The Stark and Zeeman Effects in Methyl Silane

IRVING OZIER

Department of Physics, The University of British Columbia, 6224 Agriculture Road, Vancouver, B.C., V6T 2A6, Canada

AND

W. LEO MEERTS

Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, 6525ED Nijmegen, The Netherlands

The Stark and Zeeman effects in methyl silane in the ground vibronic state have been studied in detail using the molecular-beam electric-resonance method. For a symmetric rotor without internal rotation, the rotational dependence of the effective dipole moment for matrix elements diagonal in J has been shown by Watson, Takami, and Oka to have the form $\mu_Q = \mu_0 + \mu_J J(J + 1) + \mu_K K^2$. It is shown here that, to this order, a complete characterization of the Stark effect requires only one more parameter, namely, the effective anisotropy $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$ in the polarizability. From Stark measurements alone, the true anisotropy cannot be separated from the additional dipole distortion constant shown by Aliev and Mikhaylov to enter dipole matrix elements off-diagonal in J. By studying nine different transitions $(J, K, m_J) \rightarrow (J, K, m_J \pm 1)$ in $CH_3{}^{28}SiH_3$, values were obtained for the four Stark parameters: $\mu_0 = 0.7345600(33)$ D, $\mu_J = 8.83(35)$ μD, $\mu_K = -32.82(37)$ μD, and $(\alpha_\parallel - \alpha_\perp)_{\text{eff}} = 1.99(16) \times 10^{-24}$ cm^3. These errors reflect only the internal consistency in the data; the absolute error in μ_0 is 32 μD. The modification of the Stark effect by internal rotation is discussed; it is shown that the only significant effect here is to modify the interpretation of μ_0. The change in μ_0 upon isotopic substitution of ^{30}Si for ^{28}Si was determined: $\mu_0(^{30}\text{Si}) - \mu_0(^{28}\text{Si}) = 67.0(2.0)$ μD. A study of molecular magnetic effects in $CH_3{}^{28}SiH_3$ has yielded the two molecular g factors, $g_\perp = -0.036391(21)$ nm and $g_\parallel = -0.10667(13)$ nm, as well as the anisotropy in the susceptibility $(\chi_\parallel - \chi_\perp) = -44.9(2.3) \times 10^{-30}$ J/T^2. The molecular quadrupole moment has been calculated.

I. INTRODUCTION

There are a growing number of spectroscopic techniques sensitive to the variation with rotational state of the electric dipole moment in a symmetric top. Several laser methods (*1–3*) are now available which provide very accurate Stark parameters or require such constants as input to determine zero-field energy splittings. The molecular-beam electric-resonance (MBER) method of making precision dipole measurements has recently (*4*) been extended to molecules with relatively small rotational constants. Finally, the avoided-crossing molecular-beam technique has been introduced (*5, 6*) to obtain zero-field energy separations which are inaccessible to conventional spectroscopy because of the electric dipole selection rules.

On the theoretical side, the effect of centrifugal distortion on the electric dipole matrix elements has been treated to lowest order for a symmetric top without

internal rotation in its ground vibronic state. For $\Delta J = 0$, this effect is taken into account by replacing the normal permanent moment μ by the effective dipole moment (7)

$$\mu_Q(J, K) = \mu_0 + \mu_J J(J + 1) + \mu_K K^2. \tag{1}$$

For $\Delta J = +1$, this effective moment becomes (8, 7)

$$\mu_R(J, K) = \mu_0 + \mu_J^R (J + 1)^2 + \mu_K K^2. \tag{2}$$

Here μ_0 is the equilibrium dipole moment except for a small correction. μ_J, μ_K, and μ_J^R are distortion dipole constants, which are typically four to six orders of magnitude smaller than μ_0. The physical interpretation of all four constants has been discussed in some detail (7–9).

In part because the precision methods mentioned are so new, the variation of μ with rotational state has been detected for only very few symmetric rotors. For PH$_3$ (2) and CF$_3$H (3), there is strong evidence for a change in μ with J and/or K, but not enough data to evaluate any of the individual constants. For propane-d_3, a clear variation with K was observed (10), but the experiment preceeded the establishing of Eq. (1) and so no value of μ_K was extracted from the data. The original data are reanalyzed here to determine this constant. For CH$_3$D (7) and NH$_3$ (11), both μ_J and μ_K have been obtained, while for OPF$_3$ (5) only μ_J has been measured.

In the present work, the allowed MBER spectrum of methyl silane has been investigated to obtain values of μ_0, μ_J, μ_K, and the effective anisotropy ($\alpha_\parallel - \alpha_\perp$)$_{\text{eff}}$ in the polarizability.[1] This last parameter takes into account the Stark contributions from the true anisotropy ($\alpha_\parallel - \alpha_\perp$) and from the constant μ_J^R characterizing the J dependence of the effective ($\Delta J = +1$) dipole moment in Eq. (2). As is shown in Section II.2, for all but a small class of unusual symmetric tops, μ_J^R and ($\alpha_\parallel - \alpha_\perp$) cannot be determined separately from Stark measurements alone. The modification of the linear Stark effect by internal rotation is given in the Appendix. It is shown that the only significant change introduced in the current analysis is to modify the interpretation of μ_0. The present results are summarized in Table I.

Methyl silane was selected for this Stark study because, as the prototype polar symmetric top with internal rotation (12), it has been the subject recently of a detailed study using both the new anticrossing beam technique (13) and the older microwave absorption method (14). The results of these studies will be published elsewhere (15, 16). The contributions of μ_J and μ_K are so large that, when $\mu_Q(J, K)$ is treated as a constant, the identification of many of the microwave lines cannot be made properly.

The change in μ upon isotopic substitution with ^{30}Si for ^{28}Si has also been measured. The motivation was again the interpretation of the anticrossing data (15), but this change in μ is also of interest with regard to the theory of such isotopic effects (17, 18).

---

[1] The subscript $\parallel$ on a molecular parameter indicates that the parameter is to be taken for rotation about the symmetry axis. The subscript $\perp$ similarly refers to rotation about either of the other two principal inertial axes.

TABLE I

Stark and Zeeman Constants for $CH_3{}^{28}SiH_3$

		Present Results	Others	Ref.
μ_0	(D)	0.7345600 (33)[a]	0.7380 (20)[b]	(25)
μ_J	(μD)	8.83 (35)[a]		
μ_K	(μD)	-32.82 (37)[a]		
$\mu_Q(3,2)$	(D)	0.7345365 (20)[c]		
$\mu_Q(3,2)/\mu(OCS)$		1.027057 (4)		
$(\alpha_\| - \alpha_\perp)_{eff}$	(10^{-24} cm^3)	1.99 (16)		
$g_\perp$	(nm)	-0.036391 (21)[d]	0.03583 (12)[e]	(32)
$g_\|$	(nm)	-0.10667 (13)[d]		
$(\chi_\| - \chi_\perp)$	(10^{-30} J/T^2)	-44.9 (2.3)	-39.9 (3.5)	(32)
$\Theta_\|$	(10^{-40} C m^2)	-1.2 (5)		

a - This error reflects only the internal consistency of the data. The relative signs of μ_0, μ_J and μ_K were determined here; the absolute sign for μ_0 was chosen arbitrarily to be positive.
b - This value has been referred to $\mu(OCS) = 0.71519$ D (21), rather than 0.7124 D, as used in (25).
c - The error reflects only the precision relative to the OCS measurements. The absolute error is 32 μD.
d - It was shown here that $g_\|/g_\perp > 0$. The absolute sign of the g-factors was taken from (15).
e - Only the magnitude was determined.

From a Zeeman study of the allowed MBER spectrum, the magnitudes of the two rotational g factors $g_\|$ and $g_\perp$ were determined[1] along with their relative sign. In addition, the anisotropy $(\chi_\| - \chi_\perp)$ in the susceptibility[1] was measured. By taking the absolute sign of the g factors from the avoided-crossing investigation (15), the molecular quadrupole moment $\Theta_\|$ was calculated. The results are summarized in Table I.

II. THE STARK EFFECT

1. Measurements

The variation of μ with J and K in $CH_3{}^{28}SiH_3$ was determined by observing the MBER spectrum in the high-field (19, 5) limit. The selection rules obeyed were $\Delta m_J = \pm 1$ and $\Delta J = \Delta K = 0$; in addition, the magnetic quantum numbers for the nuclear spins were conserved. As listed in Table II, nine different spectra were observed, each denoted[2] by $[J_{\pm|K|}, \mp|m_J| \rightarrow \mp(|m_J| - 1)]$, following the conventions of Ref. (4). Five of these were observed in two different electric fields. Each of the spectra is a multiplet consisting of many hyperfine components, but each appeared

---

[2] Unless otherwise indicated, it is assumed throughout that upper signs go only with upper signs, and lower with lower.

TABLE II

Stark Measurements[a]

Transition		Set A $\mathscr{E}_A$=8051.317 V/cm[b]				Set B $\mathscr{E}_B$=12389.851 V/cm[b]			
J_K	$m_J \to m'_J$	ν	σ_E^{c}	σ_T^{d}	δ^{e}	ν	σ_E^{c}	σ_T^{d}	δ^{e}
$2_{\pm 1}$	$\bar{+}1 \to 0$	490 149.8	0.5	3.0	-0.2	750 064.3	0.5	3.0	-1.2
$2_{\pm 1}$	$\bar{+}2 \to \bar{+}1$	475 474.3	0.5	3.0	-1.6	713 570.0	1.0	3.0	1.6
$3_{\pm 2}$	$\bar{+}1 \to 0$	495 341.3	1.5	1.5	0.5	761 675.4	2.0	2.0	-0.2
		495 340.0	1.5	1.5	-0.8	761 674.2	2.0	2.0	-1.4
$3_{\pm 2}$	$\bar{+}2 \to \bar{+}1$	493 392.1	2.0	2.0	0.4	756 963.2	2.0	2.0	1.7
$3_{\pm 3}$	$\bar{+}1 \to 0$	744 771.5	4.0	5.0	-0.6				
$3_{\pm 3}$	$\bar{+}2 \to \bar{+}1$	746 180.2	4.0	5.0	4.2				
$5_{\pm 1}$	$\bar{+}1 \to 0$	98 953.0	1.5	3.5	0.0	152 018.2	0.5	3.0	1.7
$5_{\pm 4}$	$\bar{+}1 \to 0$					610 590.5	2.5	4.0	-1.6
$5_{\pm 5}$	$\bar{+}1 \to 0$					763 323.0	2.5	4.0	0.0

a - All frequencies are in kHz.
b - The absolute errors in $\mathscr{E}_A$ and $\mathscr{E}_B$ are 0.34 and 0.52 volts, respectively. The ratio $\mathscr{E}_A/\mathscr{E}_B$ is accurate to ≤3 ppm. The fractional deviation ε in this ratio was allowed to vary in the fitting procedure. The best fit value for ε was -1.0(2.2) ppm.
c - σ_E is the experimental error in the peak frequency.
d - σ_T is the total error; it takes into account σ_E and an upper limit to the hyperfine shift.
e - δ is the difference between the observed and best fit values.

as a single structureless line. The peak frequency $\nu(J, K, m_J)$ measured for each line is given in Table II.

The experimental methods and conditions were very similar to those used for OPF₃ (4). The sample was made by reducing CH₃SiCl₃ with LiAlH₄. No impurities were detected in the mass spectrum; the data were taken using the ion peak with a mass-to-charge ratio of 44. To concentrate the population in the lower rotational levels, the seeded beam technique was used. For the lines with $|K| \le 3$, a 5% mixture of methyl silane in argon was expanded through a 40-μm nozzle with the source held at room temperature. For each line, the backing pressure was adjusted to give the most intense signal; these optimum values ranged from 1 to 1.5 bar. The rotational temperatures attained were ~5 to 10 K. Because A_0 is so large, the higher K levels in this prolate top were not sufficiently populated at these low temperatures. To observe the lines with $|K| = 4$ and 5, a 30% mixture of methyl silane in argon was expanded through a 430-μm nozzle at a backing pressure of ~25 mbar. Here a much more modest rotational cooling was attained. The measurements were taken in the earth's magnetic field.

The basic MBER apparatus has been described elsewhere (20). The electric field $\mathcal{E}$ was generated by the Pyrex C-field and the stabilization system developed recently (6) specifically for large electric fields of high homogeneity. The long term stability and resettability of the voltage was $\lesssim$20 ppm, while the short-term stability was $\lesssim$2 ppm. The full 10-cm length of the Pyrex plates was used as the transition region.

For each of the 16 lines measured, the observed full-width at half-height $\Delta\nu_{OBS}$ resulted from three different contributions: $\Delta\nu_T$, $\Delta\nu_{HYP}$, and $\Delta\nu_{\mathcal{E}}$. The time-of-flight linewidth $\Delta\nu_T$ was ~4.5 kHz. The second contribution $\Delta\nu_{HYP}$ arose from hyperfine shifts in the different individual transitions forming each line; it is estimated that $\Delta\nu_{HYP} \lesssim 10$ kHz. The width $\Delta\nu_{\mathcal{E}}$ due to the inhomogeneities in the electric field can be assumed to be proportional to the transition frequency ν. Because of the field distortions introduced by the slit needed for ($\Delta m_J = \pm1$) transitions, $\Delta\nu_{\mathcal{E}}/\nu$ was estimated to be ~30 ppm. The value of $\Delta\nu_{OBS}$ ranged from ~9 kHz for ν ~ 100 MHz, to ~24 kHz for ν ~ 750 MHz.

As listed in Table II, the experimental error σ_E in measuring $\nu(J, K, m_J)$ was estimated from $\Delta\nu_{OBS}$, the signal-to-noise ratio S:N, and the reproducibility. For each line, the frequency was measured at least twice, once with the frequency being swept in each direction, but many were measured four times. For $J_K = 2_{\pm1}$, one or two sweeps (one minute each) were taken on the signal averager to give S:N ~ 30:1. For $J_K = 3_{\pm2}$ and $5_{\pm1}$, four sweeps were taken and S:N ~ 10:1. For $J_K = 3_{\pm3}$, $5_{\pm4}$, and $5_{\pm5}$, 16 sweeps were used to yield S:N ~ 5:1. Although the field inhomogeneities make a large contribution to $\Delta\nu_{OBS}$, any uncertainties in the measured frequencies resulting from asymmetries in the line shape were $\lesssim\sigma_E$.

The total error σ_T assigned to each frequency must be increased over σ_E to include any possible hyperfine shifts. For each of the two $3_{\pm2}$ multiplets studied, the hyperfine splittings are symmetric about the hyperfine-free frequency (4) and the peak frequency of the single structureless line observed is determined entirely by the Stark effect. In this case, $\sigma_T = \sigma_E$. However, for each of the seven other multiplets studied, the single line observed *can* be shifted by the hyperfine contributions. This shift is generally much smaller than any hyperfine broadening $\Delta\nu_{HYP}$, which was shown to be $\lesssim$10 kHz. Consequently, an upper limit of 3 kHz for the hyperfine shift should be conservative. For each of these seven cases, σ_T was obtained by adding this upper limit to σ_E in quadrature. No frequency errors due to drift in the electric field had to be taken into account. The strongest line ($2_{\pm1}$, $m_J = \mp1 \rightarrow 0$) was used to monitor the stability of the electric field; no significant drifts were detected. The values of σ_T are given in Table II.

For the lower electric field employed (Set A), $\mathcal{E}$ was calibrated using the ($J = 1$, $m_J = \mp1 \rightarrow 0$) transition for OCS in its ground state; the OCS Stark parameters used were $\mu = 0.71519(3)$ D (21) and $(\alpha_\parallel - \alpha_\perp)_{eff} = 4.67(8) \times 10^{-24}$ cm^3 (10). As was shown for linear molecules in Ref. (22) and as discussed in Section II.4 below, it is the effective value of $(\alpha_\parallel - \alpha_\perp)$ that enters both here and in the original measurements (10). For the higher electric field employed (Set B), $\mathcal{E}$ was first calculated using the measured value of $\nu(3, 2, 1)$ in Set B, that in Set A, and the OCS calibration. The calculation was then repeated using $\nu(3, 2, 2)$. The two values of $\mathcal{E}$ agreed to 4.4 ppm and the average was used. The $3_{\pm2}$ multiplets were selected

for this purpose because their frequencies are not shifted by $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$ or the nuclear hyperfine effects. (4) The values $\mathscr{E}_A$ and $\mathscr{E}_B$ for the electric field in Set A and Set B, respectively, are given in Table II.

2. Analysis

Because the effect of internal rotation on the Stark energies only changes the interpretation of μ_0 (see Appendix), the barrier height V_3 is assumed here to be very large. The molecule-fixed frame is oriented as described for OPF_3 (5) with the silyl hydrogens corresponding to the fluorine atoms. The $\hat{z}$ direction lies along the symmetry axis with the silicon nucleus below the carbon nucleus. The yz plane contains a silyl hydrogen and, since $V_3 \to \infty$, a methyl hydrogen as well. The space-fixed frame is oriented with the $\hat{Z}$ direction along $\mathscr{E}$.

The dipole constants in Eqs. (1) and (2) can be defined in terms of the Θ_i^{jk} introduced by Watson (9):

$$\mu_0 = \mu_z^{(e)} - \Theta_y^{yz}, \tag{3a}$$

$$\mu_J = \Theta_z^{yy} + 2\Theta_y^{yz}, \tag{3b}$$

$$\mu_K = \Theta_z^{zz} - (\Theta_z^{yy} + 2\Theta_y^{yz}), \tag{3c}$$

$$\mu_J^R = \Theta_z^{yy}. \tag{3d}$$

Equation (3b) disagrees with Eq. (5b) in Ref. (5) because of a misprint in the latter. If methyl silane is treated as a symmetric rotor with C_{3v} symmetry, then expressions for the Θ_i^{jk} of Eq. (3) in terms of other molecular properties can be obtained from Ref. (9) by taking into account the differences in the two molecule-fixed frames used, as indicated in footnote (7) of Ref. (5). In Ref. (7), $\mu_Q(J, K)$ and $\mu_R(J, K)$ are referred to as $\mu_S(J, K)$ and $\mu_I(J, K)$, respectively.

The electric field dependence of the energy seems to require for its characterization five independent Stark parameters: μ_0, μ_J, μ_K, μ_J^R, and $(\alpha_\parallel - \alpha_\perp)$. However, for CH_3SiH_3, this can be reduced to four, as can be seen by considering the perturbation expansion of the Stark energy. The first-order term $E_{ST}^{(1)}$ depends only on $\mu_Q(J, K)$. The second-order term $E_{ST}^{(2)}$ receives contributions from $\mu_R(J, K)$ and $(\alpha_\parallel - \alpha_\perp)$. The leading term due to μ_J^R can be written

$$E_{ST}^{(1)}(\mu_J^R) = \frac{\mu_J^R \mu_0 \mathscr{E}^2}{3hB_0} \left[\frac{[3K^2 - J(J+1)][3m_J^2 - J(J+1)]}{J(J+1)(2J-1)(2J+3)} - 1 \right]. \tag{4}$$

The constant term is of no interest. Except for a multiplicative constant, the remaining term is identical to the contribution to $E_{ST}^{(2)}$ from $(\alpha_\parallel - \alpha_\perp)$ (4). The effect of μ_J^R on the energy can be taken into account by omitting μ_J^R from Eq. (2) and replacing $(\alpha_\parallel - \alpha_\perp)$ with

$$(\alpha_\parallel - \alpha_\perp)_{\text{eff}} \equiv (\alpha_\parallel - \alpha_\perp) + \delta\alpha, \tag{5a}$$

where

$$\delta\alpha \equiv -\mu_J^R \mu_0 / hB_0. \tag{5b}$$

A similar result was obtained earlier (22) for linear molecules.

This reduction of the number of independent Stark parameters from five to four will apply to all symmetric tops for which the spacing between rotational energy levels (J, K) and $(J + 1, K)$ can be adequately represented as being proportional to $(J + 1)$. For example, if a molecule has a large inversion splitting, then the energy denominators in the second-order perturbation terms for the dipolar Stark energy will have a different J dependence. The first term in Eq. (4) will then no longer be proportional to the Stark contribution from $(\alpha_\parallel - \alpha_\perp)$ and one could, in principle, separate $(\alpha_\parallel - \alpha_\perp)$ and μ_J^R from Stark shift measurements alone.

In calculating the Stark energy, both here for CH_3SiH_3 and in the calibration procedure with OCS, the Stark-rotation matrix was diagonalized after truncation at $\Delta J = 3$. In evaluating the rotational energy for methyl silane, the standard expression including the quartic distortion terms (23) was used. Since internal rotation is being neglected, the appropriate rotational constants are the effective parameters for the ground torsional state. These are: $B_0 = 10\,968.964$ (50) MHz, $D_J = 10.5(1.0)$ kHz, and $D_{JK} = 45.7(2.0)$ kHz. These values are preliminary results (16), but the quoted errors are small enough that they do not affect the evaluation of the Stark parameters. The fundamental constants were taken from Cohen and Taylor (24).

Our initial goal was the measurement of the four independent Stark parameters in CH_3SiH_3 relative to the dipole moment of OCS. For this purpose, it was assumed that both $\mathscr{E}_A$ and $\mathscr{E}_B$ are exactly equal to the values given in Table II. For $\mathscr{E}_A$, this is justified because it was calibrated with OCS. The absolute error in $\mathscr{E}_A$ is determined by the error of 42 ppm in the OCS dipole moment; this affects only the absolute value of μ_0, not its relative value. However, once $\mathscr{E}_A$ is fixed, any difference between the assumed value of the second field ($\mathscr{E}_B$) and the true value ($\mathscr{E}_B^T$) can bias the relative results. To solve this problem, we introduced an additional fitting parameter:

$$\epsilon = ([\mathscr{E}_B^T/\mathscr{E}_A] - [\mathscr{E}_B/\mathscr{E}_A])/(\mathscr{E}_B/\mathscr{E}_A). \tag{6}$$

A least-squares fit was made to the 16 measurements in Table II with each weighted by $1/\sigma_T^2$. The four Stark parameters discussed above were varied along with ϵ. The resulting best-fit values are given in Table I for the molecular constants and in Table II for ϵ. For each frequency, the difference δ between the observed and calculated values is given in Table II. The weighted standard deviation of the fit was 1.1 kHz, which is small compared with the uncertainties σ_T in the hyperfine-free frequencies.

Three simple arguments can be made to demonstrate that the analysis is consistent with the data. The *first* deals with the parameter ϵ. The two measurements of $\mathscr{E}_B$ described in Section II.1 show that the value of $\mathscr{E}_B/\mathscr{E}_A$ calculated from Table II should be good to ~3 ppm. The value obtained for ϵ as given in Table II is certainly consistent with this experimental error. The *second* argument involves a least-squares fit to the data at $\mathscr{E}_A$ and a second separate fit to the data at $\mathscr{E}_B$. In these, ϵ was fixed at zero. The two sets of four Stark parameters agreed with each other and with the values given in Table I for the combined fit. This is a further indication that the electric fields have been treated properly and, in addition, is strong evidence that the hyperfine effects are small. The *third* argument also deals

with the hyperfine shifts. If the values of δ are compared in Table II with the experimental errors σ_E in measuring the frequencies, then it is found that $|\delta| > |\sigma_E|$ for only 5 of the 16 measurements. This is about what one would expect if the hyperfine shifts were zero and is further evidence that these shifts have been treated conservatively.

Our second goal was to measure the value of μ_Q for a single rotational state relative to the OCS dipole moment as accurately as possible. The state $J_K = 3_{\pm2}$ was chosen because, as indicated in the calibration discussion, the spectra in this case are not shifted by $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$ or the nuclear hyperfine effects. The values obtained for the ratio $\mu_Q(3, 2)/\mu(\text{OCS})$ for the two multiplets $(3_{\pm2}, m_J = \mp1 \rightarrow 0)$ and $(3_{\pm2}, m_J = \mp2 \rightarrow \mp1)$ agreed to within 5 ppm. The average value is given in Table I. The error in the absolute value of $\mu_Q(3, 2)$ is 32 μD, as determined by the absolute error in $\mu(\text{OCS})$.

An earlier, less accurate measurement of the dipole moment of CH₃SiH₃ was made using microwave absorption (25). The constant determined was μ_0 itself. This can be shown from the discussion in Section II.4 and the fact that the polarizability effects were negligible. As can be seen from Table I, the agreement with the current value is acceptable.

3. The Dipole Moment of $CH_3{}^{30}SiH_3$

The change in the dipole moment upon isotopic substitution of ³⁰Si for ²⁸Si was determined. The sample was not isotopically enriched. Because $^{12}CH_3{}^{30}SiH_3$, $^{12}CH_3{}^{29}SiH_3$, and $^{13}CH_3{}^{28}SiH_3$ are all comparable in natural abundance, the ion peak used here had to be selected with some care. For each isotopic form, three peaks were present: $(CSiH_4)^+$, $(CSiH_5)^+$, and $(CSiH_6)^+$. The corresponding relative intensities were 100, 75, and 8. The strongest peak for ³⁰Si therefore has a mass-to-charge ratio m/e of 46. Unfortunately, this peak contains comparable contributions from ²⁹Si and ¹³C. For this reason, the present experiments were done using the peak with $m/e = 47$, which is a little weaker in the desired ³⁰Si species, but has no significant contamination from the other isotopic forms.

The measurements were made on the $(1_{\pm1}, \mp1 \rightarrow 0)$ line because $\mu_Q(1, 1)$ is the specific dipole moment that enters the anticrossing experiments on CH₃³⁰SiH₃ (15). The data were taken in electric fields of approximately 2644 and 5336 V/cm, resulting in Stark splittings of 490 and 991 MHz, respectively. Each line for the ³⁰Si species required 16 sweeps to produce the minimum acceptable signal-to-noise ratio of 5:1. As for the other transitions studied, the $(1_{\pm1}, \mp1 \rightarrow 0)$ multiplet gave a single structureless line. The experimental error σ_E in measuring the peak frequency was ~1/2 kHz for the parent species and ~3 kHz for the ³⁰Si form. The stability of the electric field was monitored by measuring the ²⁸Si spectrum before and after each ³⁰Si-scan, with all three traces being taken under identical conditions. No significant drifts were detected.

In the context of the present experiment, the isotopic substitution produces only two significant changes. In the Stark Hamiltonian, μ_0 changes by ~100 ppm. The contributions of the other three Stark parameters to the frequency are so minor that the small isotopic changes in these constants are negligible. In the rotational

Hamiltonian, B_0 changes by $\sim 1.5\%$ to 10 806.90(20) MHz (16). The isotopic changes in the distortion constants are again negligible. Because both ^{30}Si and ^{28}Si have no nuclear spin, the isotopic changes in the nuclear hyperfine energy will not be significant.

For each individual value of $\mathscr{E}$, the measurements were analysed by a simple perturbation treatment based on isolating the linear term in the Stark energy. The results were: $[\mu_0(CH_3{}^{30}SiH_3) - \mu_0(CH_3{}^{28}SiH_3)]$ equal 68.7(4.5) μD for the lower field and 66.6(2.2) μD for the higher field. The weighted mean of 67.0(2.0) μD leads to:

$$[\mu_0(CH_3{}^{30}SiH_3) - \mu_0(CH_3{}^{28}SiH_3)]/\mu_0(CH_3{}^{28}SiH_3) = 91.2(2.7) \text{ ppm.} \qquad (7)$$

The dipole moment of $CH_3{}^{28}SiD_3$ has been previously determined using microwave spectroscopy (25). It was found that

$$[\mu_0(CH_3{}^{28}SiD_3) - \mu_0(CH_3{}^{28}SiH_3)]/\mu_0(CH_3{}^{28}SiH_3) = -0.0157(38). \qquad (8)$$

As expected, the magnitude of the change produced by the substitution of ^{28}Si is much smaller than that produced by the substitution of the three silyl hydrogens. It is interesting to note that the two isotopic shifts have opposite signs in spite of the fact that the same end of the molecule is made heavier in both cases.

4. Discussion

In order to characterize the entire Stark Hamiltonian of a symmetric top at the level of accuracy where distortion effects become important, the four parameters μ_0, μ_J, μ_K, and $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$ are required. The dipole constants will enter the analysis in different ways depending on the specific transitions being studied. Transitions with $\Delta J = \Delta K = 0$ and $\Delta m_J = \pm 1$ are often studied in MBER experiments such as that done here. If $K = 0$, the quadratic Stark shift is measured and the effective dipole moment is μ_0; μ_J^R is absorbed into $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$. If $K \neq 0$, the linear contribution dominates the Stark shift; for low values of $\mathscr{E}$, this shift can be characterized entirely by the effective moment $\mu_Q(J, K)$ given in Eq. (1).

Transitions with $\Delta J = 1$ and $\Delta K = \Delta m_J = 0$ are often studied in microwave absorption experiments (10, 25). If $K = 0$ and/or $m_J = 0$, only quadratic terms enter the Stark effect and the effective moment is $(\mu_0 + K^2\mu_K)$. If both K and m_J are nonzero, the linear term dominates. The linear shift is given by

$$\Delta\nu_0^{(1)} = (2m_J K/J(J + 1)(J + 2))(\mathscr{E}/h)(\mu_0 + K^2\mu_K), \qquad (9)$$

where the subscript in $\Delta\nu_0^{(1)}$ specifies the value of Δm_J. The μ_J dependence cancels out and the effective moment is $(\mu_0 + K^2\mu_K)$, just as it is for the quadratic case.

If $\Delta m_J = \pm 1$ in these R-branch transitions as occurs in many laser experiments (26, 2), μ_J does not drop out of the problem. For $(J, K, m_J) \rightarrow (J + 1, K, m_J \pm 1)$, the linear Stark shift is given by

$$\Delta\nu_{\pm 1}^{(1)} = ((2m_J \mp J)K/J(J + 1)(J + 2))(\mathscr{E}/h)[\mu_0 + K^2\mu_K] \mp K\mu_J(\mathscr{E}/h). \qquad (10)$$

The extra shift due to μ_J is independent of J and m_J, and so makes a larger fractional contribution to the shift as J goes up. If $K \neq 0$, then, the parameters needed to

characterize the Stark shift change when the plane of polarization of the radiation is rotated from being parallel to being perpendicular to the Stark field. By observing both $(\Delta m_J = 0)$ and $(\Delta m_J = \pm 1)$ spectra, the contribution due to μ_J can be separated if sufficient accuracy is attained.

In determining μ_0, μ_J, and μ_K from an MBER experiment such as that done here, the particular states selected for study must be chosen so as to include states with $K \ll J$ as well as those with $K \sim J$. There are now values of both μ_K and μ_J for three symmetric rotors: monodeuterated methane (7), ammonia (11), and methyl silane. In these cases, $\mu_K/\mu_J \sim -1.6$, -1.9, and -3.7, respectively. For the first two values in particular, the terms in μ_K and μ_J tend to cancel in states with $K \sim J$. As a result, if only such states are studied, μ_Q will appear to be approximately constant and it will be very difficult to separate the three constants.

One of the earliest systematic changes of the dipole moment with K observed was in propyne-d_3 ($D_3C-C\equiv C-H$) with microwave absorption (10). The accuracy attained of ~ 150 ppm was not quite high enough to verify conclusively the expected K^2 dependence. Because this dependence had not been established at that time, no attempt to determine μ_K was made. The data have been reanalyzed with the methods used here for CH₃SiH₃. It was found that $\mu_K = -42(10)$ μD. The error quoted is one standard deviation, as is the case throughout the present work. The value for μ_K in propyne-d_3 is very similar to that in methyl silane. The dipole moment for the $(J_K = 3_0)$ state measured in Ref. (10) can now be identified as μ_0 and $(\alpha_\parallel - \alpha_\perp)$ in the original work should be reinterpreted as $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$.

The value of $(\alpha_\parallel - \alpha_\perp)$ cannot be obtained from Stark shift measurements alone, except for a few unusual cases. As indicated in the discussion of Eq. (5), all that can be determined is $(\alpha_\parallel - \alpha_\perp)$ plus the contribution $\delta\alpha$ from μ_J^R. This term can be important, particularly in molecules with large μ_0, small $(\alpha_\parallel - \alpha_\perp)$, and/or small B_0. In methyl silane, if $|\mu_J^R| \sim |\mu_J|$, $|\delta\alpha/(\alpha_\parallel - \alpha_\perp)| \sim 4.5\%$, which is smaller than the experimental error of 8%. On the other hand, if $|\mu_J^R| \sim |\mu_K|$, then the effect is 17%, which is clearly significant. A similar problem occurs for polar linear molecules (22). In OCS, $|\mu_J^R|$ must be $\gtrsim 4.5$ μD in order that $|\delta\alpha|$ be $\sim$ the error of 1.7% in $(\alpha_\parallel - \alpha_\perp)$.

In comparing measurements of the anisotropy in the static polarizability from Stark shifts with those at optical frequencies from depolarized-Rayleigh scattering ($27, 28$) or from intensity-dependent dispersion (29), the contribution of $\delta\alpha$ to the static values must be taken into account. In some cases, $\delta\alpha$ can be comparable in magnitude to the difference between the optical and static values. If μ_J^R is determined from the intensities of the R-branch transitions, then $\delta\alpha$ can be calculated and $(\alpha_\parallel - \alpha_\perp)$ determined.

For a symmetric rotor with $\mu \sim 1$ D, the MBER method can attain accuracies ~ 5 ppm and ~ 42 ppm for relative and absolute measurements, respectively. This has been demonstrated here for CH₃SiH₃ where nuclear hyperfine effects are small, and by Marshall and Muenter (30) using a somewhat different approach for CH₃F where the nuclear hyperfine terms are large. On this scale, the distortion effects on the dipole moment of methyl silane are rather sizable. For example, $\mu(5, 5) - \mu(5, 1) = 24\mu_K = -0.00107\mu_0$ and $\mu(5, 1) - \mu(2, 1) = 24\mu_J = 0.00029\mu_0$. However, if correlations with $(\alpha_\parallel - \alpha_\perp)_{\text{eff}}$ do not pose a serious problem, μ_J and μ_K can be

determined in a molecule like methyl silane even if these parameters are as small as 1 μD.

III. THE ZEEMAN EFFECT

The rotational g factors $g_\parallel$ and $g_\perp$ as well as the anisotropy $(\chi_\parallel - \chi_\perp)$ in the susceptibility were determined from the MBER spectrum using techniques described previously in detail (4). When a large magnetic field **B** is applied parallel $\mathscr{E}$, each of the multiplets whose spectrum appeared as a single structureless line in the earth's magnetic field will produce a doublet. If ν_U and ν_L are the peak frequencies of the upper and lower members of the doublet, respectively, then (4)

$$|\nu_U - \nu_L| = 2\mu_N B |g_{\text{eff}}|. \tag{11}$$

Since the nuclear shielding effects are negligible here,

$$g_{\text{eff}} = g_\perp + (g_\parallel - g_\perp)K^2/J(J + 1). \tag{12}$$

Let ν_0 be the common limit of ν_U and ν_L as $B \to 0$. Since the translational Stark effect is negligible here as well,

$$[(1/2)(\nu_U + \nu_L) - \nu_0] = \lambda(\chi_\parallel - \chi_\perp)B^2. \tag{13}$$

λ is a constant of proportionality whose value depends on the particular multiplet being studied. Its value can be determined from Eq. (9) of Ref. (4); $\lambda = -1/5$ for $(1_0, \mp 1 \to 0)$ and $-1/7$ for $(2_0, \mp 1 \to 0)$.

As listed in Table III, five different multiplets were studied. In all cases, B was very close to 0.8 T; it was measured to 0.02% with a calibrated NMR probe. An electric field of 1414.316 V/cm was applied with the large quartz C-field described earlier (4, 20). The transition region was 16.5 cm long, giving a time-of-flight linewidth $\Delta\nu_T \sim 2.7$ kHz. The two multiplets with quadratic Stark effect came in the low MHz region and had no significant inhomogeneity broadening. The observed

TABLE III

Zeeman Splittings and Effective g Factors

Transition		B	$|\nu_U - \nu_L|$	g_{eff} (nn)	
J_K	$m_J \to m_J'$	(T)	(kHz)		
1_0	$\mp 1 \to 0$	0.80007	443.9 (4)	$g_\perp$	-0.036394 (32)
2_0	$\mp 1 \to 0$	0.79996	443.8 (3)	$g_\perp$	-0.036387 (25)
$1_{\pm 1}$	$\mp 1 \to 0$	0.80013	870.9 (2.5)	$\frac{1}{2}g_\parallel + \frac{1}{2}g_\perp$	-0.07140 (21)
$3_{\pm 2}$	$\mp 1 \to 0$	0.80013	729.5 (7)	$\frac{1}{3}g_\parallel + \frac{2}{3}g_\perp$	-0.059805 (57)
$3_{\pm 2}$	$\mp 2 \to \mp 1$	0.80013	729.8 (7)	$\frac{1}{3}g_\parallel + \frac{2}{3}g_\perp$	-0.059830 (57)

widths of ~9 and 4½ kHz for $J_K = 1_0$ and 2_0, respectively, were dominated by the hyperfine contributions $\Delta\nu_{\mathrm{HYP}}$. The three multiplets with linear Stark effect came in the hundred MHz region and the observed widths were dominated by the inhomogeneity contribution $\Delta\nu_\mathcal{E}$.

The measurements of the g factors are summarized in Table III. The two values of $g_\perp$ agree, as do the two values of g_{eff} for $J_K = 3_{\pm2}$. The g_{eff} for $J_K = 1_{\pm1}$ is of much lower accuracy and serves primarily to establish that $g_\parallel/g_\perp > 0$. The final values for $g_\parallel$ and $g_\perp$ are given in Table I. The absolute sign was taken from the avoided-crossing study (15).

The determination of $(\chi_\parallel - \chi_\perp)$ was made from the spectra for $J_K = 1_0$ and 2_0 using Eq. (13). The values obtained were $-69.6(4.7)$ and $-68.4(5.5)$ kHz/T², respectively. The average is given in Table I, as is the molecular quadrupole moment $\Theta_\parallel$ calculated from Eq. (14) of Ref. (4). The value of B_0 used is given above in Section II.2. The value of A_0 used is 56 300 MHz, as calculated from the structure (31). The uncertainty in A_0 is negligible because the error in $\Theta_\parallel$ is determined entirely by the error in the $(\chi_\parallel - \chi_\perp)$ contribution. $\Theta_\parallel$ is small and has a relatively large error because the g factor and susceptibility contributions differ in magnitude by only ~10% and have opposite signs.

A previous microwave study of the $(J = 0 \rightarrow 1, K = 0)$ line of CH₃SiH₃ yielded values of $g_\perp$ and $(\chi_\parallel - \chi_\perp)$ (32). As can be seen from Table I, the microwave and beam values of $(\chi_\parallel - \chi_\perp)$ agree, but the two values of $g_\perp$ differ by over 4 times the quoted error. The microwave study included as well the $(J = 1 \rightarrow 2, K = 1)$ line of CH₃SiD₃. It was concluded that $g_\parallel/g_\perp < 0$; since this ratio will have the same sign in CH₃SiH₃ as in CH₃SiD₃, this conclusion is in disagreement with the present work which finds both g factors have the same sign. One possible reason for the disagreement is the distortion of the microwave spectrum by the translational Stark effect, as discussed in Ref. (33).

The form of the Zeeman energy adopted here from Ref. (4) is strictly valid only in the limit of infinite barrier. This form must be modified to take into account the internal rotation (34). An analysis similar to that given in the Appendix for the dipole moment has been carried out. At the level of accuracy attained here in the Zeeman measurements, the magnitudes of the "torsional g factors" which characterize these modifications need only be smaller than $|g_\parallel|$ and $|g_\perp|$ themselves in order that these torsional corrections not affect the current results. The only change required is to reinterpret $g_\parallel$ and $g_\perp$ as effective values for the ground torsional state in the same sense that internal rotation leads to the introduction of an effective B value B_{eff} for each torsional state (14, 23).

APPENDIX

In order to discuss the effect of internal rotation on the Stark effect, it will be necessary to introduce some notation (12, 23). When the height V_3 of the threefold barrier to internal rotation is lowered from ∞, the relative angle α between the methyl top and the silyl frame is no longer fixed. The two groups undergo small torsional oscillations about the symmetry axis and a new angular momentum must be introduced. This is represented by **p** in the internal axis method (35). To uniquely label all the energy states, there are now introduced two new quantum numbers:

$v = 0, 1, 2 \ldots$ specifying the torsional level and $\sigma = 0, +1, -1$ labeling the sublevels. If $K \neq 0$, then lowering V_3 from ∞ causes the zero-field energies to split into three groups according to whether $K\sigma$ equals zero, is positive, or is negative. If $K = 0$, the splitting is into two groups; the $(\sigma = +1)$ and $(\sigma = -1)$ levels remain degenerate, but are shifted away from the $(\sigma = 0)$ levels.

In the analysis used in Section II.2, it was assumed that the σ dependence of the Stark effect is negligible. However, two different effects can introduce such a dependence. The first results directly from the splitting just mentioned. In the second order Stark effect $E_{ST}^{(2)}$, the energy denominators for a symmetric rotor without internal rotation are proportional to B_0 (4, 10). Here, the σ splitting in the zero-field energies can be taken into account by replacing B_0 with an effective rotational[3] constant $B_{v,K,\sigma}$ with $v = 0$. This is defined in Eq. (12.115) of Ref. (23). Between one σ state and another, the fractional change in the second-order contribution $\nu^{(2)}$ to the measured frequencies will equal the fractional change in $B_{0,K,\sigma}$, which was estimated to be $\lesssim 25$ kHz out of 10 GHz or 2.5 ppm (14). Since the largest $\nu^{(2)}$ is ~ 50 MHz, this particular source of σ dependence is indeed negligible. The value of B_0 used in Section II.2 is the average of $B_{0,K,\sigma}$ over the different (K, σ) levels in the ground torsional state.

The second mechanism which can introduce a σ dependence in the Stark effect is a change in the dipole operator itself. A detailed analysis was not carried out, but rather the form of the changes were deduced by simple group theory. The complete linear Stark effect can be written:

$$E_{ST}^{(1)} = -(\mu_0 + \mu_0^T \langle (1/2)(1 - \cos 3\alpha) \rangle_{v,K,\sigma} + \mu_2^T \langle \mathbf{p}^2 \rangle_{v,K,\sigma}) \mathscr{E} m_J K / J(J + 1)$$

$$-(\mu_\perp^T + (\mu_\parallel^T - \mu_\perp^T) K^2 / J(J + 1)) \mathscr{E} m_J \langle \mathbf{p} \rangle_{v,K,\sigma}$$

$$-\mu_J \mathscr{E} m_J K - \mu_K \mathscr{E} m_J K^3 / J(J + 1). \quad \text{(A-1)}$$

Here $\langle \quad \rangle_{v,K,\sigma}$ indicates the diagonal matrix element in level (v, K, σ) (35, 15). The four new constants μ_0^T, μ_2^T, $\mu_\parallel^T$, and $\mu_\perp^T$ introduced by internal rotation are empirical torsion dipole parameters. A similar expression was used recently to discuss the effective dipole moment in the asymmetric rotor CH_3OH (36). Terms corresponding to $\mu_\parallel^T$ and $\mu_\perp^T$ have been introduced for C_2H_6 (37). In the original treatment of the effect of internal rotation on the Stark effect in symmetric rotors (38), terms similar to μ_0^T, μ_2^T, and $\mu_\perp^T$ were included, but the term corresponding to $\mu_\parallel^T$ was omitted. Equation (A-1) is similar to the corresponding expression for the rotational energy. The coefficient of $-\mathscr{E} m_J K / J(J + 1)$ in Eq. (A-1) can be considered to be the effective dipole moment $\mu_{v,K,\sigma}$ for state (v, K, σ) in analogy with the effective rotational constant $B_{v,K,\sigma}$.

The contributions to $E_{ST}^{(1)}$ from μ_0^T and μ_2^T will be considered first. The values of the corresponding matrix elements were calculated using the results of our internal rotation study (15). For $v = 0$, the averages over all three σ states and all K from 1 to 5 were $\overline{\langle (1/2)(1 - \cos 3\alpha) \rangle_0} = 0.0886$ and $\overline{\langle \mathbf{p}^2 \rangle_0} = 5.76$. The scatter in each

---

[3] Following the usual conventions (12), the quantum number dependence is written K, σ even though the actual dependence is on K and the product $K\sigma$.

of these averages was ~ 350 ppm; both the dependence on K and that on σ are very weak. As μ_0^T and μ_2^T are increased in magnitude from zero, the first effect that appears in the spectra is a slow extra variation of the frequencies $\nu(J, K, m_J)$ with K. If $|\mu_0^T| \lesssim 0.13$ D, this variation is $\sim$ the experimental error in μ_0. For $|\mu_2^T|$, the corresponding limit is 0.0014 D. Preliminary microwave measurements on the difference between the dipole moments for $(v = 0)$ and $(v = 2)$ indicate that both $|\mu_0^T|$ and $|\mu_2^T|$ are the order of or smaller than their respective limits. As a result, the only change introduced in the current analysis is the reinterpretation of μ_0 in Table I as the effective dipole moment for the ground torsional state:

$$\mu_0^{\text{eff}} = \mu_0 + \mu_0^T \langle \overline{(1/2)(1 - \cos 3\alpha)} \rangle_0 + \mu_2^T \langle \overline{\mathbf{p}^2} \rangle_0 . \tag{A-2}$$

Now the contributions of $\mu_\perp^T$ and $(\mu_\parallel^T - \mu_\perp^T)$ in Eq. (A-1) will be considered. Here a new dependence on J and K is introduced in addition to that which enters through the torsional matrix elements. A least-squares fit to the data in Table II was made adding $\mu_\perp^T$ and $(\mu_\parallel^T - \mu_\perp^T)$ to the set of parameters being varied. This yielded $\mu_\perp^T = 0.6(2.3)$ mD and $(\mu_\parallel^T - \mu_\perp^T) = -1.3(3.4)$ mD. The four original Stark parameters were virtually unchanged and the standard deviation of the fit was not improved. It is clear that these two constants do not affect the current experiment.

One curious feature of Eq. (A-1) is that a linear Stark effect is predicted for $K = 0$ due to $\mu_\perp^T$. This, of course, occurs only for $\sigma = \pm 1$, where the required degeneracy exists; for $\sigma = 0$, this term vanishes because $\langle \mathbf{p} \rangle_{v,K,0} = 0$. Furthermore, this unusual Stark effect for $\sigma = \pm 1$ is independent of J. For $K = 0$, the normal moment gives a second order Stark effect which drops rapidly with J. For high J and $K = 0$, the relative effect of the term in $\mu_\perp^T$ is magnified. A study of the conventional MBER spectrum $(3_0, \mp 1 \rightarrow 0)$ showed that $|\mu_\perp^T| \lesssim 1.2$ mD, a limit which is $\sim$ a factor of 2 smaller than the error in $\mu_\perp^T$ from the least-squares fit mentioned above.

REFERENCES

1. K. SHIMODA (Ed.), For examples of these methods, see "High-Resolution Laser Spectroscopy," Springer-Verlag, New York, 1976.
2. B. J. ORR AND T. OKA, *Appl. Phys.* **21**, 293–306 (1980).
3. S. M. FREUND, G. DUXBURY, M. RÖMHELD, J. T. TIEDJE, AND T. OKA, *J. Mol. Spectrosc.* **52**, 38–57 (1974).
4. W. L. MEERTS, I. OZIER, AND A. DYMANUS, *Canad. J. Phys.* **57**, 1163–1173 (1979).
5. I. OZIER AND W. L. MEERTS, *Canad. J. Phys.* **59**, 150–171 (1981).
6. W. L. MEERTS AND I. OZIER, *J. Chem. Phys.* **75**, 596–603 (1981).
7. J. K. G. WATSON, M. TAKAMI, AND T. OKA, *J. Chem. Phys.* **70**, 5376–5380 (1979).
8. M. R. ALIEV AND V. M. MIKHAYLOV, *J. Mol. Spectrosc.* **49**, 18–26 (1974).
9. J. K. G. WATSON, *J. Mol. Spectrosc.* **40**, 536–544 (1971).

10. L. H. SCHARPEN, J. S. MUENTER, AND V. W. LAURIE, *J. Chem. Phys.* **53,** 2513–2519 (1970).

11. K. SHIMODA, Y. UEDA, AND J. IWAHORI, *Appl. Phys.* **21,** 181–189 (1980).

12. C. C. LIN AND J. D. SWALEN, *Rev. Mod. Phys.* **31,** 841–892 (1959).

13. W. L. MEERTS AND I. OZIER, *Phys. Rev. Lett.* **41,** 1109–1112 (1978).

14. D. KIVELSON, *J. Chem. Phys.* **22,** 1733–1739 (1954).

15. W. L. MEERTS AND I. OZIER, *J. Mol. Spectrosc.*, in press.

16. M. WONG, I. OZIER, AND W. L. MEERTS, manuscript in preparation.

17. A. D. BUCKINGHAM AND W. URLAND, *Chem. Rev.* **75,** 113–117 (1975).

18. G. RILEY, W. T. RAYNES, AND P. W. FOWLER, *Mol. Phys.* **38,** 877–892 (1979).

19. N. F. RAMSEY, "Molecular Beams," Oxford Univ. Press, London, England 1956.

20. F. H. DE LEEUW AND A. DYMANUS, *J. Mol. Spectrosc.* **48,** 427–445 (1973).

21. J. M. L. J. REINARTZ AND A. DYMANUS, *Chem. Phys. Lett.* **24,** 346–351 (1974).

22. M. CHARIFI, G. GRÄFF, R. LEY, AND M. WOLF, *J. Chem. Phys.* **69,** 5020–5025 (1978).

23. W. GORDY AND R. L. COOK "Microwave Molecular Spectra," Wiley–Interscience, New York, 1970.

24. E. R. COHEN AND B. N. TAYLOR, *J. Phys. Chem. Ref. Data* **2,** 663–729 (1973).

25. J. S. MUENTER AND V. M. LAURIE, *J. Chem. Phys.* **45,** 855–858 (1966).

26. R. L. SHOEMAKER, S. STENHOLM, AND R. G. BREWER, *Phys. Rev. A* **10,** 2037–2050 (1974).

27. G. R. ALMS, A. K. BURNHAM, AND W. H. FLYGARE, *J. Chem. Phys.* **63,** 3321–3326 (1975).

28. F. BAAS AND K. D. VAN DEN HOUT, *Physica A Amsterdam* **95,** 597–601 (1979).

29. D. S. ELLIOTT AND J. F. WARD, *Phys. Rev. Lett.* **46,** 317–320 (1981).

30. M. D. MARSHALL AND J. S. MUENTER, *J. Mol. Spectrosc.* **83,** 279–282 (1980).

31. R. W. KILB AND L. PIERCE, *J. Chem. Phys.* **27,** 108–112 (1957).

32. R. L. SHOEMAKER AND W. H. FLYGARE, *J. Amer. Chem. Soc.* **94,** 684–686 (1972).

33. L. ENGLEBRECHT AND D. H. SUTTER, *Z. Naturforsch. A* **30,** 1265–1270 (1975).

34. L. ENGLEBRECHT AND D. H. SUTTER, *Z. Naturforsch. A* **33,** 1525–1545 (1978).

35. E. HIROTA, *J. Mol. Spectrosc.* **43,** 36–64 (1972).

36. L. H. JOHNSTON, R. P. SRIVASTAVA, AND R. M. LEES, *J. Mol. Spectrosc.* **84,** 1–40 (1980).

37. A. ROSENBERG AND J. SUSSKIND, *Phys. Rev. Lett.* **42,** 1613–1616 (1979).

38. D. KIVELSON, *J. Chem. Phys.* **26,** 215–216 (1957).