction product of a mixture (300 kPa) of ~2% of HCOOH (or DCOOH) and ~2% of $C_6H_{11}OH$ in He expanded through a pulse valve to create the supersonic jet. The coherent molecular emission was digitized in the time-domain and Fourier transformed in order to obtain the transition frequencies of the system under study. The coaxial arrangement of resonator and jet axes cavity causes a symmetric splitting of the molecular signals into two Doppler components. Transitions separated by more than 7 kHz are resolvable with an

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estimated accuracy of 3 kHz.

2.1. Theoretical calculations

According to the commonly reported shapes of organic six-membered rings, the most stable forms of CHF must have a chair arrangement of the ring, while the formyl group can be attached to the ring in an axial or in an equatorial position. In addition, the formyl group can rotate along the O-$C_{C=O}$ bond generating a *gauche* (doubly degenerate) and a *trans* conformation. In order to calculate the relative energies of these conformations, and to have trial spectroscopic parameters needed for the investigation of the rotational spectra, we ran MP2/6−311++G(d,p) [25] and B3LYP-D3(BJ)/def2-tzvp [26] calculations using the GAUSSIAN 16 suite of programs [27]. The results are shown in Table 1.

One can see that the *Equatorial-Gauche* (*Eg*) species is considerably more stable than the other three ones. For this reason, we limited initially the search of the rotational spectrum of the *Eg* isomer, as described below.

2.2. Rotational spectrum

According to the results of the *ab initio* calculations, the μ_a-transitions were expected to be the strongest ones. μ_a-type R-branch bands have been easily identified, indeed, with J ranging from 3 to 9. Later on, weaker μ_b- and μ_c-type transitions have been measured. Almost all of them are split into two component lines (up to a maximum splitting of a few tens of kHz), the splitting being larger for the μ_b-type transitions. This splitting arises, as described in a following section, from the tunnelling motion connecting the two equivalent *Eg* minima. All transitions have been fitted with a coupled Hamiltonian:

$$H = H_0^R + H_1^R + H^{CD} + H^{\text{int}} \quad (1)$$

where H_0^R and H_1^R are the rigid-rotor Hamiltonians for $v = 0$ and $v = 1$, respectively; H^{CD} accounts for the centrifugal distortion effects (common to both states), and H^{int} represents the interaction between $v = 0$ and $v = 1$ states, expressed as:

$$H^{int} = \Delta E_{01} \quad (2)$$

ΔE_{01} being the energy difference between the two states. Coriolis interaction terms are not determinable, as usual when ΔE_{01} is very small as in the present case. All transitions were fitted using Pickett's SPFIT program [28], with asymmetric rotor Hamiltonian, including first order centrifugal distortion constants. The I^r representation and the S reduction were chosen [29]. The fitted spectroscopic constants are reported in the left part of Table 2.

Later on, the spectrum of the CD=O species has been analyzed. It shows the same features of the spectrum of the parent species, and the obtained spectroscopic constants are reported in the right part of Table 2. No evidences of the hyperfine structure due to the quadrupolar effects of the D nucleus ($I = 1$) have been observed.

Fig. 1 shows the spectra of two transitions of CD=O species. One can note that the tunneling splitting are larger for the μ_b-transition (right), which is an interstates transition.

All measured transition frequencies are reported in the Supplementary material.

2.3. Tunnelling motion

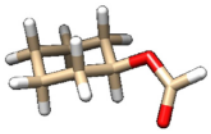
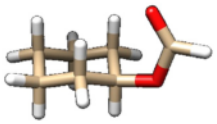
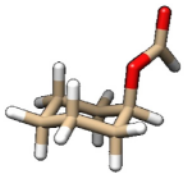
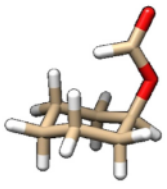
The two determined splittings ΔE_{01} are related to the barrier

Table 2
Experimental spectroscopic parameters of CHF.

	Parent		DCOO-	
	0	1	0	1
A/MHz	3403.8636(4)[a]	3403.8563(4)	3384.7903(4)	3384.7857(4)
B/MHz	1020.7402(1)	1020.7406(1)	996.0458(1)	996.0453(1)
C/MHz	874.9685(1)	874.9682(1)	856.9817(1)	856.9816(1)
D_J/kHz	0.0749(7)		0.0679(7)	
D_{JK}/kHz	0.232(9)		0.224(10)	
D_K/kHz	0.55(3)		0.51(3)	
d_1/Hz	−19.6(4)		−17.8(4)	
d_2/Hz	−3.9(5)		−4.0(5)	
ΔE_{01}/kHz	38(1)		40(1)	
σ/kHz[b]	2.5		4.5	
N[c]	154		160	

[a] Standard error in parentheses in units of the last digit.
[b] Root-mean-square deviation of the fit.
[c] Number of lines in the fit.

Table 1
Theoretical spectroscopic parameters and relative energies of the four conformers of CHF.

Eg		MP2[a]	B3LYP-D3(BJ)[b]	*Et*	MP2	B3LYP-D3(BJ)
	*A*,*B*,C/MHz	3392.7	3424.5		3027.6	3038.5
		1022.9	1009.9		1119.4	1108.4
		878.9	869.8		1032.8	1022.2
	μ_a, μ_b, μ_c/D	1.8	2.0		1.3	1.4
		0.8	0.9		0.0	0.0
		0.8	0.9		1.3	1.5
	ΔE/kJ·mol^{-1}	0[c]	0[d]		11.1	9.5
Ag				*At*		
	*A*,*B*,C/MHz	3022.8	3068.3		2553.3	2559.7
		1039.1	1015.7		1126.4	1122.0
		957.4	935.9		1102.7	1097.6
	μ_a, μ_b, μ_c/D	3.1	3.3		5.0	4.9
		0.1	0.1		0.0	0.0
		2.9	2.8		0.6	0.7
	ΔE/kJ·mol^{-1}	18.9	17.3		48.3	40.6

[a] Performed with 6−311++g** basis set.
[b] Performed with def2-tzvp basis set.
[c] Absolute energy = −423.346592 E_h.
[d] Absolute energy = −424.380788 E_h.

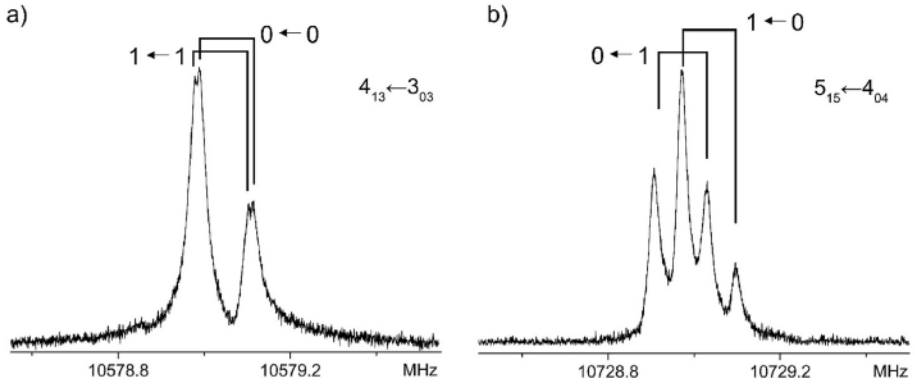


Fig. 1. Rotational electric-dipole transitions of the CD=O species: a) the $4_{13} \leftarrow 3_{03}$ *c*-type (intrastate) transition; b) the $5_{15} \leftarrow 4_{04}$ *b*-type (interstate) transition, displaying a split larger than *c*-type (intrastate) transition.

Table 3
Potential energy curve by varying τ at MP2/6−311++g(d,p) level.

τ(COCH)/°	−180	−119.3	−35.7	0.0	35.7	119.3	180
ΔE/cm^{-1}	926	2551	0	224	0.0	2551	926

height B_2 of the potential barrier connecting the two equivalent *Eg* minima and to the specific pathway and reduced mass of the tunnelling motion.

We calculated - at MP2/6−311++g(d,p) level - first the energies of the stationary point encountered along the 2π internal rotation of the HC-OC$_{C=O}$ dihedral angle (τ). The results are given − graphically and numerically − in Table 3.

From the data of Table 3, it has been possible to depict the potential energy function as a function of τ given in Fig. 2.

As expected, the ΔE_{01} values of the parent and DCOO- species are very similar to each other (ca. 40 kHz), since the reduced mass of the motion is about the same.

For this reason, we used the two ΔE_{01} values to calculate the potential energy barrier (B_2) of the intermolecular motion connecting the two equivalent minima.

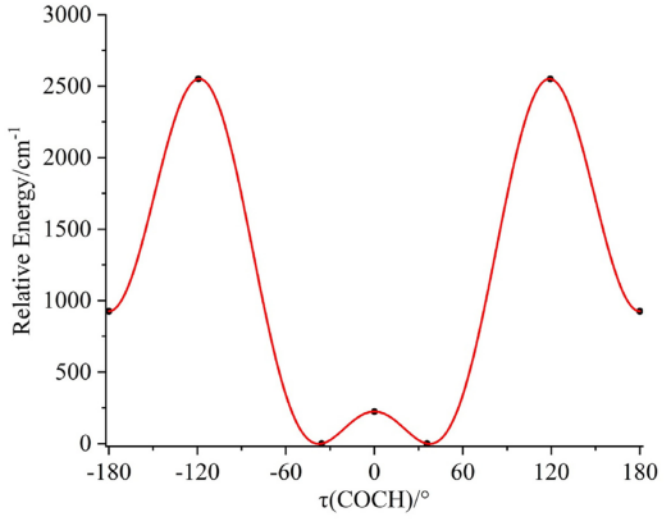


Fig. 2. Potential energy function of equatorial cyclohexylformate as function of τ(COCH) at MP2/6−311++g(d,p) level.

Meyer's flexible model [30] is particularly suitable to determine potential energy surfaces from rotational and vibrational experimental data. However, with the ΔE_{01} splittings being related to the motion across the barrier separating the two *Eg* forms, we took into account a limited portion of the torsional space τ (±65°). The double minimum potential can then be locally described by the following function:

$$V(\tau) = B_2\left[1 - (\tau/\tau_0)^2\right]^2 \quad (3)$$

where the barrier B_2 at τ = 0° and the equilibrium value of the inversion angle τ_0 (see figures in Table 3) are the two parameters required. Being the formyl group quite heavy, we did not take into account the structural relaxations of other parts of the molecule (mainly changes of the dihedral angles of the light ring hydrogens) upon the τ motion. We fixed τ_0 at its MP2/6−311++G** estimate (35.7°). The two experimental splittings were satisfactorily reproduced at a barrier B_2 ~ 267 cm^{-1}. The results of the flexible model calculations are summarized in Table 4.

In the flexible model calculations, the τ coordinate has been probed in the ±65° range and solved into 61 mesh points [30].

2.4. Structural information

Structural information has been obtained from the 6 available

Table 4
Results of the flexible model calculations.

Tunneling splittings	Obs.	Calc.
ΔE_{01}(parent)/kHz	38	39
ΔE_{01}(DCOO-)/kHz	40	39
Potential energy parameters B_2 = 267(10) cm^{-1} τ_0 = 35.7°		

Table 5
Cartesian coordinate of the hydrogen atom H11 (see Fig. 3).

	r_s	r_e[a] (specie Eg)
|*a*|/Å	3.4313(1)[b]	3.4072
|*b*|/Å	0.5937(3)	0.5825
|*c*|/Å	0.7147(2)	0.7542

[a] *Ab initio* values.
[b] Error in parenthesis are in units of the last digits.

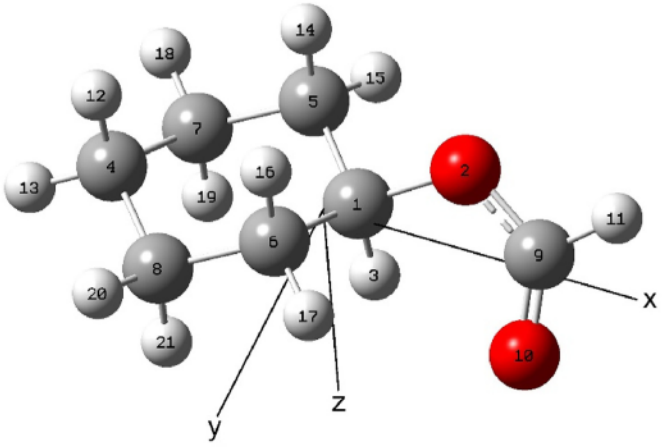


Fig. 3. Observed conformation of CHF, with atom numbering and principal axes system.

rotational constants. First, the Kraitchman [31] coordinates of the formyl hydrogen were calculated in the principal axes system of the parent species. The obtained values are reported in Table 5, where they are compared to the *ab initio* ones. The labelling of the atoms is given in Fig. 3. The *ab initio* values correspond to the localized minimum of the vibrational potential energy surface and are indicated by the notation r_e (equilibrium structure).

Since the experimental rotational constants have intermediate values between those of the MP2/6−311++G(d,p) and B3LYP-D3(BJ)/def2-tzvp methods (see Tables 1 and 2), we did not face up any attempt of structural improvement. The MP2/6−311++G(d,p) geometry is given in the Supplementary Material.

3. Conclusions

We assigned the rotational spectrum of the most stable conformer (*Eg*) of CHF and gave an accurate description of its of the formyl group internal rotation.

We would like to emphasize that the rotational spectrum of CHF was observed accidently, when trying to assign the spectrum of the molecular adduct cyclohexanol-formyc acid. This is in line with the discovery that within pulsed jet FTMW spectroscopy, carboxylic acids react to give the esters with primary and secondary alcohols, while they form the adducts with tertiary alcohols [19].

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Nothing to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2020.127952.

References

[1] R.F. Curl, J. Chem. Phys. 30 (1959) 1529.
[2] J.M. Riveros, E.B. Wilson, J. Chem. Phys. 46 (1967) 4605.
[3] G. Williams, N.L. Oven, J. Sheridan, Trans. Faraday Soc. 67 (1971) 922.
[4] D. Jelisavac, D.C. Cortés Gómez, H.V.L. Nguyen, L.W. Sutikdja, W. Stahl, I. Kleiner, J. Mol. Spectrosc. 257 (2009) 111.
[5] T. Attig, L.W. Sutikdja, R. Kannengießer, I. Kleiner, W. Stahl, J. Mol. Spectrosc. 8 (2013) 284−285.
[6] T. Attig, R. Kannengießer, I. Kleiner, W. Stahl, J. Mol. Spectrosc. 290 (2013) 24.
[7] B. Velino, A. Maris, S. Melandri, W. Caminati, J. Mol. Spectrosc. 256 (2009) 228.
[8] H.V.L. Nguyen, W. Stahl, I. Kleiner, Mol. Phys. 110 (2012) 2035.
[9] P. Ottaviani, B. Velino, W. Caminati, Chem. Phys. Lett. 428 (2006) 236.
[10] R. Meyer, W. Caminati, H. Hollenstein, J. Mol. Spectrosc. 137 (1989) 87.
[11] B. Velino, L.B. Favero, P. Ottaviani, A. Maris, W. Caminati, J. Phys. Chem. A 117 (2013) 590.
[12] V. Ilyushin, E. Alekseev, J. Demaison, I. Kleiner, J. Mol. Spectrosc. 240 (2006) 127.
[13] S. Melandri, B.M. Giuliano, A. Maris, L.B. Favero, P. Ottaviani, B. Velino, W. Caminati, J. Phys. Chem. A 111 (2007) 9076.
[14] E. Churchwell, G. Winnewisser, Astron. Astrophys. 45 (1975) 229.
[15] B. Tercero, I. Kleiner, J. Cernicharo, H.V.L. Nguyen, A. López, G.M. Muñoz Caro, Astrophys. J. Lett. 770 (2013) L13.
[16] C. Duan, M. Carvajal, S. Yu, J.C. Pearson, B.J. Drouin, I. Kleiner, Astron. Astrophys. 576 (2015) A39.
[17] I.R. Medvedev, F.C. De Lucia, E. Herbst, Astrophys. J. Suppl. 181 (2009) 433.
[18] L. Kolesniková, I. Peña, J.L. Alonso, J. Cernicharo, B. Tercero, I. Kleiner, Astron. Astrophys. 577 (2015) A91.
[19] L. Evangelisti, L. Spada, W. Li, F. Vazart, V. Barone, W. Caminati, Angew. Chem. Int. Ed. 56 (2017) 3872.
[20] L. Evangelisti, L. Spada, W. Li, I. Federici, W. Caminati, Mol. Phys. 116 (2018) 3503.
[21] L. Spada, L. Evangelisti, W. Li, R. Orlacchio, W. Caminati, J. Phys. Chem. A 123 (2019) 1785.
[22] T.J. Balle, W.H. Flygare, Rev. Sci. Instrum. 52 (1981) 33.
[23] J.-U. Grabow, W. Stahl, H. Dreizler, Rev. Sci. Instrum. 67 (1996) 4072.
[24] W. Caminati, A. Millemaggi, J.L. Alonso, A. Lesarri, J.C. Lopez, S. Mata, Chem. Phys. Lett. 392 (2004) 1.
[25] a) Chr. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618;
b) W.J. Hehre, L. Random, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
[26] a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648−5652;
b) J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533−16539;
[c] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 32 (2011) 1456;
[d] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 7 (2005) 3297−3305.
[27] C. 01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda,

O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 16, Revision, Gaussian, Inc., Wallingford CT, 2016.

[28] H.M. Pickett, J. Mol. Spectrosc. 148 (1991) 371.
[29] J.K.G. Watson, in: J R, Durig (Eds.), Vibrational Spectra and Structure, 6, Elsevier, New York/Amsterdam, 1977, pp. 1–89.
[30] R. Meyer, J. Mol. Spectrosc. 76 (1979) 266.
[31] J. Kraitchman, Am. J. Phys. 21 (1953) 17.