J. Phys. Chem. A **2002,** *106,* 7703−7706

Hyperfine Interactions in HSiCl

Wei Lin,[†] Stewart E. Novick,*,[†] Masaru Fukushima,[‡,§] and Wolfgang Jäger*,[§]

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459 and Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2 Canada

Received: March 18, 2002; In Final Form: June 10, 2002

The $J = 1-0$ transitions of the microwave spectra of $H^{28}Si^{35}Cl$, $H^{28}Si^{37}Cl$, $H^{29}Si^{35}Cl$, and $H^{30}Si^{35}Cl$ were measured at 14−15 GHz. The effective rotational constants are obtained, and the chlorine nuclear quadrupole coupling constants and nuclear spin-rotation constants of the four isotopomers are determined for the first time. These constants are compared with their values obtained from *ab initio* calculations.

Introduction

HSiCl is an important reactive intermediate in chemical vapor decomposition (CVD) of silicon from chlorosilanes,[1] and HSiCl emission can be used as a diagnostic tool in the analysis of chlorosilane CVD.[2] During our continuing study of silicon containing species, we came across a group of transitions which appeared to be due to a single chlorine nuclear quadrupole hyperfine splitting. Published rotational constants from electronic spectroscopy[3] suggested that these lines were the hyperfine structure of the $J = 1 - 0$ transition of $H^{28}Si^{35}Cl$. This hypothesis was confirmed by the measurement of the $1 - 0$ transition of three other isotopomers of HSiCl.

The first spectroscopic work on HSiCl was the partially rotationally resolved electronic absorption spectroscopy of Herzberg and Verma[4] in 1964 in which the HSiCl was produced by flash photolysis of $HSiCl_3$. A complete reinvestigation of the emission spectra of HSiCl has recently been performed in which the HSiCl was produced by a pulsed discharge of $SiHCl_3$ diluted in argon, and the vibrational frequencies, force constants, rotational constants, and the molecular structure of both the ground $\tilde{X}\ ^1A'$ state and the $\tilde{A}\ ^1A''$ state were determined.[3,5] Laser induced fluorescence of HSiCl has also been observed with the monochlorosilylene produced from the photodissociation of 2-chloroethenylsilane, $H_3SiCHCHCl$.[6] Recently, a high-level *ab initio* calculation using the CCSD(T) method has been performed in which the experimental structure and the vibrational frequencies are well reproduced.[7] The current work is the first pure rotational spectroscopy of monochlorosilylene. The ∼1 kHz resolution in the current experiment, compared to the ∼30 MHz resolution of the electronic spectroscopy, allows us to measure an improved effective rotational constant and to measure the nuclear quadrupole and nuclear spin-rotation hyperfine structure of HSiCl for the first time. In the present work, we have obtained the effective rotational constants and the chlorine nuclear quadrupole coupling constants of $H^{28}Si^{35}Cl$, $H^{28}Si^{37}Cl$, $H^{29}Si^{35}Cl$, and $H^{30}Si^{35}Cl$.

Experimental Section

The spectrum of HSiCl was measured using a pulsed-jet Fourier transform microwave spectrometer which has been described elsewhere.[8,9] Many modifications of the Wesleyan spectrometer have been made since the initial publication including coaxial expansion of the gas with the cavity axis for increased sensitivity and resolution, changes in the microwave circuitry for decrease in the microwave noise, and automatic scanning for ease of use.

In these experiments, a gas mixture of 0.5% $HSiCl_3$ or $(CH_3)_3SiCl$ in argon or neon with a total pressure of approximately 2 atm is expanded through a 0.8 mm diameter pulsed gas valve. The expanding gas then encounters a pulsed voltage of 900 V applied between electrodes separated by 1 cm. The resulting plasma discharge with a current of typically 20 ma serves to dissociate the trichlorosilane into various fragments including the monochlorosilylene. The resultant mixture of precursors and products are expanded into the high *Q* Fabry−Perot microwave cavity which is tunable between 5 and 26.5 GHz. A microwave pulse is timed to coincide with the arrival of the gas pulse in the center of the microwave cavity. If a molecular transition lies within the ∼500 kHz bandwidth of the microwave pulse/cavity combination, a macroscopic polarization is induced in the molecules. The free induction decay of this polarization is collected and averaged over multiple pulses and is Fourier transformed to yield the spectrum of the transition. The molecules are traveling coaxially with the cavity axis and thus the molecular interaction with the counter-propagating microwave radiation results in a Doppler-doubled spectral transition. The full-width-half-maximum (fwhm) of the observed lines are ∼5−7 kHz. With this fwhm, we can estimate peak centers, on most transitions, to within ∼1 kHz. The spectra of all the isotopomers were observed in natural abundance.

Observed Spectra and Analysis. The $J = 1 - 0$, $K_a = 0$ transitions for the four isotopomers were measured in the frequency range of 14−15 GHz. The $J = 2 - 1$, $K_a = 0$ transitions at 28−30 GHz are out of the range of the spectrometers. We were limited to measuring *a*-type, $K_a = 0$, $\Delta K_a = 0$, transitions because of the large value of the *A* rotational constant, which puts higher K_a states at high energy and low population, and put the *b*-type transitions out of our frequency ranges. Thus, we were only able to measure an *effective* rotational constant,

---

* To whom correspondence should be addressed.

[†] Wesleyan University.

[‡] Permanent address: Faculty of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.

[§] University of Alberta.

10.1021/jp020710m CCC: $22.00 © 2002 American Chemical Society
Published on Web 07/26/2002

the chlorine nuclear quadrupole coupling constants, and the chlorine and ^{29}Si spin-rotation constants of the ground electronic and vibrational state of HSiCl. The effective Hamiltonian used to assign and analyze the spectra is

$$H = H_{\text{rot}} + H_{\text{hf}}$$

where

$$H_{\text{rot}} = B_{\text{eff}}\, \mathbf{J}^2$$

and[10]

$$H_{\text{hf}} = \frac{{}^3/_2\, \chi_{aa}}{2I(2I-1)}[I_a{}^2 - {}^1/_3\mathbf{I}^2] + C_{bb}(Cl) I_b J_b \qquad (1)$$

with

$$B_{eff} = (B + C)/2 - 2D_J$$

for the $J = 1 - 0$ transition. B and C are the standard rotational constants, D_J is the centrifugal distortion constant, χ_{aa} is the *a* component of the chlorine nuclear quadrupole coupling constant, C_{bb}(Cl) is the *b* component of the chlorine nuclear spin–molecular rotation coupling constant, and **I** is the nuclear spin angular momentum operator of the chlorine nucleus ($I = {}^3/_2$). The inclusion of this term in the Hamiltonian was also required in the recent study of the related molecule HCCl.[11] For the H^{29}Si^{35}Cl isotopomer, there is the additional hyperfine doubling due to the nuclear spin of ^{29}Si of $^1/_2$. The required extra term in the hyperfine Hamiltonian is $C_{bb}(^{29}\text{Si})I_b^{\text{Si}}J_b$. These spin-rotation terms represent the magnetic interaction between the Cl or the ^{29}Si nuclei and the electrons of the molecule (a small but nonzero effect in closed-shell molecules) and with the magnetic moment due to the rotation of the other nuclei of the molecule.[12] Recently, McCarthy and Thaddeus have observed this extra doubling in the spectra of the ^{29}Si isotopomer of H$_2$CCSi.[13]

Table 1 lists the measured hyperfine components of the $J = 1 - 0$ rotational transition of the four isotopomers of HSiCl; F is the total angular momentum of the molecule, given by $\mathbf{F} = \mathbf{J} + \mathbf{I}$. For the H^{29}Si^{35}Cl isotopomer, the F quantum number is replaced by F_1, F, where the angular momentum is coupled as $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}$(Cl) and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(^{29}\text{Si})$. Table 2 presents the spectroscopic constants, B_{eff}, χ_{aa}, and C$_{bb}$(Cl) for H^{28}Si^{35}Cl, H^{28}Si^{37}Cl, H^{29}Si^{35}Cl, and H^{30}Si^{35}Cl, (and C$_{bb}$(^{29}Si) for H^{29}Si^{35}Cl) along with the constants available from ref 3 for comparison purposes. Because, except for H^{29}Si^{35}Cl, we have measured three hyperfine components and fit the transitions exactly with three constants, the "external" or *a posteriori* least squares estimates of the error in the constants are zero. Therefore, we have estimated the one standard deviation error of the constants by the "internal" or *a priori* estimate based on assuming that the measured frequencies can be in error by as much as 1 kHz.[14]

Discussion

Because the hyperfine structure of only one *a*-type transition was measured for each of the four isotopomers, we are able to extract only three spectroscopic constants for each isotopomer, $B_{\text{eff}} = (B + C)/2 - 2D_J$, χ_{aa}, the *a* component of the chlorine nuclear coupling constant, and C_{bb}, the *b* component of the chlorine spin-rotation tensor. However, for the H^{29}Si^{35}Cl isotopomer, we were able to extract an additional constant, $C_{bb}(^{29}\text{Si})$, the *b* component of the silicon spin-rotation tensor.

TABLE 1: Measured Hyperfine Components of the $1_{01}-0_{00}$ Transition in HSiCl

transitions				observed frequencies	obs-calc
J′	F′	J″	F″	MHz	kHz
			H^{28}Si^{35}Cl		
1	3/2	0	3/2	14526.1479	0
1	5/2	0	3/2	14532.9798	0
1	1/2	0	3/2	14538.4307	0
			H^{28}Si^{37}Cl		
1	3/2	0	3/2	14177.5292	0
1	5/2	0	3/2	14182.9136	0
1	1/2	0	3/2	14187.2109	0
			H^{29}Si^{35}Cl^a		
1	3/2, 2	0	3/2, 2	14268.4716	0.3
1	3/2, 1	0	3/2, 1	14268.4750	−0.3
1	5/2, 3	0	3/2, 2	14275.3019	−0.1
1	5/2, 2	0	3/2, 1	14275.3113	0.1
1	1/2, 0	0	3/2, 1	14280.7524	0.0
1	1/2, 1	0	3/2, 2	14280.7576	0.0
			H^{30}Si^{35}Cl		
1	3/2	0	3/2	14027.7179	0
1	5/2	0	3/2	14034.5497	0
1	1/2	0	3/2	14040.0017	0

[a] For the H^{29}Si^{35}Cl isotopomer, the F quantum number is replaced by F_1, F, where the angular momentum is coupled as $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}$(Cl) and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(^{29}\text{Si})$.

TABLE 2: Spectroscopic Constants for HSiCl in MHz^a

isotopomer	$B_{\text{eff}}{}^b$	$B_{\text{eff}}{}^c$	$\chi_{\text{aa}}(\text{Cl})^b$	$C_{bb}(\text{Cl})^{b,d}$	$C_{bb}(^{29}\text{Si})^{b,d}$
H^{28}Si^{35}Cl	7265.8051(3)	7264.(4)	−27.303(3)	0.0052(7)	
H^{28}Si^{37}Cl	7090.9173(3)	7087.(4)	−21.521(3)	0.0036(7)	
H^{29}Si^{35}Cl	7136.9679(2)		−27.306(2)	0.0057(5)	−0.015(2)
H^{30}Si^{35}Cl	7016.5902(3)		−27.305(3)	0.0048(7)	

[a] One standard deviation in parentheses. This is based on an "internal" estimate of the fit assuming the transitions frequencies are accurate to 1 kHz. [b] This work. [c] Reference 3, $(B+C)/2$, D_J not given. [d] Assuming $C_{cc} = 0$. What is actually being reported is $C_{bb} + C_{cc}$.

Rotational Constants and Molecular Structure. As seen in Table 2, the values of $(B + C)/2$ from the electronic spectroscopy of ref 3 are in good agreement with our more accurate measurement for H^{28}Si^{35}Cl and H^{28}Si^{37}Cl. The B_{eff} of H^{29}Si^{35}Cl and H^{30}Si^{35}Cl were measured for the first time to be 7136.9666(6) and 7016.5895(11) MHz, respectively.

Fixing the Si − H bond length at 1.5275 Å and the Cl − Si − H angle at 95° from ref 5, our values of B_{eff} for the four isotopomers we studied yield a substitutional, r_s, Si−Cl bond length of 2.0716(21) Å and an average, r_0, Si−Cl bond length of 2.0722(22) Å, essentially identical to the values of refs 3 and 5.

Chlorine Nuclear Quadrupole Coupling Constants. We will use the newly measured value of the *a* component of the chorine nuclear quadrupole coupling constant in H^{28}Si^{35}Cl to examine the bonding of silicon to chlorine in HSiCl. If we assume that the electron distribution is cylindrically symmetrical about the Si−Cl bond, then we calculate that the chlorine nuclear quadrupole coupling constant along the bond is given by

$$\chi_{zz} = \frac{\chi_{aa}}{{}^3/_2\cos^2\theta - {}^1/_2} \qquad (2)$$

where the z is the bond axis and θ is the angle between the *a* inertial axis of the molecule and z axis and is equal to 1.68°

given the geometry from ref 5 . This gives $\chi_{zz} = -27.338(3)$ MHz for $H^{28}Si^{35}Cl$. Because this angle of rotation is small, this value for χ_{zz} is approximately correct even for the likely event that the assumption of electronic cylindrical symmetry about the SiCl bond is not correct. Anticipating a result given below, if χ_{bb} is large and positive (say +29 MHz) and χ_{cc} is small and negative (the traceless tensor requires that $\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$) and that the quadrupole coupling tensor is diagonal in a coordinate system oriented along the Si−Cl bond, then $\chi_{zz} = -27.351$ MHz, which differs from the original estimate of χ_{zz} by only 13 kHz. Thus, we take χ_{zz}, the quadrupole coupling constant of ^{35}Cl in $H^{28}Si^{35}Cl$ along the Si−Cl bond axis, to be −27.35(1) MHz.

The nuclear quadrupole coupling constant measured along the bond axis can be used to understand the bonding between the chlorine and silicon atoms. The Townes and Dailey model relates the value of χ_{zz} to the *p* electron density around nucleus in question and thus to the percent ionic character of the bond.[15] This model is described in some detail in the two standard monographs of microwave spectroscopy, Townes and Schawlow[16] and Gordy and Cook,[17] and thus, we will not repeat the outlines of the model here. If we include some *s* hybridization of the p_σ orbital of chlorine and also include the effect of π-electron "back-donation" from the chlorine to the silicon atom, then we can modify the equations given in ref 17 to read

$$i_c = 1 + \frac{\chi_{zz}}{(1 - f_s - {}^{1}/_{2}\, f_\pi) e q_{310} Q(\mathrm{Cl})} \tag{3}$$

for the relationship between the ionic character of the Si−Cl bond, i_c, and the nuclear quadrupole coupling constant of chlorine along the Si−Cl bond axis, χ_{zz}. Here, f_s is the fractional *s* character of the bonding p_z (p_σ) orbital of chlorine; f_π is the fraction of a π electron which is transferred from chlorine to silicon in covalent bonding; and $eq_{310}Q$ (Cl) is contribution to the nuclear quadrupole coupling constant (along the *z* axis) of ^{35}Cl of a chlorine $3p_z$ electron, whose value is 109.74 MHz.[18]

Tanimoto et. al. suggest that for SiCl[19] and $SiCl_2$[20] f_π has the values of 0.27 and 0.19, respectively. If we take the amount of back-donation, f_π, to be 0.27, as in SiCl, and fractional amount of *s* character in the p_σ orbital, f_s, to be 0.15,[12,16] eq 2 gives a value of 0.65 for the fraction of ionic character in the Si−Cl bond of HSiCl. This value of i_c is in agreement with that given by the simple linear relationship between the ionic character of a bond and the electronegativity difference of the atoms,[21] $i_c = {}^{1}/_{2}|x_{\mathrm{Cl}} - x_{\mathrm{Si}}| = 0.63$.

We note that the inclusion of π back-donation from chlorine to silicon implies that the cylindrical symmetry of the electronics along the Cl−Si bond may be broken, and thus, the χ_{xx} and χ_{yy} components of the chlorine nuclear quadrupole coupling constant may be unequal. Using these values of f_s and f_π, assuming, arbitrarily, that the back-donation is from the p_x orbital, and using a fractional covalent character of 0.35 that we "fit" from the measured value of χ_{zz}, we obtain estimates of the chlorine nuclear quadrupole coupling constants of χ_{xx} and χ_{yy} to be +5.9 and +21.5 MHz, respectively.

The nuclear quadrupole coupling constant was also investigated by ab initio calculations performed on the HSiCl set to the experimental geometry using the Gaussian 98 package.[22] The B3LYP density functional method was used with the triple-ζ, correlation consistent, basis set augmented with diffuse functions. Multiplying the calculated electric field gradient by the known electric quadrupole moment of ^{35}Cl of -8.249×10^{-26} cm^2,[23] gives $\chi_{aa}(^{35}Cl) = -25.8$ MHz,[24] in relatively good agreement with our measurement. Furthermore, χ_{bb} at +29.3 MHz and χ_{cc} at −3.5 MHz are calculated to be quite unequal. These values are similar to those obtained above by invoking π back-donation; the donating orbital is thus the nonbonding *p* orbital along the *c* axis, the axis perpendicular to the plane of the molecule.

TABLE 3: Comparison of the ^{35}Cl Nuclear Quadrupole Coupling Constants as Measured along the Si − Cl Bond of Some Chlorosilylenes and Chlorosilanes[a]

	SiCl[b]	HSiCl[c]	$SiCl_2$[d,e]	H_3SiCl[f]	H_2SiCl_2[g,e]	$HSiCl_3$[h,e]
χ_{zz}(Cl)	−23.13(32)	−27.35(1)	−36.08(35)	−39.74	−38.33(13)	−36.4

[a] In MHz. The number in parentheses represents the one-standard-deviation error, where known. [b] Reference 19. [c] This work, see text. [d] Reference 20. [e] It is assumed that the Si−Cl bond is a principal axes of the quadrupole tensor. [f] Reference 30. [g] Reference 31. [h] Reference 32.

It has recently been suggested that electron correlation effects may need to be included for a full recovery of the electric field gradients at heavy nuclei in *ab initio* calculations.[25,26] We have therefore also explored the use of self-consistent field and electron correlation methods for the *ab initio* determination of the ^{35}Cl nuclear quadrupole coupling constant in HSiCl. The built-in capability of the Gaussian 98 package to calculate electric field gradients at the SCF, MP2, and MP3 levels of theory was utilized, using Sadlej's basis sets for H,[27] Si, and Cl.[28] The values obtained for $\chi_{aa}(^{35}Cl)$ are −29.2 MHz (SCF), −25.3 MHz (MP2), and −26.3 MHz (MP3). The MP3 value is within 4% of the experimental value (−27.303 MHz), thus validating this approach. Treatment of electron correlation at higher levels of theory, such as MP4 and CCSD(T), may further improve the agreement with experiment. Techniques exist to calculate the electric field gradient at these levels of theory,[29] but their application is beyond the scope of this work.

Table 3 lists the chlorine nuclear quadrupole coupling constants measured along the Si−Cl bond of a series of chlorosilylenes already mentioned and the chlorosilanes, H_3SiCl,[30] H_2SiCl_2,[31] and $HSiCl_3$.[32] In the cases of $SiCl_2$, H_2SiCl_2, and $HSiCl_3$, the measured nuclear quadrupole coupling constant was rotated onto the Si−Cl bond. To do this, it was assumed that the Si−Cl bond is a principal axis of the quadrupole tensor and that the electronic distribution of the Si−Cl bond is of cylindrical symmetry. The chlorine nuclear quadrupole coupling constant range from about −23 to −40 MHz in these molecules, corresponding to percent ionic character in the Si−Cl bond of ~70% to ~49%. The Si−Cl bonds in the chlorosilylenes are slightly more ionic in character than those in the chlorosilanes.

Chlorine and Silicon Spin-Rotation Constants. The frequencies of the hyperfine components of the $J = 1-0$ transition (whose energy is approximately $B + C$) are equally sensitive to the value of the spin rotation constants C_{bb}(Cl) and C_{cc}(Cl) but insensitive to the value of C_{aa}(Cl). The value for $C_{bb}(^{35}Cl)$ in $H^{28}Si^{35}Cl$ given in Table 2 as 5.2(7) kHz is based on (arbitrarily) setting $C_{cc}(^{35}Cl)$ equal to zero. If, in eq 1 for the hyperfine Hamiltonian, we were to substitute the scalar interaction, $C_I(\mathrm{Cl})[I_aJ_a + I_bJ_b + I_cJ_c]$, for $C_{bb}(\mathrm{Cl})I_{bb}J_{bb}$, then the value of C_I(Cl) would be exactly ${}^{1}/_{2}$ of the value we report for C_{bb}(Cl). In this case, we would be, in effect, including the $I_bJ_b + I_cJ_c$ terms with coefficients forced to be equal, the I_aJ_a term having no effect on the frequencies of the 1−0 transition.

We can estimate the main contribution to the value of C_{bb} via the second-order equation[11−13]

$$C_{bb} = \frac{4Ba_{XA}|\langle X|L_b|A\rangle|^2}{E_\mathrm{A} - E_\mathrm{X}} \qquad (4)$$

where B is the rotational constant, a_{XA} is is the off-diagonal nuclear-spin−orbit interaction constant, L_b is the orbital angular momentum operator, and the energy denominator is the energy between the first excited singlet state (A) and the ground (singlet) state (X). In ref 11 on HCCl, the matrix element is assumed to be unity and the spin−orbit constant is estimated by the authors to be 102 MHz (the value in the $^1\Delta$ state of the isoelectronic NCl radical). If we take those values here (because the $^1\Delta$ state of PCl has not been investigated and so the appropriate a_XA value is not available), and use the appropriate rotational constant and take the energy denominator to be $\mathrm{E}(\tilde{A}\ ^1A'') - \mathrm{E}(\tilde{X}\ ^1A') = 20718\ \mathrm{cm}^{-1}$,[3] we estimate $C_{bb}(^{35}\mathrm{Cl})$ in $\mathrm{H}^{28}\mathrm{Si}^{35}\mathrm{Cl}$ to be 4.8 kHz compared to our measured value of 5.2 kHz, perhaps a fortuitous agreement given that the 100 MHz estimate for a_{XA} is really appropriate for HCCl and not HSiCl and that we have arbitrarily set C_{cc}(Cl) to be zero.

We can also estimate the spin-rotation constants by ab initio calculation. There is a new version of the Gaussian program under development which currently can calculate the spectroscopic hyperfine constants for singlet states ($\boldsymbol{\chi}$ and $\boldsymbol{C}$, the nuclear quadrupole coupling, and nuclear spin-rotation interaction tensors) along with the more complete set of fine and hyperfine constants for doublet radicals ($\boldsymbol{\epsilon}$, a_F, $\boldsymbol{T}$; electron spin-rotation, Fermi contact, and nuclear spin-electron spin interactions).[33] Using this program, we calculate for the chlorine nucleus in $\mathrm{H}^{28}\mathrm{Si}^{35}\mathrm{Cl}$ $C_{aa} = 131$ kHz, $C_{bb} = 5.7$ kHz (experimental, 5.2(7) kHz with C_{cc} assumed zero), and $C_{cc} = 0.04$ kHz; we calculate for the silicon nucleus in $\mathrm{H}^{29}\mathrm{Si}^{35}\mathrm{Cl}$ $C_{aa} = -485$ kHz, $C_{bb} = -7.9$ kHz, and $C_{cc} = -5.0$ kHz. Our experimental value for $C_{bb}(^{29}\mathrm{Si})$ is −15(2) kHz with C_{cc} assumed to be zero which should be compared with the sum of the calculated values for the bb and cc components of the tensor which is −13 kHz. These calculations were performed using the B3LYP density functional method using an augmented, correlation consistent, polarized valence, triple-ζ basis set. This same calculation (geometry optimized rather than set at the experimental geometry) directly gives $\chi_{aa}(^{35}\mathrm{Cl}) = -27.658$ MHz which is to be compared with our experimental value −27.303(3) MHz.

Acknowledgment. This work was supported by the National Science Foundation and by the Natural Sciences and Engineering Research Council of Canada. M.F. gratefully acknowledges the support by Hiroshima City University President-Designated Grant for Long-Term Research Abroad for Young Researchers. We thank Jim Cheeseman, Mike Frisch, and John Montgomery for help with the *ab initio* calculations.

References and Notes

(1) Ho, P.; Breiland, W. G. *Appl. Phys. Lett.* **1983**, *43*, 125.

(2) Ho, P.; Breiland, W. G.; Carr, *Chem. Phys. Lett.* **1986**, *132*, 422.

(3) Harper, W. W.; Clouthier, D. J. *J. Chem. Phys.* **1997**, *106*, 9461.

(4) Herzberg, G.; Verma, R. D. *Can. J. Phys.* **1964**, *42*, 395.

(5) Hostutler, D. A.; Ndiege, N.; Clouthier, D. J.; Pauls, S. W. *J. Chem. Phys.* **2001**, *115*, 5485.

(6) de Nalda, R.; Mavromanolakis, A.; Couris, S.; Castillejo, M. *Chem. Phys. Lett.* **2000**, *316*, 449.

(7) Vàzquez, J.; Stanton, J. F. *J. Phys. Chem. A* **2002**, *106*, 4429.

(8) Hight Walker, A. R.; Chen, W.; Novick, S. E.; Bean, B. D.; Marshall, M. D. *J. Chem. Phys.* **1995**, *102*, 7298.

(9) Xu, Y.; Jäger, W. *J. Chem. Phys.* **1997**, *106*, 7968.

(10) Hirota, E.; Brown, J. M.; Hougen, J. T.; Shida, T.; Hirota, N. *Pure Appl. Chem.* **1994**, *66*, 571.

(11) Yamamoto, S.; Habara, H.; Kim, E.; Nagasaka, H. *J. Chem. Phys.* **2001**, *115*, 6007.

(12) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; McGraw-Hill: New York, 1955; pp 215−219.

(13) McCarthy, M. C.; Thaddeus, P. *J. Mol. Spectrosc.* **2002**, *211*, 228.

(14) Tellinghuisen, J. *J. Mol. Spectrosc.* **1996**, *179*, 29. The "internal" estimate of the standard deviation of the derived spectroscopic constants is a standard feature of the SPFIT program of Herb Pickett used in the current study.

(15) Townes, C. H.; Dailey, B. P. *J. Chem. Phys.* **1949**, *17*, 782.

(16) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; McGraw-Hill: New York, 1955; pp 233−237.

(17) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; John Wiley & Sons: New York, 1984; pp 738−758.

(18) Jaccarino, V.; King, J. G. *Phys. Rev.* **1951**, *83*, 471. The constant $eq_{310}Q$ (^{35}Cl) is twice the value of b^{35} of this reference.

(19) Tanimoto, M.; Saito, S.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1984**, *103*, 330.

(20) Tanimoto, M.; Takeo, H.; Matsumura, C.; Fujitake, M.; Hirota, E. *J. Chem. Phys.* **1989**, *91*, 2102.

(21) Gordy, W. *J. Chem. Phys.* **1951**, *19*, 792.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Sternheimer, R. M. *Phys. Rev. A* **1972**, *6*, 1702. Note that the values for the electric quadrupole moments of ^{35}Cl and ^{37}Cl have been inadvertently switched in this reference.

(24) Given the esoteric units and choice of sign of the Gaussian 98 package, multiplication by the conversion factor of -2.35×10^{26} bohr^2 cm^{-2} MHz Hartree^{-1} is also required. J. Montgomery, private communication.

(25) Kellö, V.; Sadlej, A. J. *Mol. Phys.* **1996**, *89*, 127.

(26) Schwerdtfeger, P.; Pernpointer, M.; Laerdahl, J. K. *J. Chem. Phys.* **1999**, *111*, 3357.

(27) Sadlej, A. J. *Collec. Czech. Chem. Commun.* **1988**, *53*, 1995.

(28) Sadlej, A. J. *Theor. Chim. Acta* **1992**, *79*, 123.

(29) Pernpointner, M.; Seth, M.; Schwerdtfeger, P. *J. Chem. Phys.* **1998**, *108*, 6722.

(30) Kewley, R.; McKinney, P. M.; Robiette, A. G. *J. Mol. Spectrosc.* **1970**, *34*, 390.

(31) Hensel, K. D.; Jaeger, W.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1993**, *158*, 131.

(32) Mitzlaff, M.; Holm, R.; Hartmann, H. *Z. Naturforschg.* **1967**, *22 A*, 1415.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Stratmann, R. E.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Iyengar, S.; Petersson, G. A.; Ehara, M.; Toyota, K.; Nakatsuji, H.; Adamo, C.; Jaramillo, J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; 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.; Gomperts, R.; 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.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 01 Development Version*; Gaussian, Inc.: Pittsburgh, PA, 2002.