Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intramolecular Hydrogen tunneling in 2-Chloromalonaldehyde trapped in solid para-hydrogen

Supporting Information

Alejandro Gutiérrez-Quintanilla[a,b#], Michèle Chevalier[a], Rasa Platakyte[a,c], Justinas Ceponkus[c] and Claudine Crépin[a]*

[a] Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405, Orsay, France

[b] Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Universidad de La Habana. Ave. Salvador Allende No. 1110, Quinta de los Molinos, La Habana 10400, Cuba.

[c] Institute of Chemical Physics, Vilnius University, Sauletekio av. 9 bat. III, L-10222 Vilnius, Lithuania.

[#]Present address: Aix-Marseille Université, Laboratoire PIIM, Team ASTRO, Service 252, Saint Jérôme, Ave. Escadrille Normandie Niemen, 13013 Marseille, France

* claudine.crepin-gilbert@u-psud.fr

1. C_s-C_{2v} comparison and mode analysis

We propose to comment the experimental results given in Table 2 by a crude analysis of the mode behavior based on theoretical predictions in C_s and C_{2v} point groups corresponding respectively to the description of the equilibrium structure and the transient structure in the H transfer. We used DFT calculations at two different levels of theory, (M06-2X/6-311++G(3df,3pd))[1] and (B3LYP/6-311++G(3df,3pd)).[2] Table S1 reports the mode frequencies of these two structures at the (B3LYP/6-311++G(3df,3pd)) level and their correspondence based on the similarities of the atomic motions at play. The same correspondence is obtained with both methods.

We focus our interest in the 800-1800 cm^{-1} spectral range. The high frequency modes, corresponding to X-H stretching modes cannot be analyzed. The O-H stretching is not experimentally observed and the C-H stretching modes (modes 19 and 20 in Table S1 below) are not the same when predicted with one method or the other. Moreover, the experimental bands are broad and cannot be clearly assigned whatever the set of theoretical frequencies used. A Fermi resonance is also not exclude in this range.[3] Consequently, there is no clear information to extract from these stretching modes.

The symmetry of the modes is obtained from their symmetry in the transient geometry (C_{2v}) when the correspondence is straightforward. We have not performed any sophisticated calculations in order to get a degree of similarity or a theoretical prediction of correspondence. Within this rough approach, the symmetry in the G_4 molecular group is obtained for all the modes of interest (column 5 in Table S1), except four modes between 1250 and 1450 cm^{-1} including two A1 and two B2 modes. The main components of $\boldsymbol{\mu}$ (μ_x, μ_y or μ_z) deduced from C_s calculations are also reported in Table S1 (column 6). In-plane modes are generally hybrid modes. The ratio μ_y/μ_z is method dependent but shows similar tendencies, given in Table S1, with both methods. From these tendencies and the G_4 mode symmetries, one can predict the behavior of the vibrational transition for each mode, in terms of cases ①, ②, or ③ (see Fig. 5). It is reported in Table S1 as "transition type (theo.)", column 7. On the other hand, the transition type can be deduced from the observed bands, after mode assignments, except when $\Delta\nu_1 \sim 0$. It is reported in Table S1 as "transition type (exp.)", column 8. The comparison is perfect for the modes where all the data are available, confirming our assignments.

Only one component of mode 11 is very weakly detected corresponding to the transition from l_0 (at 1016 cm^{-1}). Its large shift (5 cm^{-1}) from the component induced by complexation with oH_2 suggests that it corresponds to l_0-u_1, leading to a ② case, as predicted by symmetry considerations.

The intense mode 17 is predicted as a ① case. Case ① is obtained in the association of ν_u=1583 cm^{-1} with ν_l=1563 cm^{-1}. This association is also in agreement with the variation of the intensities observed when heating the sample. It leads to $\Delta\nu_1$=28 cm^{-1}. Such an enhancement of the tunneling process with this mode is not predicted because of the similarity of the mode frequencies in C_s and C_{2v} geometries (see Table S1). Redington et al.,[4,5] in their work on tropolone, show that when these frequencies are close, the vibration has very little influence on proton transfer. The second ν_l band at 1608 cm^{-1} could be due to a combination of two modes (theoretically predicted at 1383cm^{-1} and 270cm^{-1}) in Fermi resonance with the mode calculated at 1613 cm^{-1}.[1] In that case another doublet is expected. A possible value for a second ν_u could be around 1608 cm^{-1} with $\Delta\nu_1$ close to $\Delta\nu_0$. On the one hand, a very weak line at 1601 cm^{-1} seems to appear in the difference spectrum, on the other hand a large band below the water band at 1630 cm^{-1} is not excluded. In summary, it is difficult to conclude on mode 17.

The mode of lowest frequency (13) among the puzzling 13-16 modes has a main ① behavior, in agreement with the A1 symmetry of the suggested corresponding C_{2v} mode. The suggested B2 symmetry for mode 16 is not in contradiction with experimental observations. The suggested symmetries of the last modes are not in agreement with the ① case deduced from the experiment. Taking into account that two modes are calculated, with high hybrid character, and that only one band is observed with a very weak $\Delta\nu_1$, no conclusion can be done. Most sophisticated theoretical calculations are necessary to rationalize the observations in this spectral range.

Table S1: Characteristics of vibrational modes of 2-ClMA. Frequencies (cm^{-1}) in C_s (equilibrium geometry) and C_{2v} (transient state geometry) symmetries obtained at the (B3LYP/6-311++G(3df,3pd)) level of theory. Calculated intensities (km/mol) in parenthesis. Modes are numbered in the C_s geometry. Corresponding modes in C_{2v} and C_s geometries are on the same lines. C_{2v} mode symmetry is reported together with the guessed G_4 symmetry. C_{2v} mode characteristics *in italic* refer to modes for which the correspondence with C_s modes is doubtful. The main components of the transient dipole moment of the mode in C_s symmetry are also reported, noted μ_x, μ_y, μ_z. The transition type, as defined in Fig. 5 of the main text, is deduced from considerations on symmetry and predicted $\boldsymbol{\mu}$ (Transition type (theo.)), and from the experimental vibrational bands (Transition type (exp.)). The measured tunneling splittings in the various vibrational levels are reported in the last column (cm^{-1}).

N°	C_s		C_{2v}		C_{2v} sym.	G_4 sym.	$\boldsymbol{\mu}$ comp (C_s)	Trans. type (theo.)	Trans. type (exp.)	$\Delta\nu_1$
	Freq.	Int.	Freq.	Int.						
1	224	(5)	239	(3)	B1	B1	μ_x			
2	270	(7)	651	(2)	A1	A1	$\mu_y \geq \mu_z$			
3	283	(3)	282	(3)	B2	B2	$\mu_y > \mu_z$			
4	300	(2)	374	(0)	A2	A2	μ_x			
5	387	(3)	381	(11)	B1	B1	μ_x			
6	475	(6)	453	(1)	A1	A1	μ_z			
7	520	(17)	575	(20)	B2	B2	$\mu_y >> \mu_z$			
8	909	(53)	1287	(78)	B1	B1	μ_x	①	①	1.9
9	926	(34)	972	(29)	A1	A1	$\mu_y > \mu_z$	② (③)	② (③)	7.8
10	997	(41)	985	(0)	B1	B1	μ_x	①	①	5.1
11	1035	(5)	1034	(0)	A2	A2	μ_x	②	②?	
12	1080	(81)	1146	(28)	A1	A1	$\mu_y \sim \mu_z$	③	③	8.3
13	1272	(200)	*1375*	*(144)*	*A1*	A1 [a]	$\mu_z > \mu_y$		① (③)	3.2
14	1371	(64)	*1320*	*(128)*	*B2*		$\mu_z \geq \mu_y$			
15	1383	(102)	*1878*	*(134)*	*A1*		$\mu_y \geq \mu_z$		①/③	0.4
16	1422	(26)	*1435*	*(43)*	*B2*	B2 [a]	$\mu_y > \mu_z$		①/②/③	0
17	1613	(237)	1601	(618)	B2	B2	μ_y	①		28 [b]
18	1701	(154)	1635	(120)	A1	A1	μ_z	①	①	8.4
19	3002	(50)	3108	(17)	B2				①	1
20	3169	(113)	3110	(8)	A1				②	7
21	3215	(105)	*i*1223	(270)	B2	B2				

[a] symmetries deduced from experimental results (see text); [b] value discussed in the text, not certain.

2. Comparison with malonaldehyde

The $\Delta\nu_1$ tunneling splitting of various vibrational levels of malonaldehyde has been measured in jet experiments by Suhm et al..[6–8] Consequently, we think that it could be interesting to the readers to compare the vibrational effect on tunnelling in 2-ClMA and MA. Table S2 reports the vibrational frequencies of MA modes, in comparison with those of 2-ClMA. The numbering is the same as in Table S1 and corresponds to the 2-ClMA molecule. Similar modes are reported in the same line. Bold values correspond to C-H (olefinic) motions in MA and are of course very different from the corresponding C-Cl motions in 2-ClMA. Once again, the correspondence is not straightforward in the 1300-1450 cm^{-1} frequency range. These uncertainties are underlined by values in italic. Table S2 reports $\Delta\nu_1$ values (experimental values) for MA and 2-ClMA. Additionally, $\Delta\nu_1/\Delta\nu_0$ values are also reported for a better comparison because $\Delta\nu_0$ values are quite different in MA (21.6 cm^{-1})[9] and in 2-ClMA (7.9 cm^{-1}).

In ref. 10, the author established a correspondence in MA modes obtained in C_s (equilibrium structure) and C_{2v} (transient structure) geometries. Similarly to the case of tropolone,[4,5] modes with similar frequencies in both geometries exhibit a negligible change in the tunneling splitting. It concerns modes 1, 3 and 17 in the numbering of Table S2. Modes 1 and 3 are related to olefinic C-H, specific to MA. Modes 17 look like very similar in MA and 2-ClMA. This comparison brings another argument to discard the possibility of $\Delta\nu_1$=28 cm^{-1} in this vibrational level in 2-ClMA. However, the strong enhancement of the splitting with mode 15 (Table S2 numbering) in MA is not at all reproduced in 2-ClMA. As the splitting depends on the barrier for the H transfer, if a vibrational mode promotes the transfer the barrier is lowered compared to that in the ground state and the splitting is larger. Modes 15 in MA and 2-ClMA (Table S2 numbering) are “mechanically” very similar, as modes 17 are. In both cases, the different behavior of the tunneling upon vibrational excitation is surprising. However, our view is based on C_s calculations where the tunneling process is absent. A more sophisticated approach is definitively required to explain the observed differences in the MA and 2-ClMA vibrational behaviors. However, except for these specific modes, the comparison given in Table S2 shows many similar effects for similar modes in both molecules.

Table S2: Comparison of vibrational modes in 2-ClMA and MA. Frequencies (cm^{-1}) in C_s (equilibrium geometry) symmetries obtained at the (B3LYP/6-311++G(3df,3pd)) level of theory. Calculated intensities (km/mol) in parenthesis. The mode numbering is the same as in Table S1 and corresponds to the 2-ClMA molecule. Corresponding modes in 2-ClMA and MA are on the same lines. G_4 mode symmetries are those of Table S1. MA mode characteristics in italic refer to modes for which the correspondence with 2-ClMA is doubtful. Bold values correspond to C-H (olefinic) motions in MA. The measured tunneling splittings (cm^{-1}) in the various vibrational levels of 2-ClMA (this paper) and MA (refs 6-8), together with relative $\Delta\nu_1/\Delta\nu_0$ values are reported in the last four columns.

N°	C_s frequency (intensity) 2ClMA		C_s frequency (intensity) MA		G_4 sym.	$\Delta\nu_1$ 2-ClMA	$\Delta\nu_1$ MA	$\Delta\nu_1/\Delta\nu_0$ 2-ClMA	$\Delta\nu_1/\Delta\nu_0$ MA
1	**224**	**(5)**	**789**	**(36)**	B1		20-23 [a]		1
2	270	(7)	276	(9)	A1		265/57 [b]		>2.6
3	**283**	**(3)**	**1119**	**(11)**	B2		17 [b]		0.8
4	300	(2)	288	(4)	A2		6-9 [b]		~0.3
5	387	(3)	401	(4)	B1		15 [b]		0.7
6	**475**	**(6)**	**3221**	**(2)**	A1				
7	520	(17	523	(18)	B2		15 [b]		0.7
8	909	(53)	943	(53)	B1	1.9	3-5 [a]	0.25	~0.2
9	926	(34)	897	(7)	A1	7.8	27 [b]	1	1.25
10	997	(41)	1021	(18)	B1	5.1		0.65	
11	1035	(5)	1045	(17)	A2				
12	1080	(81)	1003	(45)	A1	8.3	14 [b]	1.0	0.65
13	1272	(200)	1289	(158)		3.2	8 [c]	0.4	0.4
14	1371	(64)	*1406*	*(17)*			0 [c]		0
15	1383	(102)	1391	(100)		0.4	69 [c]	0.05	3.2
16	1422	(26)	*1478*	*(49)*		0	4-7 [a]	0	~0.25
17	1613	(237)	1627	(277)	B2	28 [e]	21 [b]	3.5	1.0
18	1701	(154)	1697	(213)	A1	8.4	7 [b,d]	1.1	0.3 [d]
19	3002	(50)	2973	(105)	B2	*1*	*3* [b]	*0.1*	*0.1*
20	3169	(113)	3116	(229)	A1	*7*	*22* [b]	*0.9*	*1.0*
21	3215	(105)	3179	(16)	B2				

[a]ref. 6. [b]ref. 8. [c]ref. 7. [d]this mode appears as an hybrid mode in ref. 8 whereas case ① is clearly predicted, as for 2-ClMA. [e]value discussed in the text, not certain.

References:

1 A. Gutiérrez-Quintanilla, M. Chevalier, R. Platakyte, J. Ceponkus, G. A. Rojas-Lorenzo and C. Crépin, 2-Chloromalonaldehyde, a model system of resonance-assisted hydrogen bonding: Vibrational investigation, *Phys. Chem. Chem. Phys.*, 2018, **20**, 12888–12897.

2 A. Gutiérrez-Quintanilla, M. Chevalier, R. Platakyte, J. Ceponkus and C. Crépin, Selective photoisomerisation of 2-chloromalonaldehyde, *J. Chem. Phys.*, 2019, **150**, 034305.

3 P. Zielke and M. A. Suhm, Raman jet spectroscopy of formic acid dimers: Low frequency vibrational dynamics and beyond, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4528–4534.

4 R. L. Redington and R. L. Sams, State-specific spectral doublets in the FTIR spectrum of gaseous tropolone, *J. Phys. Chem. A*, 2002, **106**, 7494–7511.

5 R. L. Redington, T. E. Redington and R. L. Sams, Quantum tunneling in the midrange vibrational fundamentals of tropolone, *J. Phys. Chem. A*, 2006, **110**, 9633–9642.

6 T. N. Wassermann, D. Luckhaus, S. Coussan and M. A. Suhm, Proton tunneling estimates for malonaldehyde vibrations from supersonic jet and matrix quenching experiments, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2344–2348.

7 N. O. B. Luttschwager, T. N. Wassermann, S. Coussan and M. A. Suhm, Periodic bond breaking and making in the electronic ground state on a sub-picosecond timescale: OH bending spectroscopy of malonaldehyde in the frequency domain at low temperature, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8201–8207.

8 N. O. B. Lüttschwager, T. N. Wassermann, S. Coussan and M. A. Suhm, Vibrational tuning of the Hydrogen transfer in malonaldehyde – a combined FTIR and Raman jet study, *Mol. Phys.*, 2013, **111**, 2211–2227.

9 T. Baba, T. Tanaka, I. Morino, K. M. T. Yamada and K. Tanaka, Detection of the tunneling-rotation transitions of malonaldehyde in the submillimeter-wave region, *J. Chem. Phys.*, 1999, **110**, 4131–4133.

10 F. Wu, Quantum mechanical investigation of mode-specific tunneling upon fundamental excitation in malonaldehyde, *J. Phys. Chem. A*, 2016, **120**, 3849–3854.