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Microwave spectroscopy and large amplitude motion of chlorosulfonic acid ($ClSO_2OH$)

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ABSTRACT

The high-resolution rotational spectrum of chlorosulfonic acid ($ClSO_2OH$) has been studied using both broadband and cavity-based Fourier transform microwave spectrometers over the frequency range of 5–18 GHz. *a*-, *b*-, and *c*-type transitions have been recorded for both the ^{35}Cl and ^{37}Cl isotopologues. The observation of *c*-type lines establishes that the molecule lacks a plane of symmetry and suggests that the OH group can undergo large amplitude motion between equivalent structures. Interconversion between these structures can be achieved via internal rotation through two inequivalent barriers occurring at Cl-S-O-H torsional angles of 0 or 180 degrees. As in previous work on triflic and methanesulfonic acids, two states are observed and are treated as tunneling states which are presumed to arise primarily due to motion through the lower of the two barriers. The *a*- and *c*-type transitions occur within each of these states while the *b*-type transitions cross between them. Rotational, centrifugal distortion, and chlorine nuclear quadrupole coupling constants, as well as the energy difference between the two tunneling states and associated coupling constants, have been determined. The experimental tunneling energies, ΔE, for the ^{35}Cl and ^{37}Cl isotopologues are 52.6926(16) MHz and 52.6397(46) MHz, respectively. Quantum chemical calculations were carried out using MP2 and B3LYP density functional theory (DFT) methods with an aug-cc-pVTZ basis set. The rotational constants from the optimized structures were in good agreement with the experimental values. The lowest energy barrier for OH motion was calculated to be 2.63 kcal/mol at the B3LYP/aug-cc-pVTZ level. The effects of the large amplitude motion are similar to those recently reported for triflic acid (CF_3SO_2OH) and methanesulfonic acid (CH_3SO_2OH). However, while the tunneling splittings in chlorosulfonic and triflic acids are virtually identical, they differ significantly from that of methanesulfonic acid.

1. Introduction

Chlorosulfonic acid ($ClSO_2OH$) is a superacid that is commonly used in a variety of reactions such as sulfonation, esterification, and dehydration. Industrially, it finds application in the synthesis of sulfonic acid derivatives and is widely used in the production of detergents, dyes, and pharmaceuticals. Reyes *et al.* [1], Lane and Kjaergaard [2], and Gupta *et al.* [3] have performed calculations on OH-stretching overtone-induced photodissociation, while Li *et al.* [4] have reported a computational study on the ionic dissociation of the acid in micro-solvated clusters. The infrared spectrum has been recorded [5], and Badawi [6] has presented a complete vibrational analysis based on computed frequencies. The deprotonation energy has also been calculated by *ab initio* methods [7]. Experimentally, Canagaratna *et al.* [8] have reported the microwave spectrum of the weakly bound complex $HCl \cdot SO_3$, which is the van der Waals isomer of $ClSO_2OH$.

In this work, we report a combined theoretical and rotational spectroscopic study of the ^{35}Cl and ^{37}Cl isotopologues of chlorosulfonic acid. The acid is structurally similar to triflic [9] and methanesulfonic [10] acids, which have been previously studied by microwave techniques. Since the OH hydrogen does not lie on any symmetry plane, a particularly interesting feature of all of these systems is the torsional motion of the OH moiety. The resulting splittings (treated as tunneling splittings) have been measured for CF_3SO_2OH, CF_3SO_2OD, and CH_3SO_2OD, though that for CH_3SO_2OH has only been estimated, as it was likely outside the range of the spectrometer used in those studies. In this paper, the analogous tunneling splittings are measured for both $^{35}ClSO_2OH$ and $^{37}ClSO_2OH$, and complementary computational work investigating the tunneling path and the barrier to the hydroxyl large amplitude motion is reported. To the best of our knowledge, this study represents the first

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report of a high-resolution spectroscopic investigation of this species.

1.1. Computational methods and results

Density functional theory and MP2 calculations were carried out by the Gaussian 16 program [11] using the cluster computers from the Texas Advanced Computing Center (TACC) to determine the conformations and structural parameters of chlorosulfonic acid. The B3LYP (Becke's three-parameter hybrid functional using the LYP correlation functional) method [12,13] was implemented with the aug-cc-pVTZ basis set [14] to scan the dihedral angles of τ(Cl4-S1-O5-H6) for 36 steps at 10° per step, to identify the stable configurations. See Fig. 1 for atom numbering and for the structure obtained after full optimization. The result of the potential energy scan at the B3LYP/aug-cc-pVTZ level is given in Fig. 2 where it may be seen that the calculated equilibrium values of τ are ± 86 deg. The two energetically equivalent forms have identical rotational constants and are obtained when the hydroxyl group is oriented roughly parallel to the S1=O2 or S1=O3 bond. A rotation of OH around the S1-O5 bond allows the interconversion between these two structures. After further optimization, the calculated energy barriers to this interconversion are at $\tau = 180^\circ$ 2.63 kcal/mol (DFT) and 2.67 kcal/mol (MP2) and, with the zero-point energy correction, 2.10 kcal/mol (DFT) and 2.13 kcal/mol (MP2). At $\tau = 0^\circ$, they are 3.12 kcal/mol (DFT) and 3.52 kcal/mol (MP2) and after zero-point energy correction, 2.59 kcal/mol (DFT) and 2.97 kcal/mol (MP2). Thus, in cm^{-1}, the lower barrier is in the 920–934 cm^{-1} range (735–745 cm^{-1} with zero-point corrections) and the higher barrier is in the 1090–1230 cm^{-1} range (906–1040 cm^{-1} with zero-point corrections). The calculated rotational constants, dipole moment components (μ_g, $g = a, b, c$), and nuclear quadrupole coupling constants at the optimized geometry of the ^{35}Cl isotopologue are summarized in Table 1.

1.2. Experimental methods and results

Spectra were taken using a tandem cavity [15] and chirped-pulse [16] Fourier transform microwave spectrometer, details of which have been provided in prior publications [17,18]. Chlorosulfonic acid (Sigma Aldrich, 99 %) was placed in a reservoir and heated to approximately 80 °C. The vapor was entrained in a flowing stream of argon at 0.5 atm and passed into a 0.016 in. inner diameter needle, as described elsewhere [19]. The outlet of the needle was positioned just below the nozzle orifice and bent to direct the flow along the axis of a pulsed argon expansion with the stagnation pressure held at ~ 1.1 atm. Due to the corrosive nature of chlorosulfonic acid, all metal surfaces in contact with liquid or vapor were made of 316 stainless steel. A 6–18 GHz chirped-pulse spectrum was collected in 3 GHz segments, with each segment the average of between 170,000 and 900,000 free induction decay (FID) signals, and each FID collected for 20 μs. Constants obtained from preliminary fits of the resulting spectrum enabled subsequent cavity measurements which targeted weaker transitions. Both ^{35}Cl and ^{37}Cl species were observed in natural abundance. Uncertainties in the measured transition frequencies are estimated to be 3 kHz and 15 kHz

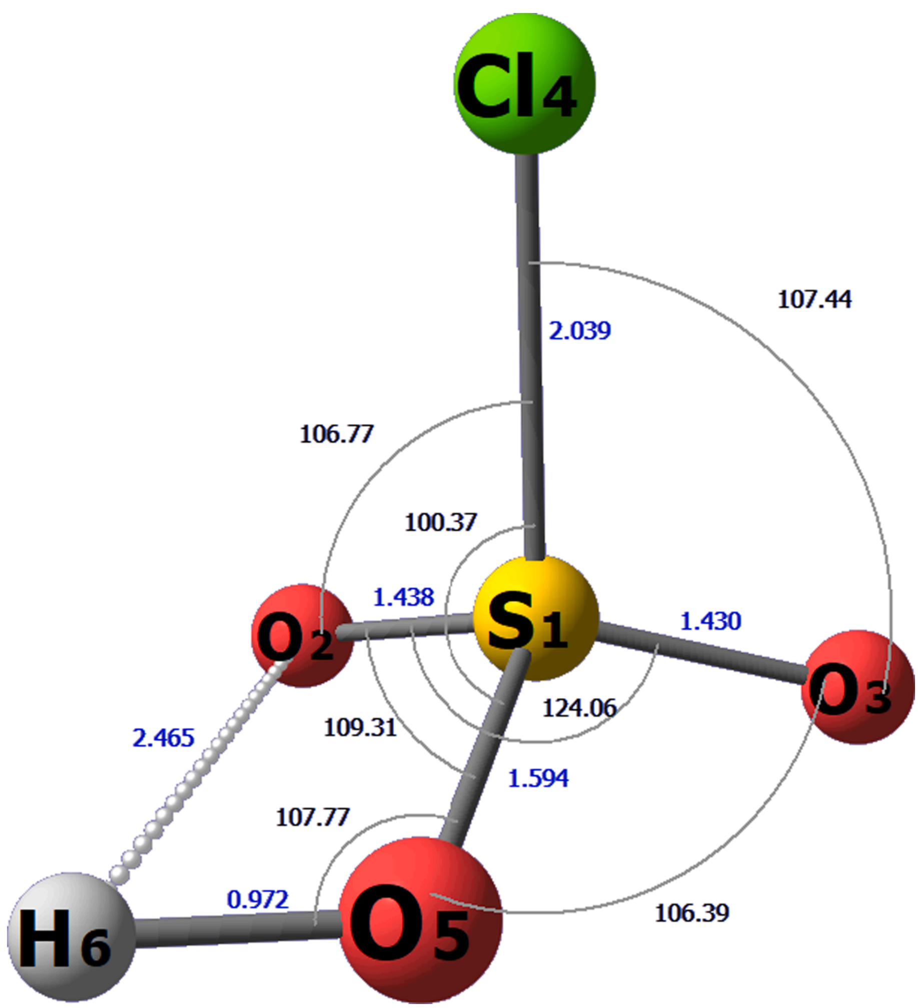

Fig. 1. Calculated geometry of chlorosulfonic acid at the MP2/aug-cc-pVTZ level of theory with atom labeling. This structure is one of two energetically equivalent configurations, the other having H6 pointed toward the right.

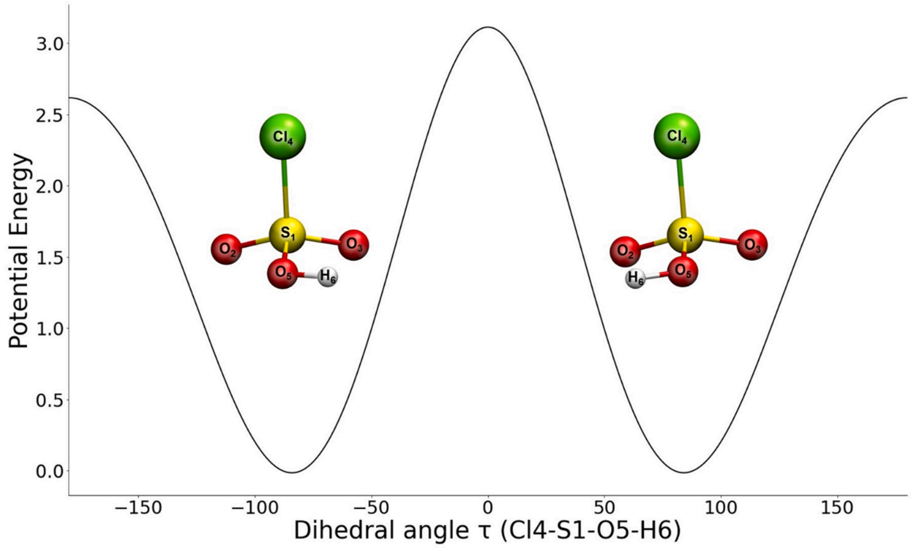

Fig. 2. The DFT potential energy scan at 10° intervals along Cl4-S1-O5-H6 dihedral angle for chlorosulfonic acid. Potential energy is given in kcal/mol and the dihedral angle is in degrees. The 2.6 kcal/mol barrier corresponding to rotation away from the S-Cl bond are seen at the far left and the far right. Rotation toward the S-Cl bond, through $\tau = 0$, has a slightly higher barrier. Since the potential energy maxima do not exactly correspond to any of the dihedral angles of the grid, transition state energies were further optimized to give the numbers cited in the text.

Table 1
Calculated spectroscopic constants of chlorosulfonic acid at the B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels of theory.

Parameters	B3LYP/ aug-cc-pVTZ	MP2/ aug-cc-pVTZ
A (MHz)	4907.12	4928.69
B (MHz)	2746.35	2824.43
C (MHz)	2727.35	2795.87
μ_a (Debye)	0.58	0.69
μ_b (Debye)	2.21	1.88
μ_c (Debye)	1.6	1.95
χ_{aa} (MHz)	−72.84	−67.22
$(\chi_{bb} - \chi_{cc})$ (MHz)	0.998	2.15

for the cavity measurements and the chirped-pulse system, respectively. Representative cavity spectra are shown in Fig. 3.

The calculated dipole moment of the molecule has non-zero components along each of the inertial axes and thus, *a*-, *b*-, and *c*-type spectra were observable. The *a*-, and *c*-type transitions appeared as closely spaced pairs and were, therefore, assigned as occurring within tunneling states, while the *b*-type transitions were significantly displaced from their rigid rotor values and were assigned as crossing between them. The separation of 109 MHz for the strongest hyperfine component of the $1_{11} \leftarrow 0_{00}$ transition is approximately twice the value of the tunneling splitting, ΔE. The *b*-type and *c*-type transitions were relatively strong and *a*-type transitions were relatively weak, in agreement with the calculated dipole moment components listed in Table 1.

The following Hamiltonian was used to treat the observed spectrum:

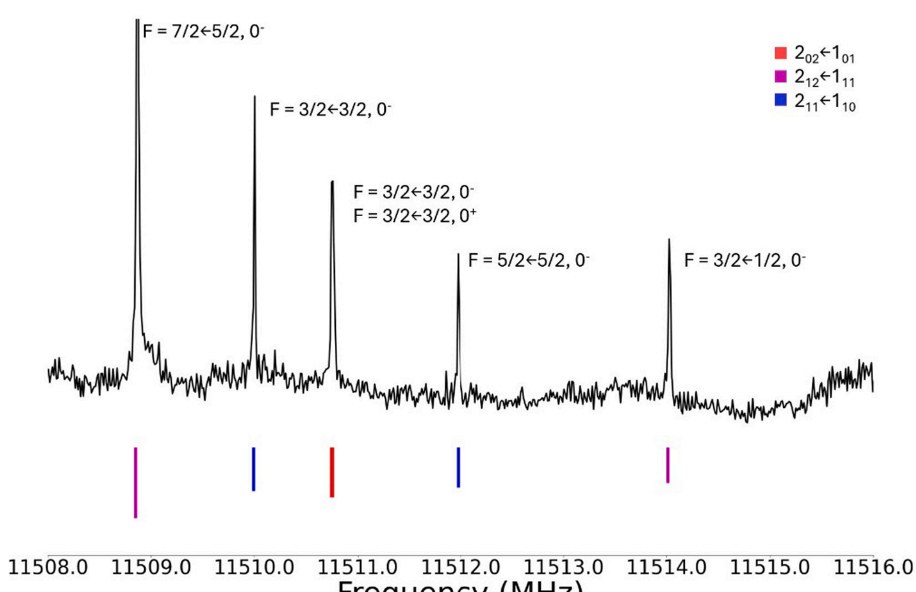

Fig. 3. A sample spectrum of ^{35}Cl chlorosulfonic acid. This spectrum is the result of stitching together several scans taken on the cavity spectrometer.

$$\mathrm{H} = \sum_{n=0}^{1}\left[H_{ROT}^{(n)} + H_{CD}^{(n)} + H_{NQC}^{(n)} + \delta_{n,1}\Delta E\right] + H_{INT} \quad (1)$$

where H_{ROT} and H_{CD} are the rigid rotor and centrifugal distortion Hamiltonians, respectively, and $n = 0$ and 1 for the two tunneling states, designated 0^+ and 0^-, respectively. H_{NQC} is the Hamiltonian for the nuclear quadrupole coupling for the $I = 3/2$ ^{35}Cl or ^{37}Cl nucleus, $\delta_{n,1}$ is the Kronecker delta, and ΔE is the energy separation between the tunneling states. The Watson-A reduced Hamiltonian in the I^r representation [20] was used for the centrifugal distortion terms. H_{INT}, which is the Hamiltonian describing the interaction between the 0^+ and 0^- states, accounts for Coriolis coupling [21,22]. The following form was used:

$$H_{INT} = F_{bc}(P_bP_c + P_cP_b) + G_aP_a \quad (2)$$

In principle, both terms have the correct symmetry but it is unknown *a priori* whether one or the other or both are necessary to fit the observed data. After numerous attempts to determine the best form of H_{INT}, it was found necessary to retain both terms in order to obtain an acceptable fit. It is noteworthy that in the case of triflic acid, the parent form could be fit using only the F_{bc} term while the deuterated form required only the G_a term [9]. This difference was attributed to the different selection rules for the matrix elements of $(P_bP_c + P_cP_b)$ and P_a which, therefore, render the different operators best able to describe the strongest couplings that manifest in the spectrum. Evidentially, given the pairs of levels that interact in chlorosulfonic acid, the use of both terms provides the best description. Indeed, with only the F_{bc} term, the fits for the ^{35}Cl isotopologue achieved an rms residual of 50 kHz, which dropped to 10.7 kHz after adding the G_aP_a term and its K-dependent correction, $G_a^K K^2$).

Fits were performed using Pickett's SPFIT program [23,24]. In total, 215 hyperfine components between 5 and 18 GHz were included for the ^{35}Cl species and the fitted constants are summarized in Table 2. The rms error is seen to be 10.7 kHz, which is comparable to the frequency accuracy of the chirped-pulse spectrum. It is interesting to note that in the analysis of deuterated triflic acid, the fitted values of Δ_K for the two tunneling states were of approximately equal magnitude but opposite signs. This is also the case for chlorosulfonic acid, and may result from some additional untreated interaction absorbed in these constants and/or neglect of the full 360 degree internal rotation through both potential energy barriers. Spectral frequencies, their assignments, and residuals from the least squares fits are given in the Supplementary Material.

For the ^{37}Cl isotopologue, a total of 76 hyperfine components between 5 and 15 GHz were assigned and fit. Due to lower intensities, fewer hyperfine components were measured and two of the centrifugal distortion constants, Δ_{JK} and Δ_K, were not determinable from the data. Thus, they were constrained to their ^{35}Cl values in the fit. The resulting spectroscopic parameters are listed in Table 3 and a table of the observed frequencies, assignments, and residuals is given in the Supplementary Material. Assuming identical electric field gradients around the ^{35}Cl and ^{37}Cl nuclei and the same location of the *a*-, *b*-, and *c*-inertial axes, the ratio of their nuclear quadrupole coupling constants should equal the nuclear quadrupole moment ratio of ^{35}Cl and ^{37}Cl. Indeed, the ratio of the fitted values of χ_{aa} is 1.268624(79), which agrees well with the literature value of 1.26878(15) [25]. For (χ_{bb}− χ_{cc}), the ratio is 1.2751(34), which slightly outside the experimental uncertainties, but still acceptable given the rotation of the inertial axes upon substitution.

Table 2
Experimental spectroscopic constants from the combined fit of the 0^+ and 0^- states for $^{35}ClSO_2OH$.

	0^+		0^-
A (MHz)	5069.493(16)		5066.031(16)
B (MHz)	2876.939(19)		2876.940(20)
C (MHz)	2871.273(19)		2871.269(20)
Δ_J (kHz)	0.536(49)		0.703(45)
Δ_{JK} (kHz)	2.31(28)		1.82(29)
Δ_K (kHz)	8.6(26)		−12.0(21)
χ_{aa} (MHz)	−72.6350(27)		−72.6399(25)
$(\chi_{bb} - \chi_{cc})$ (MHz)	3.9856(68)		3.9788(52)
ΔE (MHz)		52.6926(16)	
$\lvert F_{bc}\rvert$(MHz)		11.5273(48)	
$\lvert G_a\rvert$ (MHz)		9.545(45)	
G_a^K(MHz)		−0.1845(47)	
N[a]		215	
σ[b] (kHz)		10.7	

[a] Total number of transitions used in the fit.
[b] Standard deviation of the fit.

Table 3
Experimental spectroscopic constants from the combined fit of the 0^+ and 0^- states for $^{37}ClSO_2OH$.

	0^+		0^-
A (MHz)	5069.428(33)		5066.072(33)
B (MHz)	2800.188(39)		2800.194(39)
C (MHz)	2794.719(39)		2794.709(39)
Δ_J (kHz)	0.68(14)		0.502(26)
Δ_{JK} (kHz)	[2.31] [c]		[1.82] [c]
Δ_K (kHz)	[8.6] [c]		[-12.0] [c]
χ_{aa} (MHz)	−57.2549(29)		−57.2587(35)
$(\chi_{bb} - \chi_{cc})$ (MHz)	3.1256(64)		3.112(10)
ΔE (MHz)		52.6397(46)	
$\lvert F_{bc}\rvert$(MHz)		10.9044(99)	
$\lvert G^a\rvert$ (MHz)		9.392(92)	
G_a^K(MHz)		−0.1748(53)	
N[a]		76	
σ[b] (kHz)		10.4	

[a] Total number of transitions used in the fit.
[b] Standard deviation of the fit.
[c] Fixed at the corresponding values from ^{35}Cl isotopologue fit.

2. Discussion

The theoretical rotational constants for $^{35}ClSO_2OH$ are in good agreement with experiment, with the MP2 values within 2.8 % of the observed values. The B3LYP results are slightly worse, but still acceptable, with the calculated constants within 5 % of those observed. In making these comparisons, it should be noted that the calculated structural parameters reflect the equilibrium structure, whereas the experimental parameters correspond to the vibrationally averaged structure of the ground vibrational state. Interestingly, the B3LYP calculations show better agreement with experimental χ_{aa}, which is within 0.3 % of the observed value (compared with the MP2 result which is only within 7.5 % of the measured value). The calculated values of $(\chi_{bb} - \chi_{cc})$ are significantly worse, with percent errors of 75 % and 46 % for the B3LYP and MP2 calculations, respectively. However, this may not be too surprising inasmuch as the values themselves are small and thus small absolute errors manifest as large percent errors.

The results of this study show that chlorosulfonic acid is remarkably similar to triflic acid. The measured tunneling splittings are virtually identical, 52.6926(16) MHz and 52.96784(65) MHz for $^{35}Cl^{32}SO_3H$ and $CF_3^{32}SO_3H$, respectively. The barrier interconnecting the two equivalent minima are also virtually identical, 2.6 and 2.8 kcal/mol for chlorosulfonic and triflic acids, respectively. (We note however that slightly different methods were used to obtain these results: B3LYP/aug-cc-pVTZ for chlorosulfonic acid and M06-2X/6–311++G(3df,3pd) for triflic acid). In both systems, the *b*-type transitions cross between tunneling states. While, at first, this latter point may not seem surprising, the selection rules for the triflic acid spectrum were observed to change upon deuteration such that it was the *c*-type transitions that crossed between the tunneling states. This effect was attributed to subtle changes in the vibrationally averaged geometry upon deuterium substitution which gave rise to a switching of the definitions of the *b*- and *c*-inertial axes [9]. Thus, in this light, the exact parallel between the selection rules in chlorosulfonic and triflic acids seems not guaranteed, though it apparently holds true. It would be interesting to know if it is the *c*-type transitions that cross between tunneling states in the $ClSO_2OD$ spectrum. Note that, as in the cases of triflic and methanesulfonic acids, the chlorosulfonic acid spectrum is treated here as a tunneling problem between two equivalent minima in which (presumably) only the lower of the two barriers in Fig. 2 is relevant. This approach has been quite successful in all three cases, but we note that it is possible that the spectra could be alternatively treated as an internal rotation problem involving a full 360 degree rotation through two inequivalent potential barriers. In light of the overall success of the tunneling approach, however, this possibility has not been pursued.

In contrast with the similarities between chlorosulfonic and triflic acids, the substitution of Cl or CF_3 with a CH_3 group produces dramatic changes. The barrier to the torsional motion in methanesulfonic acid has been calculated to be only ~ 0.7 kcal/mol (245 cm^{-1}) [10], and the tunneling splitting is, correspondingly, much larger. Indeed, the energy separation between the tunneling states for the CH_3SO_2OH has been estimated to be ~ 150 GHz [2] and was, therefore, too large to measure in previously reported microwave work [10]. The tunneling splitting for the OD species, however, was within the range of the spectrometer and was determined to be 6471.9274(18) MHz. Thus, it is safe to expect that the value for the OH form is much higher than that. Clearly, the 53 MHz tunneling splitting observed for both chlorosulfonic and triflic acids is extremely small in comparison. While Cl and CF_3 are both electron withdrawing, the CH_3 group is electron donating and this, evidently, has a profound effect on the torsional energy barrier and OH torsional frequency.

3. Conclusions

In this work, the first combined theoretical and high-resolution spectroscopic study on chlorosulfonic acid ($ClSO_2OH$) has been conducted. Torsional motion of the OH group about the S-O bond in a double minimum potential results in the observation of a pair of tunneling states for both ^{35}Cl and ^{37}Cl isotopologues. Of the observed transitions, *a*-, and *c*-type transitions are within each of the tunneling states, while the *b*-type transitions cross between them. The lowest barrier height to this motion was calculated to be 2.63 kcal/mol (920 cm^{-1}) at the B3LYP/aug-cc-pVTZ level of theory and is surmounted along a path in which the O-H group rotates through a configuration in which the O-H bond is *anti* to the S-Cl bond. The experimentally determined tunneling energies, ΔE, for the ^{35}Cl and ^{37}Cl isotopologues are 52.6926(16) MHz and 52.6397(46) MHz, respectively. These values are nearly identical to those for triflic acid but strikingly different from those of methanesulfonic acid. Taken together, the results for chlorosulfonic, triflic, and methanesulfonic acids provide good benchmarks for calculations aimed at predicting these tunneling splittings.

CRediT authorship contribution statement

Aaron J. Reynolds: Writing – review & editing, Validation, Investigation, Formal analysis, Data curation. **Diego E. Rodriguez:** Investigation. **Wei Lin:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Investigation, Formal analysis, Data curation, Conceptualization. **Kenneth R. Leopold:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jms.2024.111927.

References

[1] J.Y. Reyes, S. Brickel, O.T. Unke, T. Nagy, M. Meuwly, Phys. Chem. Chem. Phys. 18 (2016) 6780–6788.
[2] J.R. Lane, H.G. Kjaergaard, J. Phys. Chem. A 111 (2007) 9707–9713.
[3] P. Gupta, J.R. Lane, H.G. Kjaergaard, Phys. Chem. Chem. Phys. 10 (2010) 8277–8284.
[4] S. Li, F. Tao, R. Gu, Sci. China Ser B: Chem. 51 (2008) 305–315.
[5] S.M. Chackalackal, F.E. Stafford, J. Am. Chem. Soc. 88 (1966) 4815–4819.
[6] H.M. Badawi, Spectrochimica Acta Part A 66 (2007) 194–198.
[7] A.H. Otto, S. Schrader, T. Steigler, M. Schneider, J. Chem. Soc. Faraday Trans. 93 (1997) 3927–3930.
[8] M. Canagaratna, J.A. Phillips, H. Goodfriend, D.L. Fiacco, M.E. Ott, B. Harms, K. R. Leopold, J. Mol. Spectrosc. 192 (1998) 338–347.
[9] A.K. Huff, N. Love, K.R. Leopold, J. Mol. Spectrosc. 385 (2022), 111623-1–9.
[10] A.K. Huff, N. Love, K.R. Leopold, J. Phys. Chem. A 127 (2023) 3658–3667.
[11] Gaussian 16, Revision 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, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
[12] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
[13] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.
[14] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007–1023.
[15] T.J. Balle, W.H. Flygare, Rev. Sci. Instrum. 52 (1981) 33–45.
[16] G.G. Brown, B.C. Dian, K.O. Douglass, S.M. Geyer, S.T. Shipman, B.H. Pate, Rev, Sci. Instrum 79 (2008) 053103.
[17] J.A. Phillips, M. Canagaratna, H. Goodfriend, A. Grushow, J. Almlöf, K.R. Leopold, J. Am. Chem. Soc. 117 (1995) 12549–12556.
[18] C.T. Dewberry, R.B. Mackenzie, S. Green, K.R. Leopold, Rev. Sci. Instrum. 86 (2015), 065107–1-7.
[19] M. Canagaratna, J.A. Phillips, H. Goodfriend, K.R. Leopold, J. Am. Chem. Soc. 118 (1996) 5290–5295.
[20] J.K.G. Watson, Aspects of Quartic and Sextic Centrifugal Effects on Rotational Energy Levels, in: J.R. Durig (Ed.), Vibrational Spectra and Structure, Elsevier Scientific Publishing, Amsterdam, 1977, pp. 1–89.
[21] H.M. Pickett, J. Chem. Phys. 56 (1972) 1715–1723.
[22] C.R. Quade, J. Chem. Phys. 47 (1967) 1073–1090.
[23] H.M. Pickett, J. Mol. Spectrosc. 148 (1991) 371–377.
[24] S.E. Novick, J. Mol. Spectrosc. 329 (2016) 1–7.
[25] R. Livingston, Phys. Rev. 82 (1951) 289.