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Ground-State Electric Dipole Moment of Methane*

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Linear Stark shifts and allowed electric dipole transitions have been observed for the first time in the *ground* electronic and vibrational state of a *conventionally nonpolar* molecule. By means of molecular-beam techniques, the electric dipole moment of CH_4 in its ground vibronic state has been determined to have a magnitude of $(5.38 \pm 0.10) \times 10^{-6}$ D.

It is commonly assumed that the electric dipole moment of a tetrahedral molecule in its ground electronic and vibrational state is identically zero. However, recent theoretical calculations[1-3] have shown that centrifugal distortion effects produce a small permanent moment whose magnitude is the order of 10^{-5} to 10^{-6} D. This mechanism should be operative not only for tetrahedral molecules, but also for virtually all symmetry types which do not contain a center of inversion.[3]

A direct experimental verification of these theoretical treatments is of particular interest because of the various implications associated with the existence of this type of electric dipole moment (EDM). First, of course, the magnitude of these moments would allow one to study the distortion mechanism itself. Second, and perhaps of greater importance, a series of otherwise forbidden spectra would be allowed, thereby providing a new tool for measuring the constants which appear in the rotational Hamiltonian for the ground vibronic state. Finally, such EDM's can significantly affect the distribution over rotational levels of interstellar molecules.[4]

It is the purpose of the present Letter to report the first measurement of a centrifugal-distortion dipole moment of this nature. It is here determined that the electric dipole moment μ_ϵ of CH_4 in the *ground* vibronic state has a magnitude of $(5.38 \pm 0.10) \times 10^{-6}$ D. This determination was made by measuring Stark shifts in the ortho-para spectrum[5] of CH_4 in the $(J=2)$ rotational level. A conventional molecular-beam magnetic-resonance spectrometer[6] was used with an electric field $\vec{\mathcal{E}}$ applied parallel to the usual magnetic field $\vec{H}$ in the Z direction. The sensitivity of the method developed here is such that effects due to a methane EDM as small as 10^{-8} D could have been detected. By comparison, the smallest molecular EDM previously measured,[7a] namely, that of HD, is $(5.85 \pm 0.17) \times 10^{-4}$ D.

In Fig. 1(a), the ortho-para spectrum of CH_4 for $\epsilon = 0$ and $H = 1982.81$ G is shown. Each of the two high-frequency lines is an unresolved doublet. The remaining three lines are completely resolved. All seven transitions follow the selection rule $\Delta m = 0$, where m is the eigenvalue of the Z component of the total angular momentum. However, only the two unresolved doublets result from magnetic dipole (MD) transitions.[7b] The three resolved lines result from *allowed electric dipole* (ED) transitions, the first such transitions observed in the *ground* vibronic state of a *conventionally nonpolar* molecule.

In Fig. 1(b), the magnetic-dipole ortho-para spectrum for $\epsilon = 324.4$ V/cm and $H = 1982.73$ G is shown. The labels above each line show the correspondence between the two spectra. Note that the two unresolved doublets in Fig. 1(a) have been split by the Stark effect and are clearly re-

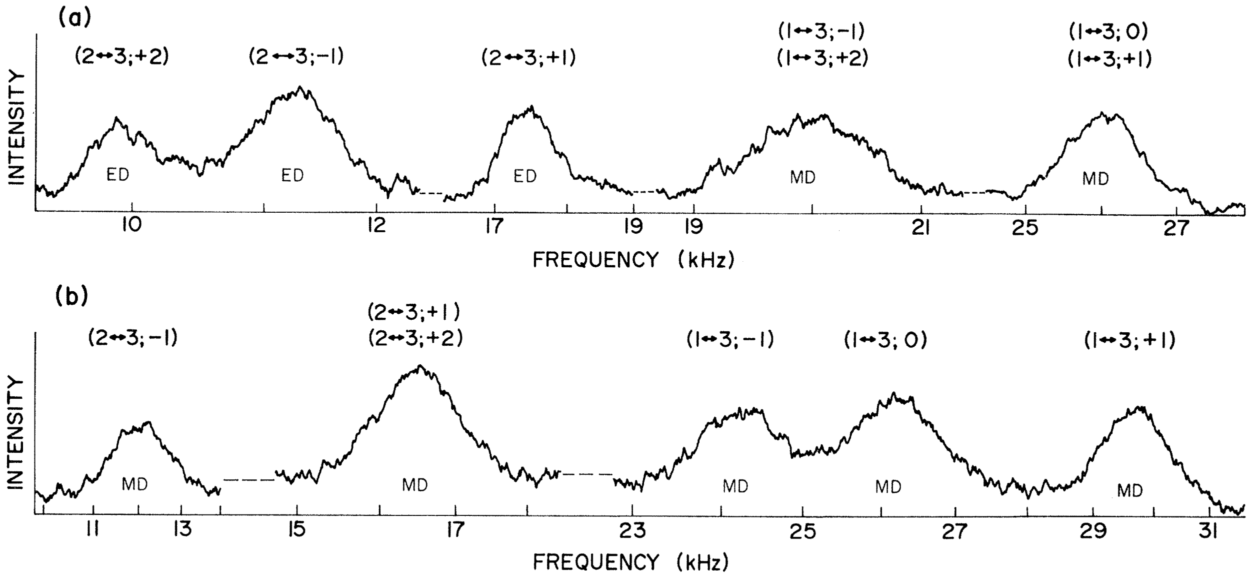

FIG. 1. The ortho-para spectrum of CH_4: (a) for $\epsilon = 0$ V/cm and $H = 1982.81$ G, and (b) for $\epsilon = 324.4$ V/cm and $H = 1982.73$ G. See Ref. 8. Each line is labeled as to whether it arises from a magnetic dipole (MD) or electric dipole (ED) transition. Each spectrum was taken in several sections with different frequency sweep rates but the same intensity scale.

solved[8] for $\epsilon = 324.4$ V/cm. All the spectra taken for $\epsilon \neq 0$ were MD induced.

In order to interpret these data, we first calculate the Hamiltonian matrix in the Γ representation,[5, 9, 10] which is characterized by the quantum numbers (I, m_I, m_J, ρ). I is the total nuclear spin and for $J = 2$ can equal 1 (ortho) or 0 (para). m_I and m_J are, respectively, the eigenvalues of I_Z and J_Z. ρ is a parity index which takes the values 1 or 2 corresponding, respectively, to even and odd parities of the ($J = 2$) rotational wave functions[9] under inversion of the *space-fixed* frame.[11]

The effective Hamiltonian W can be written as a 3×3 matrix,[12] diagonal in $m = m_I + m_J$, of the form shown in Table I. B arises from the Stark effect. It can be shown directly from the Wigner-Eckart theorem that $B = \mu_\epsilon \epsilon \eta m_J 6^{-1/2}$. The value of the constant η depends on the details of the physical mechanism producing the EDM and the definition of μ_ϵ. For the Watson-Fox mechanism[1-3] with $\mu_\epsilon = C_{34}$,[2] which equals $(20)^{-1/2}\Theta_z^{xy}$,[3] $\eta = -i6 \times (10)^{1/2}$ and

$$B = -i\mu_\epsilon \epsilon m_J (60)^{1/2}. \qquad (1)$$

TABLE I. The form of the effective Hamiltonian matrix in the representation $\Gamma \equiv (I, m_I, m_J = m - m_I, \rho)$. α, γ, A, and B are all functions of m.

(I, m_I, m_J, ρ)	$(1, 1, m-1, 2)$	$(0, 0, m, 2)$	$(0, 0, m, 1)$
$(1, 1, m-1, 2)$	α	A	0
$(0, 0, m, 2)$	A^*	γ	B
$(0, 0, m, 1)$	0	B^*	γ

In Table I, A is a constant ≈ 10 kHz which arises from the tensor part of the spin-rotation interaction. α and γ are functions of H. For a detailed discussion of α, γ, and A, the reader is referred to Refs. 5, 9, and 10.

Because I, m_I, and ρ cannot be treated as good quantum numbers here, we introduce a second representation $\Lambda \equiv (\lambda, m)$ and write the eigenvalues of W as $E(\lambda, m)$. λ is an artificial index which can take the values 1, 2, and 3 such that $E(\lambda, m) < E(\lambda' m)$ if $\lambda < \lambda'$. The transition $(\lambda m) \leftrightarrow (\lambda' m)$ occurs at frequency $\nu_\epsilon(\lambda \leftrightarrow \lambda'; m)$. It is this notation which is used to label the lines in Figs. 1(a) and 1(b). As will be explained below, Fig. 1 of paper I (Ref. 5) shows $E(1,1)$, $E(2,1)$, and $E(3,1)$ as functions of H for $B = 22.2$ kHz.[13]

For $\epsilon = 0$ and $H \gtrsim 3000$ G, $B = 0$ and $|\alpha| \sim |\gamma| \sim |\alpha - \gamma| \gg |A|$. The $E(\lambda, m)$ can be approximated by the diagonal elements of W: The lowest energy $E(1, m) \rightarrow W(I = 1, m_I = 1, m_J = m - 1, \rho = 2)$; the highest energy $E(3, m) \rightarrow W(0, 0, m, 2)$; and the intermediate energy $E(2, m) \rightarrow W(0, 0, m, 1)$. Notice that the one level $E(2, m)$ of even parity ($\rho = 1$) lies between the two levels of odd parity ($\rho = 2$). For these fields, no transitions are MD allowed and only $(2 \leftrightarrow 3; m)$ is ED allowed. When H is lowered to a value near the crossing field[5] $H_{\text{CR}} \approx 1982$ G, $|\alpha - \gamma| \approx |A|$, and the basis functions $\Psi(1,1,m-1,2)$ and $\Psi(0,0,m,2)$ are strongly mixed. Now $(1 \leftrightarrow 3; m)$ is MD allowed; both $(2 \leftrightarrow 3; m)$ and $(2 \leftrightarrow 1; m)$ are ED allowed.

If ϵ is increased from 0, the Stark effect will mix[14] $\Psi(0,0,m,2)$ and $\Psi(0,0,m,1)$. $(1 \leftrightarrow 3; m)$, $(2 \leftrightarrow 1; m)$, and $(2 \leftrightarrow 3; m)$ are all both ED and MD allowed. The level $E(2,m)$ remains "trapped" between the other two, repelling $E(1,m)$ downwards and $E(3,m)$ upwards. The resultant Stark shift in the line $(1 \leftrightarrow 3; m)$ will be quadratic or linear as $|B| \ll$ or $\gg |\nu_{\epsilon=0}(1 \leftrightarrow 3; m)|$, respectively.

In identifying a new spectrum, the number of lines observed must be carefully accounted for. There are six possible values of m ranging from -2 (with $I=0$, $m_I=0$, $m_J=-2$) to $+3$ (with $I=1$, $m_I=1$, $m_J=+2$). For $m=-2$, the ortho state does not occur and, for $m=+3$, the two para states do not occur. Only for $m=-1,0,+1,+2$ can a 3×3 matrix of the form shown in Table I occur. For each m, there are three pairs (λ, λ'); so there appear to be 12 transitions possible. However, $B=0$ for $m=0$. Thus $(2 \leftrightarrow 1; 0)$ and $(2 \leftrightarrow 3; 0)$ are both MD and ED forbidden; $(1 \leftrightarrow 3; 0)$ is only MD allowed and will have zero Stark shift [see Figs. 1(a) and 1(b)]. Under the conditions used for the MD spectrum shown in Fig. 1(b), ten transitions can occur. (For the corresponding ED spectrum, only nine transitions are possible.)

In order to detect a transition in our spectrometer, the net change $\Delta(\lambda \leftrightarrow \lambda'; m)$ in the magnitude of the Z component of the effective magnetic moment must be appreciable.[6] From paper I (see Fig. 1 in particular), $\Delta(1 \leftrightarrow 3; m) = \Delta(1 \leftrightarrow 2; m) = (g_I - g_J)\mu_N$, where g_I is the proton g factor, g_J is the rotational g factor, and μ_N is the nuclear magneton. Since $|g_I - g_J| \sim |g_I|$,[5] the transitions $(1 \leftrightarrow 3; m)$ and $(1 \leftrightarrow 2; m)$ should be detected easily[6] and with equal efficiency. On the other hand, $\Delta(2 \leftrightarrow 3; m) = 0$ and $(2 \leftrightarrow 3; m)$ cannot be detected directly. Thus three transitions which can occur will not be detected, leaving a total of seven MD lines.

Indeed, in the spectrum shown in Fig. 1(b), seven lines were observed.[8] All four $(1 \leftrightarrow 3; m)$ were detected,[8] but the three $(2 \leftrightarrow 3; m)$ were observed rather than the three $(1 \leftrightarrow 2; m)$. Such an interchange of lines has been noted previously in the low-field spectrum[15] of H_2. After the rf field induces $(2 \leftrightarrow 3; m)$, a nonadiabatic Majorana transition follows the $(1 \leftrightarrow 2; m)$ rf transition and yields a total $\Delta \approx 0$.

In paper I, an error[11] was made which does not affect any of the major points in the earlier work but which is critical to the current problem. It was incorrectly argued[16] that the parity operator P associated with ρ inverts the molecule-fixed frame. This would allow an internal interaction to mix $\Psi(0,0,m,2)$ and $\Psi(0,0,m,1)$. B was then attributed to $D_U \mathcal{O}_{\text{dist}}^{(3)}$ where $\mathcal{O}_{\text{dist}}^{(3)}$ is a third-rank distortion tensor and D_U is the associated effective coupling constant.[17] However, P inverts the *space*-fixed frame[11] and so must commute with all internal interactions. This eliminates the possibility of any such contribution from $D_U \mathcal{O}_{\text{dist}}^{(3)}$ to B. This same point permits the Stark effect to mix $\Psi(0,0,m,2)$ and $\Psi(0,0,m,1)$. If we correct the definition of ρ and replace $D_U \mathcal{O}_{\text{dist}}^{(3)}$ with the Stark effect, then the essential features of paper I can be carried over for use here.

The basic beam apparatus used is thoroughly described elsewhere.[18, 19] The Stark plates had a gap of 0.15416 ± 0.00005 cm.[19] The Stark voltage was measured to better than 0.1% with a digital voltmeter. Approximately optimum rf power was used for each methane transition.[7b] For the source temperature employed (77°K), the instrumental full width at half-height for MD transitions was ≈ 1.5 kHz. The line positions were determined typically to 150 Hz. H was calibrated to typically 50 mG with the $(J=0)$ line D_2. A detailed description of the rf coils will be published elsewhere.

The value of μ_ϵ was initially determined by fitting the data taken on $\nu_\epsilon(1 \leftrightarrow 3; 1)$ for seven different values of ϵ from 324.4 to 908.8 V/cm with H held essentially constant at 1982.70 G. The Stark shift was observed to be approximately linear for $\epsilon \gtrsim 650$ V/cm. All $\nu_\epsilon(\lambda \leftrightarrow \lambda'; m)$ depend only on $\alpha - \gamma$, $|A|$, and $|B|$. It was recently determined[20] that, for $(1 \leftrightarrow 3; 1)$, $A = 12.25 \pm 0.15$ kHz. The rms deviation σ between the calculated and observed $\nu_\epsilon(1 \leftrightarrow 3; 1)$ was subjected to a full three-parameter search for the minimum deviation $\sigma_{\min}$, subject only to the constraint that A fall within twice the error limits (i.e., 300 Hz) of the value given above. The error limits on μ_ϵ were then set using the statistical analysis given in Ref. 10. It was found that $|\mu_\epsilon| = (5.38 \pm 0.10) \times 10^{-6}$ D and that $\sigma_{\min} = 85$ Hz with $A = 12.25$ kHz. Using the values of $\alpha - \gamma$, A, and B corresponding to $\sigma_{\min}$, we then evaluated the rms deviation $\tilde{\sigma}$ for twenty mean frequencies measured on other lines for values of ϵ in the range above and values of H from 1982.31 to 1982.81 G. We found $\tilde{\sigma} = 97$ Hz. Since each mean frequency was measured typically to only 150 Hz, the overall fit must be regarded as excellent. The various systematic errors that can occur in the use of a Stark field to shift lines in a magnetic-resonance beam experiment have been examined in detail by MacAdam.[19] The possible errors from such sources and from the neglect of certain small terms in W have been estimated and found to be negligible here.

The unique feature of the molecular-beam technique used here to measure μ_ϵ lies in the fact that the ortho-para transitions simultaneously (i) have frequencies which are very sensitive to ϵ, and (ii) produce changes in the beam trajectory which are easily detected. A conventionally applied[6] magnetic-resonance spectrometer does not meet conditions (i) or (ii), and current conventional[6] electric-resonance spectrometers cannot meet condition (ii).[21]

The present experiment has several important implications for molecular spectroscopy. First, the value of μ_ϵ obtained here is in excellent agreement with the estimate of 4×10^{-6} D by Fox[2] and of 5.8×10^{-6} D by Watson.[3] This is strong evidence that the Watson-Fox mechanism[1-3] is the dominant one generating μ_ϵ and adds considerable confidence to their other predictions.[2,4] Second, the value of μ_ϵ can be used to calculate[2,3] the strengths of the far-infrared and microwave spectra associated with this EDM. Third, the techniques developed here can be used to measure μ_ϵ for other tetrahedral molecules for which the ($\epsilon = 0$) ortho-para spectrum can be observed. Finally, the Stark ortho-para spectrum provides, for a tetrahedral molecule, the most sensitive means yet demonstrated for measuring the distortion constant D_T and the nuclear hyperfine coupling constants,[9] and for putting an upper limit on the inversion splitting.

This work is being continued to refine the present measurement and develop further its beam applications. A full report will be published elsewhere. There is also underway in our laboratory an experiment to observe for CH_4 the far-infrared spectrum associated with this dipole moment.

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[7b] In contrast to Ref. 5, the axis of the coil used to induce the MD methane transitions was parallel to $\vec{H}$.

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[12] We can neglect here the $(I=1)$ levels with $m_I \neq 1$.

[13] The levels $E(\lambda, 0)$ shown in Fig. 1 of Ref. 5 cannot be interpreted in a similar manner because $B=0$ for $m=0$.

[14] It is assumed here that $m \neq 0$.

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[16] This error does not occur in Refs. 9 and 10. See Ref. 14 of Ref. 5.

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