

AJP

ISSN : 0971 - 3093

Vol 23, No 6, December, 2014

ASIAN JOURNAL OF PHYSICS

An International Quarterly Research Journal



ANITA PUBLICATIONS

FF-43, 1st Floor, Mangal Bazar, Laxmi Nagar, Delhi-110 092, India
B O : 2, Pasha Court, Williamsville, New York-14221-1776, USA

Vibrational assignments, theoretical calculations, structural parameters and conformer stability determinations of cyclobutyldichlorosilane

James R Durig^{a*}, Ikhlas D Darkhalil^{1a}, Bhushan S Deodhar^{2a}, Gamil A Guirgis^b, Justin K Wyatt^b,
Carson W Reed^b and Joshua J Klaassen^a

^aDepartment of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110 USA

^bDepartment of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424, USA

Dedicated to Professor Dr. S Mohan

The infrared spectra of the gas (3500 to 80 cm⁻¹) and Raman spectra of the liquid (1500 to 1100 cm⁻¹) of cyclobutyldichlorosilane (c-C₄H₇SiHCl₂) have been recorded and complete vibrational assignments are given for all four conformers. To support the spectroscopic study, ab initio calculations by the Møller-Plesset perturbation method to second order MP2 (full) and density functional theory calculations by the B3LYP method have been carried out. The infrared intensities, Raman activities, vibrational frequencies and band contours have been predicted from MP2 (full)/6-31G(d) calculations and these theoretical values are compared to the experimental ones when available. The conformational stabilities (t-Eq > g-Eq > t-Ax > g-Ax) have been predicted from theoretical calculations with basis sets up to 6-311+G(2d,2p) from both MP2(full) and density functional theory calculations by the B3LYP method. The results are discussed and compared to the corresponding properties of some related molecules. © Anita Publications. All rights reserved.

Keywords: cyclobutyldichlorosilane; vibration; conformations.

1 Introduction

The structure of the cyclobutane molecule generated controversy whether it was a puckered or planar molecule. Several different methods were used to try to obtain conclusive evidence of the structure of the molecule. This controversy continued for several years until finally a vibrational study showed conclusively that the molecule was puckered [1].

There was no controversy concerning the structure of the ring for the cyclobutyl molecules which had monosubstituted additions but there was a different controversy. There was an interesting controversy that developed when studies were reported from the infrared vibrations investigation of cyclopropyl chloride and bromide. From the study of these two molecules it was reported that both of these molecules had both axial and equatorial molecules present from infrared vibrational investigations [2-3]. However, one of these investigators carried out a microwave investigation of cyclobutylbromide [4] but the equatorial conformer was the only form identified. Additionally, a subsequent microwave investigation of cyclobutyl chloride which was very extensive with several isomers from a well known scientist (Prof. W. D. Gwinn) and it was clearly shown that there was only the axial conformer present [5]. Continuing microwave studies did not provide evidence of a second conformer whereas the vibration spectrum clearly showed the presence of the second conformer [6-7]. This difference persisted until the 80s when cyclobutyl halides and silane reported to have both the axial and equatorial conformers present in the monosubstituted cyclobutyl molecules.

The utilization of microwave spectroscopy for the determination of structural parameters of significant organic molecules became in use in the 60's. Of particular interest was the excellent study of the microwave investigation of chlorocyclobutane. The structural parameters were reported for this chloride where in addition to the rotational constants for the ³⁵Cl species there were rotational constants from eight

¹Taken in part from the theses of I D Darkhalil which will be submitted in partial fulfillment of the Ph.D. degrees.

²Taken in part from the theses of B S Deodhar which will be submitted in partial fulfillment of the Ph.D. degrees.

Corresponding author :

e-mail: durigj@umkc.edu ; 01 816-235-6038, fax: 01 816-235-2290, (James R Durig)

of the isotopes of this molecule. By using these data the r_0 parameters were obtained for this molecule. However, the CH distance ranged from 1.090 to 1.110 Å which is a very large difference. Therefore, the utilization of a significant number of hydrogen isotopes to obtain molecular distances results for many molecules with unusual structural parameters.

An attempt was made to obtain more realistic parameters by combining *ab initio* predicted values and the experimentally determined rotational constants to determine the r_0 structural parameters more accurately by utilization of diagnostic least square [8]. However, many of the A rotational constants of the isotopomers could not be fitted but from a later microwave study [9] the spectrum of both the axial and equatorial conformers were assigned and the A rotational constants for the ^{35}Cl and ^{37}Cl isotopomers were significantly different from those previously reported [5]. Therefore, by using these new values of the rotational constants and by combining them with *ab initio* calculations again parameters were obtained which seemed more reasonable.

The data of greatest interest in connection with the geometrical structure are the internuclear distances. Initially the r_s method was derived in 1953 directly from rotational-vibrational spectroscopy. When the rotational constants for various isotopic species are observed then the r_s structure can be determined by Kraitchman's method [10]. The major problem with the r_s structure is that it assumes the geometry to be isotope invariant. This would be true if the harmonic approximation were exactly obeyed but it is not and an uncertainty in the r_s structure arises from anharmonicity. Additionally if the atom lies on the axis then there is no way to obtain the r_s structural parameters for that species. Thus it is reasonable to imply that there is no real way to relate r_s to other kinds of experimental structures.

Another method for estimating an equilibrium structure from ground state rotational constants was developed by Watson [11] in 1973 who proposed a mass dependent method (r_m) and applied it to a number of diatomic and triatomic molecules. The advantage of this mass dependent method over the conventional r_e method is insensitive to the perturbations and resonances that affect excited vibrational states. This method was utilized by Nakata and coworkers [12] for determination of the r_m structure of phosgene. It was observed in the analysis that the r_m structure derived from different combination of isotopic species were different from one another and exceeded their experimental error. This systematic uncertainty can be reduced or practically cancelled [13-14] by taking proper average of r_m parameters obtained from different isotopic species. Nevertheless the need for significant isotopic species has led to few determinations of r_m parameters. Thus the r_0 parameters are the ones mainly used in the last decade. Therefore, we initiated some adjustments to improve the ability to obtain the heavy atom parameters of molecule with two or more conformers by the use of *ab initio* predictions.

We have found that good structural parameters for hydrocarbons and many substituted ones can be determined by adjusting the structural parameters obtained from the *ab initio* MP2(full)/6-311+G(d,p) calculations to fit the rotational constants obtained from microwave experimental data by using the computer program "A&M" (*Ab initio* and Microwave) developed [15] in our laboratory. To reduce the number of parameters that are necessary for completed structural data we have shown that the C-H distance can be obtained by theory predictions. We [16] have shown that *ab initio* MP2(full)/6-311+G(d,p) calculations predict the carbon-hydrogen r_0 structural parameters for more than fifty hydrocarbons to at least 0.002 Å compared to the experimentally determined [17] values from isolated CH stretching frequencies which agree with previously determined values from earlier microwave studies. Therefore, all of the carbon-hydrogen parameters can be taken from the MP2 (full)/6-311+G(d,p) predicted values for the respective conformer. However, in order to further reduce the number of independent variables, the structural parameters are separated into sets according to their types where bond distances in the same set keep their relative ratio, whereas bond angles and torsional angles in the same set keep their difference in degrees. This assumption is based on the fact that errors from *ab initio* calculations are systematic.

Additionally, we have also shown that the differences in predicted distances and angles from the *ab initio* calculations for different conformers of the same molecule can usually be used as one parameter with the *ab initio* predicted differences except for some dihedral angles. Therefore, if we have complete set of rotational constants then the adjusted r_0 structural parameters for a molecule can be obtained. The germane-hydrogen and silicon-hydrogen r_0 structural parameter values can be experimentally determined [17] from isolated SiH and GeH stretching frequencies. The conformers of cyclobutyldichlorosilane are shown in Fig 1.

2 Experimental and Computational Methods

The sample of cyclobutyldichlorosilane was prepared by coupling trichlorosilane to the Grignard reagent of cyclobutyl magnesiumbromide in dry diethyl ether under dry nitrogen. After stirring over night at room temperature the sample was filtered under nitrogen and the ether was distilled off. The product was originally purified by trap-to-trap distillation twice and the final purification was obtained at low pressure and low temperature by a sublimation column. The sample was further purified by a fractionation column and the purity of the sample was verified from the infrared spectra of the gas and NMR spectrum of the liquid.

The mid infrared spectrum of the gas (Fig 2) was obtained from 4000 to 250 cm^{-1} on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapour was removed from the spectrometer housing by purging with dry nitrogen. The theoretical resolution used to obtain the spectrum of the gas was 0.5 cm^{-1} . One hundred twenty eight interferograms were added and transformed with a boxcar truncation function.

The Raman spectra (Fig 3) were recorded on a Spex model 1403 spectrometer equipped with a Spectra-Physics model 2017 argon laser operating on the 514.5 nm line. The laser power used was 0.5 W with a spectral bandpass of 3 cm^{-1} . The spectrum of the liquid was recorded with the sample sealed in a Pyrex glass capillary. The measurements of the Raman frequencies are expected to be accurate to $\pm 2 \text{ cm}^{-1}$.

The LCAO-MO-SCF restricted Hartree-Fock calculations were performed with the Gaussian-03 program [19] with Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters by using the gradient method of Pulay [20]. Several basis sets as well as the corresponding ones with diffuse functions were employed with the Møller-Plesset perturbation method [21] to second order (MP2 (full)) as well as with the density functional theory by the B3LYP method.

The infrared spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra. Infrared intensities determined from MP2(full)/6-31G(d) calculations were obtained based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were transformed with respect to normal coordinates by $(\partial\mu_w/\partial Q_i) = \sum (\partial\mu_w/\partial X_j)L_{ij}$, where Q_i is the i^{th} normal coordinate, X_j is the j^{th} Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $[(N\pi)/(3c^2)] [(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$. The predicted spectrum of the mixture of conformers should be compared to the infrared spectra of the gas (Fig 2).

The *ab initio* calculations were carried out for this molecule and the energy differences [Table 1] for the four possible forms were obtained with the t-Eq form as the most stable conformer followed by the g-Eq, t-Ax and g-Ax forms. The *ab initio* predicted energy difference from the MP2(full)/6-311G(d,p) calculations with 198 basis sets gives the t-Eq conformer as the more stable form by 57 cm^{-1} (0.68 kJ/mol) than the g-Eq form. The B3LYP method with all the basis sets used in this study consistently predicts t-Eq

as the more stable conformer followed by g-Eq, t-Ax and g-Ax forms, respectively. From the band intensities of the t-Eq and g-Eq SiCl_2 symmetric stretch fundamentals assigned at 519 and 481 cm^{-1} , respectively, an initial ΔH can be determined with a value of 271 cm^{-1} . The accuracy of this value is likely to be very poor as there are underlying fundamentals from the t-Ax and g-Ax fundamentals in near coincidence with these two bands but this can give an idea of which conformer is more stable and it gives a value to compare the predicted energy differences.

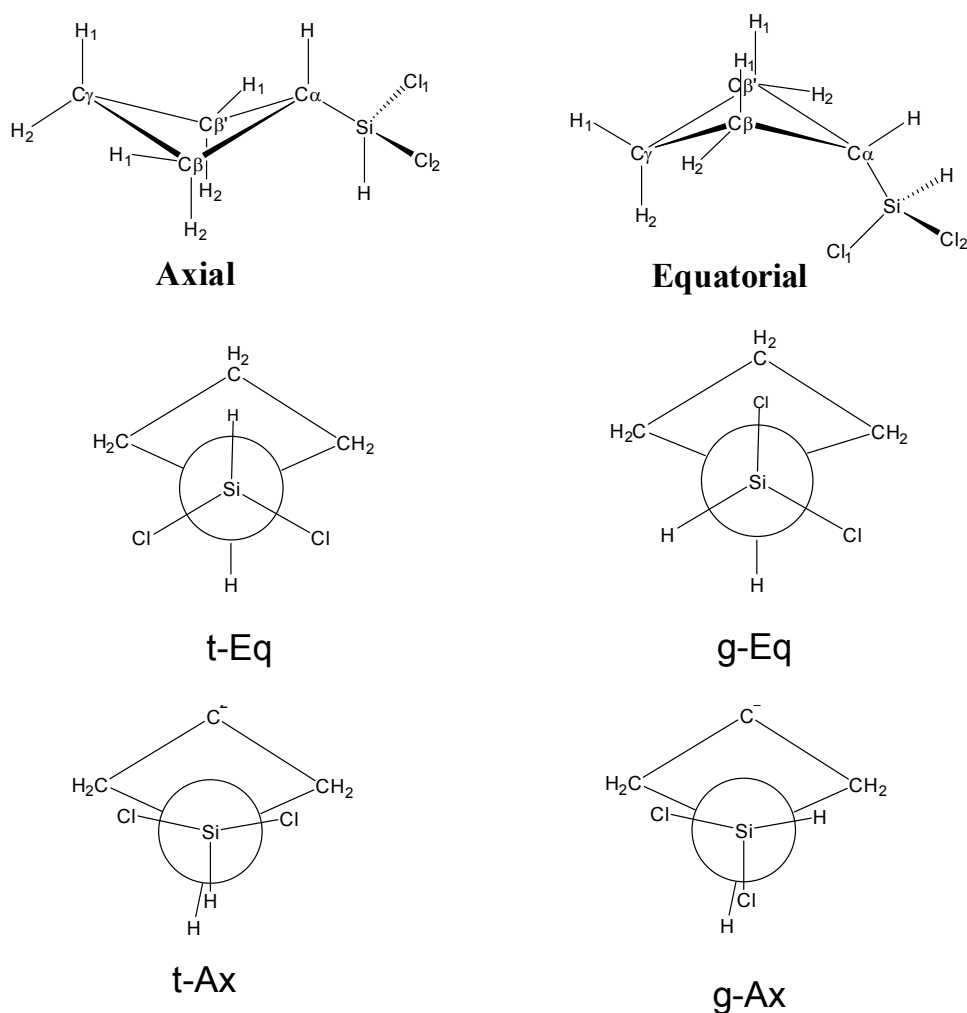


Fig 1. Conformers of cyclobutyldichlorosilane

3 Results and Discussion

It is interesting to note that when we proceed to a higher basis set like MP2 (full)/6-311+G(2d,2p) it predicts the g-Eq form to be more stable than the t-Eq conformer by 82 cm^{-1} . This is an interesting phenomenon where the addition of more functions into the *ab initio* basis sets actually causes poorer results. The same basis set but with B3LYP method gave instead the t-Eq form as the most stable conformer from

the four possible ones. These values are both far off in magnitude and the *ab initio* predicted MP2(full) values even predicts the Eq-g conformer as being the more stable form. Thus the B3LYP method gives more consistent results for conformational stability predictions in this study compared to the MP2(full) calculation which was not able to predict a specific conformer as the more stable form. The experimentally determined enthalpy differences if obtained later should be comparable to the *ab initio* predicted energy values and also can be compared with other enthalpy differences obtained for other molecules of the form $c\text{-C}_4\text{H}_7\text{SiHX}_2$. The B3LYP predictions appear to correspond much better with the experimental result and so are thought to be more reliable for the determination of the energy differences.

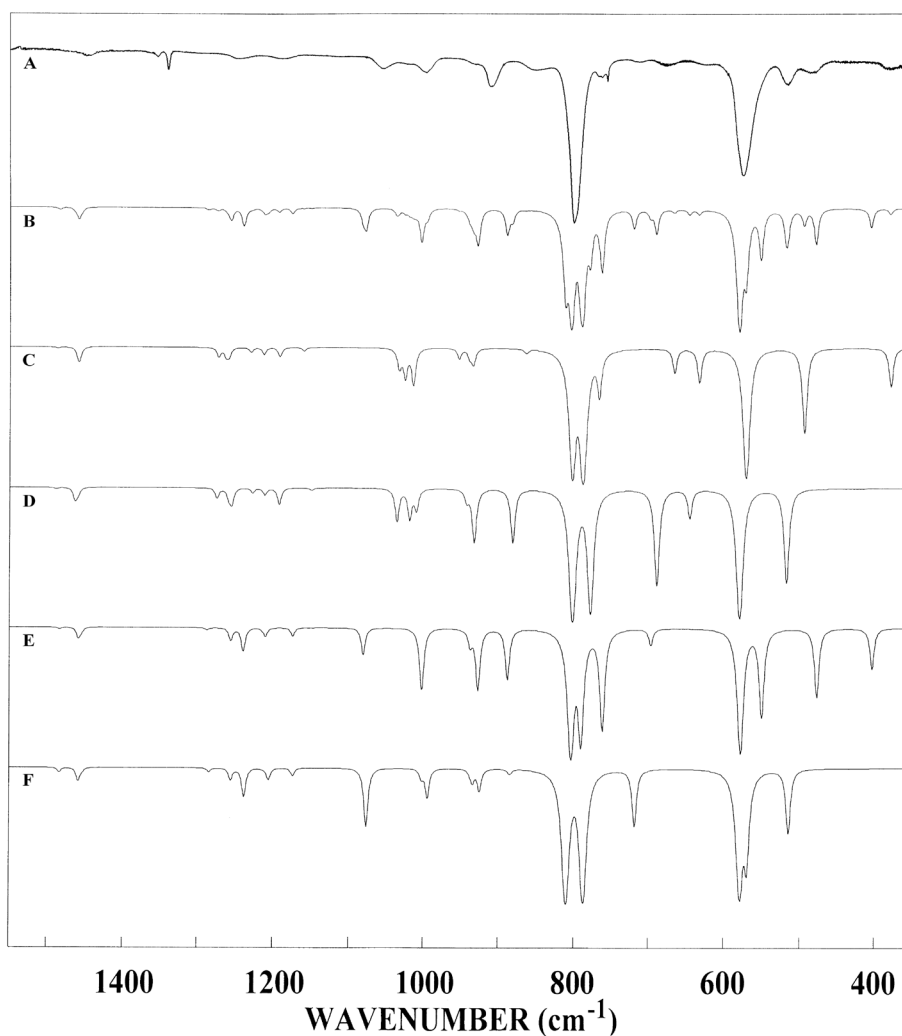


Fig 2. Comparison of experimental and calculated infrared spectra of cyclobutyldichlorosilane: (A) observed spectrum of gas; (B) simulated spectrum of a mixture of the four stable conformers of cyclobutyldichlorosilane at 25°C; (C) simulated spectrum of g-Ax conformer; (D) simulated spectrum of t-Ax conformer; (E) simulated spectrum of g-Eq conformer; (F) simulated spectrum of conformer t-Eq

Table 1. Calculated Electronic Energies (Hartree) for the t-Eq and Energy Differences (cm^{-1}) for g-Eq, t-Ax, and g-Ax Forms of cyclobutyldichlorosilane

Method/Basis Set	t-Eq ^a	Energy Difference ^b		
		g-Eq	t-Ax	g-Ax
MP2(full)/6-31G(d)	0.000684	12	164	286
MP2(full)/6-31+G(d)	0.0175112	-6	258	226
MP2(full)/6-31G(d,p)	0.0669021	14	182	331
MP2(full)/6-31+G(d,p)	0.0827558	6	267	259
MP2(full)/6-311G(d,p)	0.456566	57	112	306
MP2(full)/6-311+G(d,p)	0.467003	-35	214	185
MP2(full)/6-311G(2d,2p)	0.5953155	-19	48	90
MP2(full)/6-311+G(2d,2p)	0.6013542	-82	69	26
B3LYP/6-31G(d)	2.2093142	64	266	336
B3LYP/6-31+G(d)	2.2164985	75	280	343
B3LYP/6-31G(d,p)	2.2203848	61	258	331
B3LYP/6-31+G(d,p)	2.2272266	71	271	331
B3LYP/6-311G(d,p)	2.3313051	92	226	308
B3LYP/6-311+G(d,p)	2.3346166	70	235	292
B3LYP/6-311G(2d,2p)	2.3489741	84	207	266
B3LYP/6-311+G(2d,2p)	2.3509751	65	212	251

^a Energy of conformer is given as $-(E + 1365)$ H.

^b Energy difference related to the t-Eq conformer.

There has been no vibrational investigation previously reported on the cyclobutyldichlorosilane. In the current study, with the aid of MP2(full)/6-31G(d) predicted vibrational wavenumbers, *ab initio* predicted intensities along with infrared band contours it has been possible to assign a significantly large number of the fundamentals for the most stable conformers of $c\text{-C}_4\text{H}_7\text{SiHCl}_2$ Tables (2-5). The vibrational assignments reported herein are based on a significant amount of information with the mid infrared spectrum of the gas and predictions from the scaled *ab initio* MP2(full)/6-31G(d) calculations. The *ab initio* infrared band intensities were also used but they seemed to be the least reliable of the data utilized.

For the t-Eq conformer the average error for the fixed scaled predicted frequencies for the A' block fundamentals was 9 cm^{-1} which represent 0.6% error. The average error for the A'' modes for the t-Eq form was 7 cm^{-1} which represent 0.55% error. Thus, the relatively small basis set of 6-31G(d) by the MP2(full) calculations with two scaling factors provides excellent predicted frequencies for aiding the vibrational assignments.

Table 2. Observed and calculated^a frequencies (cm⁻¹) for Eq-t cyclobutyldichlorosilane.

Vib. No.	Approximate Descriptions	<i>ab initio</i>	fixed scaled ^b	IR int.	Raman act.	dp ratio	IR Gas	Band Contours ^d	
								A	C
A' v1	β-CH2 antisymmetric stretch	3198	3000	36.3	68.2	0.67	2986	-	100
v2	γ-CH2 antisymmetric stretch	3182	2985	8.1	81.0	0.35	2975	100	-
v3	CH stretch	3129	2935	11.4	32.3	0.63	2943	16	84
v4	γ-CH2 symmetric stretch	3126	2932	33.8	123.3	0.14	2938	100	-
v5	β-CH2 symmetric stretch	3113	2921	6.7	148.0	0.14	2926	8	92
v6	SiH stretch	2343	2222	107.6	95.2	0.12	2202	-	100
v7	β-CH2 deformation	1575	1483	1.7	6.3	0.67	-	34	66
v8	γ-CH2 deformation	1549	1458	4.9	20.0	0.73	1451	9	91
v9	β-CH2 wag	1351	1284	1.5	5.9	0.60	1268	100	-
v10	CH in-plane bend	1301	1237	10.2	4.6	0.75	1248	75	25
v11	β-CH2 twist	1266	1205	4.4	5.7	0.75	1189	93	7
v12	β-CH2 rock	1128	1076	26.8	2.6	0.01	1056	98	2
v13	Ring breathing	1055	1002	3.4	14.7	0.16	998	2	98
v14	Ring deformation 1	959	924	8.6	2.1	0.27	910	81	19
v15	Ring deformation 2	912	884	2.0	3.8	0.06	856	-	100
v16	SiH in-plane bend	828	787	160.3	9.5	0.73	800	100	-
v17	γ-CH2 rock	751	718	26.5	3.3	0.10	717	98	2
v18	Si-C stretch	588	569	60.1	1.4	0.61	578	100	-
v19	SiCl2 symmetric stretch	537	514	31.0	8.7	0.08	519	60	40
v20	SiHCl2 Ring bending	306	296	2.5	3.3	0.12	295	34	66
v21	SiCl2 deformation	239	234	4.1	3.1	0.31	-	95	5
v22	β-CH2 antisymmetric stretch	161	161	6.5	3.9	0.72	-	4	96
v23	β-CH2 symmetric stretch	122	120	10.1	0.4	0.71	-	-	100
A'' v24	β-CH2 deformation	3190	2992	18.6	62.4	0.75	2980	-	-
v25	γ-CH2 wag	3113	2920	27.0	3.6	0.75	2926	-	-
v26	β-CH2 wag	1544	1453	0.9	5.4	0.75	1445	-	-
v27	CH out-of-plane bend	1321	1255	4.4	3.5	0.75	1248	-	-
v28	γ-CH2 twist	1305	1238	1.3	0.4	0.75	1248	-	-
v29	β-CH2 twist	1279	1214	0.2	7.4	0.75	1208	-	-
v30	Ring deformation 1	1235	1173	2.9	6.6	0.75	1168	-	-
v31	Ring deformation 2	1041	994	11.8	1.0	0.75	993	-	-
v32	SiH out-of-plane bend	985	936	1.2	10.8	0.75	935	-	-
v33	β-CH2 rock	972	933	4.6	3.4	0.75	912	-	-
v34	SiCl2 antisymmetric stretch	853	810	168.0	9.8	0.75	800	-	-
v35	SiHCl2 Ring bending	812	772	0.0	0.0	0.75	770	-	-
v36	Ring puckering	607	578	140.0	4.7	0.75	578	-	-
v37	SiCl2 wag	293	290	0.0	3.4	0.75	295	-	-
v38	SiCl2 twist	85	84	0.2	0.7	0.75	-	-	-
v39	SiCl2 rock	47	45	0.2	0.3	0.75	-	-	-

^aMP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/amu), depolarization ratios and potential energy distributions (P.E.D.s)

^bMP2(full)/6-31G(d) fixed scaled frequencies with factors of 0.88 for CH and SiH stretches and CH2 deformations, 1.0 for heavy atom bends, and 0.90 for all other modes.

^cA and C values in the last two columns are percentage infrared band contours.

Table 3. Observed and calculated^a frequencies (cm⁻¹) for Eq-g cyclobutyldichlorosilane.

Vib. No.	Approximate Descriptions	<i>ab initio</i>	fixed scaled ^b	IR int.	Raman act.	dp ratio	IR Gas	Band Contours ^c		
								A	B	C
v1	β-CH2 antisymmetric stretch	3201	3003	33.8	53.0	0.68	2986	-	84	16
v2	β-CH2 antisymmetric stretch	3193	2995	17.0	64.0	0.75	2980	5	3	92
v3	γ-CH2 antisymmetric stretch	3182	2985	8.0	75.5	0.45	2975	95	2	3
v4	β-CH2 symmetric stretch	3128	2934	9.4	147.8	0.04	2943	36	2	62
v5	β-CH2 symmetric stretch	3126	2932	35.0	45.9	0.12	2938	66	7	27
v6	γ-CH2 symmetric stretch	3125	2931	26.7	45.0	0.66	2938	30	31	39
v7	CH stretch	3107	2914	11.6	84.0	0.31	2907	13	53	34
v8	SiH stretch	2343	2223	136.5	138.5	0.16	2202	9	2	89
v9	β-CH2 deformation	1575	1483	0.7	5.5	0.70	-	36	51	13
v10	γ-CH2 deformation	1549	1458	3.9	21.4	0.72	1451	15	70	15
v11	β-CH2 deformation	1544	1454	1.2	5.2	0.75	1445	7	26	67
v12	β-CH2 wag	1354	1287	0.9	4.9	0.70	1268	6	80	14
v13	γ-CH2 wag	1322	1255	4.9	3.2	0.75	1248	14	20	66
v14	β-CH2 wag	1306	1239	1.9	1.2	0.70	1248	45	53	2
v15	CH in-plane bend	1302	1238	7.5	3.4	0.75	1248	26	41	33
v16	CH out-of-plane bend	1279	1214	0.3	7.9	0.75	1208	32	12	56
v17	β-CH2 twist	1270	1209	3.2	7.3	0.73	1189	68	17	15
v18	γ-CH2 twist	1235	1173	3.1	6.7	0.75	1168	22	18	60
v19	β-CH2 rock	1132	1080	10.7	2.6	0.18	1056	97	-	3
v20	β-CH2 twist	1055	1002	19.3	6.7	0.24	998	58	2	40
v21	Ring breathing	1049	1001	10.8	9.5	0.16	998	3	94	3
v22	Ring deformation 2	986	937	1.3	7.0	0.75	935	-	14	86
v23	Ring deformation 1	975	936	4.7	6.9	0.75	935	56	7	37
v24	Ring deformation 1	961	926	29.2	1.4	0.11	910	67	32	1
v25	Ring deformation 2	917	887	23.0	3.6	0.14	856	20	72	8
v26	SiH out of plane bend	846	803	139.4	9.2	0.75	800	22	78	-
v27	SiH in of plane bend	831	790	91.7	4.8	0.75	800	82	12	6
v28	β-CH2 rock	800	761	65.4	4.0	0.72	765	100	-	-
v29	γ-CH2 rock	726	696	6.4	6.9	0.40	693	33	55	12
v30	SiCl2 antisymmetric stretch	605	577	115.1	4.1	0.75	578	10	90	-
v31	Si-C stretch	573	549	50.4	5.1	0.58	557	79	5	16
v32	SiCl2 symmetric stretch	497	476	34.5	9.8	0.02	481	2	21	77
v33	SiHCl2 Ring bending	412	402	17.4	1.9	0.61	387	35	52	13
v34	SiHCl2 Ring bending	297	291	2.4	4.4	0.35	295	55	2	43
v35	Ring puckering	210	208	0.6	1.4	0.71	-	-	75	25
v36	SiCl2 deformation	181	180	5.0	3.0	0.70	-	35	20	45
v37	SiCl2 wag	116	115	3.1	0.8	0.63	-	50	-	50
v38	SiCl2 twist	97	96	1.8	1.0	0.73	-	14	66	20
v39	SiCl2 rock	46	44	0.4	0.4	0.74	-	33	4	63

^aMP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/amu), depolarization ratios and potential energy distributions (P.E.D.s)

^bMP2(full)/6-31G(d) fixed scaled frequencies with factors of 0.88 for CH and SiH stretches and CH2 deformations, 1.0 for heavy atom bends, and 0.90 for all other modes.

^cA and C values in the last two columns are percentage infrared band contours.

Table 4. Observed and calculated^a frequencies (cm⁻¹) for Ax-t cyclobutyldichlorosilane.

Vib. No.	Approximate Descriptions	<i>ab initio</i>	fixed scaled ^b	IR int.	Raman act.	dp ratio	IR Gas	Band Contours ^c		
								A	C	
A'	v ₁	γ-CH ₂ antisymmetric stretch	3198	3000	40.0	71.1	0.52	2986	77	23
	v ₂	β-CH ₂ antisymmetric stretch	3173	2977	13.2	60.4	0.75	2971	-	100
	v ₃	γ-CH ₂ symmetric stretch	3132	2938	10.4	167.9	0.06	2943	54	46
	v ₄	CH stretch	3127	2933	24.4	48.6	0.23	2938	41	59
	v ₅	β-CH ₂ symmetric stretch	3117	2924	4.4	114.5	0.26	2926	96	4
	v ₆	SiH stretch	2345	2225	104.2	92.8	0.12	2207	5	95
	v ₇	β-CH ₂ deformation	1580	1488	0.5	8.0	0.64	-	53	47
	v ₈	γ-CH ₂ deformation	1554	1463	4.6	16.8	0.75	-	-	100
	v ₉	β-CH ₂ wag	1341	1274	3.8	1.8	0.57	1248	72	28
	v ₁₀	CH in-plane bend	1316	1254	5.7	1.9	0.44	1248	60	40
	v ₁₁	β-CH ₂ twist	1250	1191	6.2	8.9	0.74	1189	100	-
	v ₁₂	β-CH ₂ rock	1087	1035	13.5	4.6	0.48	1125	100	-
	v ₁₃	Ring breathing	1063	1009	8.4	20.4	0.12	1009	62	38
	v ₁₄	Ring deformation 1	966	931	24.4	0.1	0.34	912	100	-
	v ₁₅	Ring deformation 2	909	880	24.7	3.3	0.56	856	90	10
	v ₁₆	SiH in-plane bend	816	777	114.8	9.7	0.75	770	100	-
	v ₁₇	Si-C stretch	718	688	59.7	3.7	0.16	681	97	3
	v ₁₈	γ-CH ₂ rock	668	644	11.9	2.3	0.40	631	78	22
	v ₁₉	SiCl ₂ symmetric stretch	540	516	56.3	10.1	0.09	519	81	19
	v ₂₀	SiHCl ₂ Ring bending	289	282	0.2	4.1	0.14	-	100	-
	v ₂₁	SiCl ₂ wag	224	220	5.7	1.4	0.67	-	-	100
	v ₂₂	β-CH ₂ antisymmetric stretch	165	165	6.1	3.4	0.74	-	81	19
	v ₂₃	β-CH ₂ symmetric stretch	141	139	5.0	0.1	0.46	-	21	79
A''	v ₂₄	β-CH ₂ deformation	3178	2981	3.1	66.8	0.75	2971	77	23
	v ₂₅	γ-CH ₂ wag	3118	2925	44.9	2.8	0.75	2926	-	100
	v ₂₆	β-CH ₂ wag	1550	1459	2.2	7.4	0.75	-	54	46
	v ₂₇	γ-CH ₂ twist	1324	1258	3.6	0.6	0.75	1248	41	59
	v ₂₈	CH out-of-plane bend	1291	1226	1.8	3.9	0.75	1233	96	4
	v ₂₉	β-CH ₂ twist	1273	1210	2.5	8.7	0.75	1189	5	95
	v ₃₀	Ring deformation 1	1209	1148	1.0	4.7	0.75	1140	53	47
	v ₃₁	Ring deformation 2	1070	1018	12.2	0.5	0.75	1019	-	100
	v ₃₂	SiH out-of-plane bend	991	941	4.4	13.2	0.75	935	72	28
	v ₃₃	β-CH ₂ rock	963	925	0.4	0.6	0.75	910	60	40
	v ₃₄	SiCl ₂ antisymmetric stretch	844	801	158.8	8.4	0.75	800	100	-
	v ₃₅	SiHCl ₂ Ring bending	811	773	0.0	0.0	0.75	770	100	-
	v ₃₆	SiCl ₂ deformation	608	578	138.0	5.0	0.75	578	62	38
	v ₃₇	Ring puckering	297	295	0.0	2.6	0.75	295	100	-
	v ₃₈	SiCl ₂ twist	97	97	0.2	1.0	0.75	-	90	10
	v ₃₉	SiCl ₂ rock	39	37	0.1	0.1	0.75	-	100	-

^aMP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/amu), depolarization ratios and potential energy distributions (P.E.D.s)

^bMP2(full)/6-31G(d) fixed scaled frequencies with factors of 0.88 for CH and SiH stretches and CH₂ deformations, 1.0 for heavy atom bends, and 0.90 for all other modes.

^cA and C values in the last two columns are percentage infrared band contours.

Table 5. Observed and calculated^a frequencies (cm⁻¹) for Ax-g cyclobutyldichlorosilane.

Vib. No.	Approximate Descriptions	<i>ab initio</i>	fixed scaled ^b	IR int.	Raman act.	dp ratio	IR Gas	Band Contours ^c		
								A	B	C
v1	γ-CH2 antisymmetric stretch	3210	3011	26.6	46.5	0.66	2996	63	37	-
v2	β-CH2 antisymmetric stretch	3180	2984	4.1	67.2	0.75	2975	22	25	53
v3	β-CH2 antisymmetric stretch	3175	2978	14.5	65.6	0.67	2971	13	85	2
v4	γ-CH2 symmetric stretch	3143	2948	26.0	124.7	0.11	2955	70	9	21
v5	β-CH2 symmetric stretch	3123	2930	16.2	105.7	0.11	2938	5	58	37
v6	β-CH2 symmetric stretch	3116	2924	35.8	59.5	0.10	2926	10	5	85
v7	CH stretch	3102	2910	19.7	51.0	0.56	2907	53	26	21
v8	SiH stretch	2344	2223	131.5	130.7	0.16	2202	7	2	91
v9	β-CH2 deformation	1578	1486	0.4	10.0	0.68	-	79	0	21
v10	γ-CH2 deformation	1550	1459	3.5	16.4	0.74	1451	4	88	8
v11	β-CH2 deformation	1548	1457	2.9	6.9	0.74	1451	6	3	91
v12	CH in-plane bend	1340	1272	3.4	2.0	0.60	1248	27	50	23
v13	γ-CH2 wag	1328	1262	3.2	0.6	0.75	1248	20	12	68
v14	β-CH2 wag	1321	1258	3.1	2.0	0.42	1248	79	21	0
v15	β-CH2 wag	1294	1228	1.8	3.9	0.75	1233	22	11	67
v16	γ-CH2 twist	1274	1211	2.6	8.8	0.75	1189	13	9	78
v17	β-CH2 twist	1249	1190	3.5	7.9	0.73	1189	87	5	8
v18	CH out-of-plane bend	1221	1158	1.4	4.1	0.75	-	44	6	50
v19	β-CH2 rock	1084	1032	7.5	5.3	0.44	1025	11	20	69
v20	β-CH2 twist	1075	1024	11.7	1.5	0.49	1025	31	55	14
v21	Ring breathing	1067	1013	15.2	19.7	0.11	1019	51	46	3
v22	Ring deformation 1	1002	951	3.9	13.4	0.75	935	19	4	77
v23	Ring deformation 1	973	937	3.4	0.4	0.23	935	95	1	4
v24	Ring deformation 2	968	932	6.0	0.4	0.69	912	100	-	-
v25	Ring deformation 2	889	862	1.7	6.0	0.63	-	22	74	4
v26	SiH out of plane bend	844	801	139.6	7.6	0.72	800	6	94	-
v27	SiH in of plane bend	827	787	177.8	7.2	0.72	800	92	5	3
v28	β-CH2 rock	805	765	18.9	0.9	0.67	765	93	3	4
v29	γ-CH2 rock	685	664	9.7	1.3	0.69	663	53	45	2
v30	Si-C stretch	662	631	14.0	6.3	0.44	631	24	74	2
v31	SiCl2 antisymmetric stretch	598	569	134.2	5.6	0.74	557	41	59	-
v32	SiCl2 symmetric stretch	516	492	46.6	11.4	0.02	490	7	24	69
v33	SiHCl2 Ring bending	383	376	16.3	1.9	0.73	369	39	36	25
v34	SiHCl2 Ring bending	287	282	0.7	3.6	0.34	-	39	6	55
v35	SiCl2 deformation	190	189	3.3	3.0	0.69	-	31	15	54
v36	Ring puckering	165	163	0.9	0.8	0.54	-	3	63	34
v37	SiCl2 wag	131	129	2.9	1.0	0.70	-	64	-	36
v38	SiCl2 twist	111	110	0.5	1.2	0.75	-	3	71	26
v39	SiCl2 rock	41	39	0.3	0.3	0.75	-	45	9	46

^aMP2(full)/6-31G(d) *ab initio* calculations, scaled frequencies, infrared intensities (km/mol), Raman activities (Å⁴/amu), depolarization ratios and potential energy distributions (P.E.D.s)

^bMP2(full)/6-31G(d) fixed scaled frequencies with factors of 0.88 for CH and SiH stretches and CH₂ deformations, 1.0 for heavy atom bends, and 0.90 for all other modes.

^cA and C values in the last two columns are percentage infrared band contours.

The assignment of the fundamentals for the four conformers of cyclobutyldichlorosilane was complicated due to their close proximity and similar intensities. In the infrared spectra of the gas the fundamentals could not be sufficiently resolved to assign them to different bands, which leads to the assignment of multiple fundamentals to single bands. However, if the Raman spectra of the liquid (Fig 3) is compared to the infrared spectra of the gas (Fig 2) it can be seen that additional bands can be resolved. For example, in the region of $1300 - 1100 \text{ cm}^{-1}$ in the infrared spectra of the gas (Fig 2) one can see two bands, whereas, in the spectra of the Raman liquid one can see at least five well resolved bands in the same region. For a more complete assignment of the fundamentals of the conformers of cyclobutyldichlorosilane further Raman spectra of the liquid and infrared spectra of additional phases and solutions should be obtained.

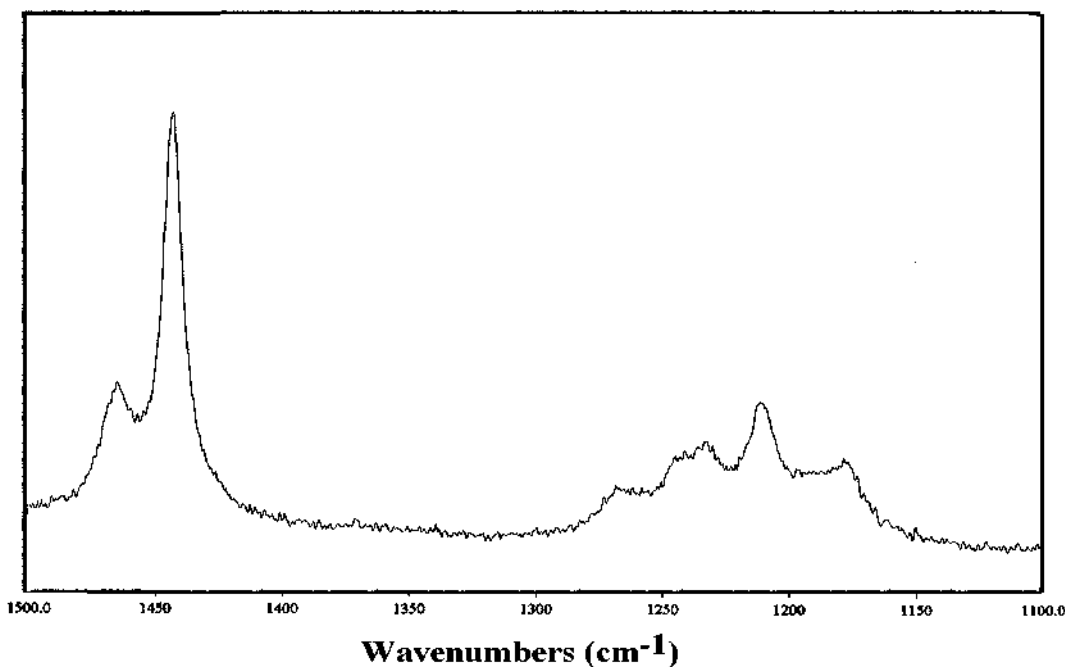


Fig 3. Raman spectra of the liquid from $1500 - 1100 \text{ cm}^{-1}$

It would be of interest to obtain the enthalpy differences for the $c\text{-C}_4\text{H}_8\text{SiCl}_2$ molecule since it has never been studied and a spectroscopy investigation would be of interest to see how different substituents affect the conformational stability of four membered ring molecules and whether the experimental work will agree with the *ab initio* calculation results. Therefore, a continuation of this study would be excellent in order to obtain a more reliable experimental value for the conformational enthalpy difference by using a variable temperature spectra of the sample dissolved in the liquefied xenon. Some of the advantages behind carrying such an experiment is that a very little interaction of the solute with the solvent molecules so the frequencies observed in the solution were shifted very little from those observed in the gas. Also, the bands will be relatively narrow particularly when the data was recorded at relatively low temperatures. Thus, it will be possible to resolve relatively close frequency fundamentals so individual bands could be assigned for very complex gas phase contours. Also, relative intensities of bands which are extensively overlapped in the gas will be obtainable when they are recorded in low temperature rare gas solutions. Therefore, such spectra are very good for making vibrational assignments particular for molecules where more than one conformer is present and many fundamentals are closely spaced.

Table 6. Structural parameters^a (Å and degrees) and rotational constants (MHz) of cyclobutyldichlorosilane.

Structural Parameters	t-Eq	g-Eq	t-Ax	g-Ax
rC _α -Si	1.845	1.849	1.849	1.849
rC _α -C _β	1.559	1.558	1.559	1.560
rC _α -C _{β'}	1.559	1.558	1.559	1.556
rC _γ -C _β	1.546	1.546	1.546	1.547
rC _γ -C _{β'}	1.546	1.546	1.546	1.547
rSi-Cl ₁	2.050	2.050	2.049	2.052
rSi-Cl ₂	2.050	2.051	2.049	2.050
rC _α -H	1.096	1.098	1.096	1.098
rC _β -H ₁	1.091	1.092	1.094	1.094
rC _{β'} -H ₁	1.091	1.092	1.094	1.094
rC _β -H ₂	1.095	1.094	1.094	1.093
rC _{β'} -H ₂	1.095	1.094	1.094	1.093
rC _γ -H ₁	1.093	1.094	1.093	1.091
rC _γ -H ₂	1.092	1.093	1.092	1.092
∠C _α SiCl ₁	109.9	108.9	109.1	111.1
∠C _α SiCl ₂	109.9	108.8	109.1	108.8
∠Cl ₁ SiCl ₂	109.3	108.7	109.4	108.4
∠C _β C _α Si	118.6	119.8	114.2	116.5
∠C _{β'} C _α Si	118.6	120.7	114.2	116.5
∠C _β C _α C _β	87.3	87.4	87.5	88.0
∠C _γ C _β C _α	87.8	87.8	88.3	88.7
∠C _γ C _{β'} C _α	87.8	87.8	88.3	88.7
∠C _β C _γ C _β	88.2	88.2	88.4	88.9
∠HC _α C _β	109.7	109.0	116.0	114.9
∠HC _α C _{β'}	109.7	109.2	116.0	114.8
∠HC _α Si	110.7	108.9	107.9	105.8
∠HSiC _α	111.9	114.9	114.0	113.3
∠H ₁ C _β C _α	111.2	117.4	118.8	118.6
∠H ₁ C _{β'} C _α	111.2	117.6	118.8	118.3
∠H ₁ C _β C _γ	110.7	118.7	118.3	117.6
∠H ₁ C _{β'} C _γ	110.7	118.6	118.3	117.6
∠H ₂ C _β C _α	117.5	111.2	110.1	110.4
∠H ₂ C _{β'} C _α	117.5	111.2	110.1	110.4
∠H ₂ C _β C _γ	118.8	110.8	111.3	111.7
∠H ₂ C _{β'} C _γ	118.8	110.7	111.3	111.8
∠H ₁ C _β H ₂	109.2	109.4	108.7	108.7
∠H ₁ C _{β'} H ₂	109.2	109.4	108.7	108.7
∠H ₁ C _γ C _β	118.2	110.6	111.1	111.4
∠H ₁ C _γ C _{β'}	118.2	110.6	111.1	111.3
∠H ₂ C _γ C _β	110.4	118.2	117.9	117.3
∠H ₂ C _γ C _{β'}	110.4	118.2	117.9	117.4
∠H ₁ C _γ H ₂	109.5	109.5	109.0	109.2
τC _γ C _β C _{β'} C _α	148.5	148.3	150.9	154.6
τHC _α -SiCl	60.2	63.3	59.7	61.0
A(MHz)	1991.28	1986.82	1925.35	1997.63
B(MHz)	996.60	1030.34	1087.77	1115.48
C(MHz)	698.58	794.54	751.43	862.16

^aPredicted structural parameters obtained from MP2(full)/6-311+G(d,p) calculation.

It would be interesting to obtain the complete adjusted r_0 structural parameters for the stable conformers of cyclobutyldichlorosilane. To do so we must predict the rotational constants to be fit from the microwave spectra using a suitable predicted structures (Table 6). We [16] have shown that *ab initio* MP2(full)/6-311+G(d,p) calculations predict the carbon-hydrogen r_0 structural parameters for more than fifty hydrocarbons to at least 0.002 Å compared to the experimentally determined [17] values from isolated CH stretching frequencies which agree to previously determined values from earlier microwave studies. Therefore, all of the carbon-hydrogen parameters can be taken from the MP2(full)/6-311+G(d,p) predicted values for the conformers of cyclobutyldichlorosilane. The silane-hydrogen r_0 structural parameter value was experimentally determined [17] for the t-Eq conformer to be 1.477(2) Å from isolated SiH stretching frequency listed in Table 2. This leaves 9 independent structural parameters to be determined for a completed adjusted r_0 structural parameters. Therefore, a minimum of 9 rotational constants would be desirable to obtain such an experimental structure. Additionally, we have also shown that the differences in predicted distances and angles from the *ab initio* calculations for different conformers of the same molecule can usually be used as one parameter with the *ab initio* predicted differences except for some dihedral angles. This would mean that each additional conformer would only increase the minimum number of rotational constants by three. Such a microwave study would be desirable as there are few cyclobutylsilane structures determined, but the study of the microwave spectra of cyclobutyldichlorosilane will be a challenging investigation with a high degree of difficulty. This difficulty is due to the Cl atoms on the Si substituent where each chlorine nucleus has a spin quantum number $I = 3/2$ and, therefore, a nuclear quadrupole moment which interacts with the electric field gradient created by the electrons of the rotating molecule.

Acknowledgments

J R D acknowledges the University of Missouri-Kansas City for a Faculty Research Grant for partial financial support of this research. We are thankful to have the opportunity to submit this article in honor of Prof S Mohan who has been an outstanding spectroscopist and who is a very wonderful friend to large number of young scientists.

References

1. Miller F A, Capwell R J, Lord R C, Rea D G, *Spectrochim Acta*, 28A(1972)603.
2. Rothschild W G, *J Chem Phys*, 45(1966)1214.
3. Durig J R, Green W H, *J Chem Phys*, 47(1967)673.
4. Rothschild W G, Dailey B P, *J Chem Phys*, 36(1962)2931.
5. Kim H, Gwinn W D, *J Chem Phys*, 44(1966)865.
6. Wurstner-Rock A, Rudolph H D, *J Mol Struct*, 97(1983)327.
7. Durig J R, Geyer T J, Groner P, Dakkouri M, *Chem Phys*, 125(1988)299.
8. Durig J R, Lee M J, Little T S, *Struct Chem*, 2(1991)195.
9. Velino B, Favero L B, Caminati W, *J Mol Spectrosc*, 179(1996)168.
10. Kraitchman J, *Am J Phys*, 21(1953)17.
11. Watson J K G, *J Mol Spectrosc*, 48(1973)479.
12. Nakata M, Sugie M, Takeo H, Matsumura C, Fukuyama T, Kuchitsu K, *J Mol Spectrosc*, 86(1981)241.
13. Nakata M, Fukuyama T, Kuchitsu K, Takeo H, Matsumura C, *J Mol Spectrosc*, 83(1980)118.
14. Smith J G, Watson J K G, *J Mol Spectrosc*, 69(1952)47.
15. van der Veken B J, Herrebout W A, Durig D T, Zhao W, Durig J R, *J Phys Chem A*, 103(1999)1976.
16. Durig J R, Ng K W, Zheng C, Shen S, *Struct Chem*, 15(2004)149.
17. McKean D C, *J Mol Struct*, 113(1984)251.

18. [Klaassen J J, Panikar S S, Guirgis G A, Dukes H W, Wyatt J K, Durig J R, *J Mol Struct*, 1032\(2013\)254.](#)
19. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb, M A, Cheeseman, J R, Montgomery Jr, J A, Vreven, T, Kudin, K N, Burant, J C, Millam, J M, Iyengar, S S, Tomasi, J, Barone, V, Mennucci, B, Cossi, M, Scalmani, G, Rega, N, Petersson, G A, Nakatsuji, H, Hada, M, Ehara, M, Toyota, K, Fukuda, R, Hasegawa, J, Ishida, M, Nakajima, T, Honda, Y, Kitao, O, Nakai, H, Klene, M, Li, X, Knox, J E, Hratchian, H P, Cross, J B, Adamo, C, Jaramillo, J, Gomperts, R, Stratmann, R E, Yazyev, O, Austin, A J, Cammi, R, Pomelli, C, Ochterski, J W, Ayala, P Y, Morokuma, K, Voth, G A, Salvador, P, Dannenberg, J J, Zakrzewski, V G, Dapprich, S, Daniels, A D, Strain, M C, Farkas, O, Malick, D K, Rabuck, A D, Raghavachari, K, Foresman, J B, Ortiz, J V, Cui, Q, Baboul, A G, Clifford, S, Cioslowski, J, Stefanov, B B, Liu, G, Liashenko, A, Piskorz, P, Komaromi, I, Martin, R L, Fox, D J, Keith, T, Al-Laham, M A, Peng, C Y, Nanayakkara, A, Challacombe, M, Gill, P M W, Johnson, B, Chen, W, Wong, M, W, Gonzalez, C, Pople, J A, Gaussian 03, Revision E.01 Gaussian, Inc., Wallingford CT, 2004.
20. [Pulay P, *Mol Phys*, 17\(1969\)197.](#)
21. [Møller C, Plesset M S, *Phys Rev*, 46\(1934\)618.](#)

[Received: 01.05.2014 ; accepted: 30.05.2014]