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Publication Date

1974-11-01

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November, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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ELECTRIC FIELD DEFLECTION OF MOLECULES
WITH LARGE AMPLITUDE MOTIONS

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(ABSTRACT)

The Stark effect is derived for several plausible models for molecules such as XeF_6 and IF_7 which are believed to show pseudorotation or other large-amplitude internal motion. These results are related to the behavior of these molecules in electric-field-deflection molecular beam experiments. The absence of focusing of XeF_6 is compatible with an effective dipole moment of distorted XeF_6 of up to 1.2D for free pseudorotation but only 0.2D if pseudorotation is restricted by a potential barrier with C_{4v} orientation 770 cm^{-1} above C_{3v} . Additional examples are treated for XeF_6 as well as models appropriate to the MX_7 molecules.

The deflection of molecular beams in an inhomogeneous electric field is an important method of determining electrical polarity. A special problem arises if the molecule is non-rigid and exhibits large-amplitude motion in one or more coordinates. We are particularly interested in molecules such as XeF_6 and IF_7 , but there are many other examples. Falconer, et al.¹ presented experimental results for XeF_6 and IF_7 and discussed their interpretation.

For molecules with only a one-dimensional inversion, such as NH_3 , the treatment of Falconer, et al. is quite satisfactory. For cases with two or three dimensional distortion, however, a more thorough analysis is required such as that given below.

The earlier treatment implicitly assumed that in cases of two or three dimensional distortion the molecule could invert only by passing over or tunneling through the central potential barrier. In many cases, however, such a molecule can invert by pseudorotation around the central potential barrier. In these cases of pseudorotation, the pattern of internal energy levels is very different from that of a double-minimum vibration in one dimension, and the analysis of deflection properties must be made in terms of the quantum states for pseudorotation.

Method of Electric Field Deflection

The experimental method and the general method of analysis of results are presented by Falconer, et al.¹ For our purposes

it is sufficient to consider the effect of an electric field on the energy levels, i.e., the Stark effect. The molecules of interest here show no first order effect, and the energy of a given state in field E can be written

$$W = W^{(0)} + W^{(2)} E^2 \quad (1)$$

where $W^{(0)}$ is the unperturbed energy of the molecule in a particular quantum state and $W^{(2)}$ is the second order perturbation of that state.

In the electric deflection experiments, molecules will focus on the detector only if they have a sufficiently positive Stark effect, i.e., if $W^{(2)}$ is positive and sufficiently large. The minimum required magnitude of $W^{(2)}$ is determined by comparison with NH_3 which was used in calibration. Falconer, et al., report that molecules should show focusing provided

$$(\mu^2/\Delta) > 0.01 D^2/(\text{cm}^{-1}) \quad (2)$$

where μ is the effective dipole moment in the distorted state and Δ is the separation of the inversion doublet.

MX_3 Molecules with a Double Minimum Vibration

It is useful to start the analysis with molecules of the type MX_3 , such as NH_3 , which undergo a double minimum vibration that inverts their pyramidal structure. The wave function for inversion may be written

$$\psi_{\text{inv.}} = |n, p\rangle \quad (3)$$

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where n denotes the number of quanta of vibration (ignoring inversion) and $p = +$ or $-$ indicates the parity to inversion. Let the inversion coordinate be S_2 and the angle between the electric field and the symmetry axis be β . Then the energy of the dipole in the field is

$$\epsilon = -E c S_2 \cos \beta \quad (4)$$

where c is a constant related to the electrical polarity of the molecule.

The rotational wave function is

$$\psi_{\text{rot}} = |JKM\rangle \quad (5)$$

where J is the total angular momentum quantum number, K is the component of J along the molecular symmetry axis, and M is the component of J along a space fixed axis, in this case the field direction.

To second order, the interaction term $W^{(2)}$ for the state J, K, M, n, p is

$$W^{(2)} = \sum_{J', K', \dots} \frac{\langle JKMnp | cS_2 \cos \beta | J'K'M'n'p' \rangle \langle J'K'M'n'p' | cS_2 \cos \beta | JKMnp \rangle}{(E_{JKM} - E_{J'K'M'}) + (E_{np} - E_{n'p'})} \quad (6)$$

where the sum covers all sets of quantum numbers except J, K, M, n, p . Also E_{JKM} is the energy of the $|JKM\rangle$ rotational state and E_{np} is the energy of the $|np\rangle$ state. The conditions for non-zero matrix elements are

$$\langle np | S_2 | n'p' \rangle \neq 0, \quad p' \neq p \quad (7a)$$

$$\langle JKM | \cos\beta | J'K'M' \rangle \neq 0, \quad J'=J \text{ or } J\pm 1, \quad K'=K, \quad M'=M. \quad (7b)$$

For experiments at or below room temperature, we can ignore the contribution of higher vibrational levels ($n>0$) because of the denominator of equation (6). $W^{(2)}$ now simplifies to

$$W^{(2)} = c^2 |\langle 0- | S_2 | 0+ \rangle|^2 \sum_{J'} \frac{\langle JKM | \cos\beta | J'KM \rangle \langle J'KM | \cos\beta | JKM \rangle}{(E_J - E_{J'}) + (E_{0-} - E_{0+})} \quad (8)$$

where we have chosen $|0-\rangle$ as the reference vibrational state. We can identify the term, $c^2 |\langle 0- | S_2 | 0+ \rangle|^2$, as the effective dipole moment squared, μ_{eff}^2 , where upon Equation (8) becomes

$$W^{(2)} = \mu_{\text{eff}}^2 \sum_{J'} \frac{\langle JKM | \cos\beta | J'KM \rangle \langle J'KM | \cos\beta | JKM \rangle}{(E_J - E_{J'}) + (E_{0-} - E_{0+})}. \quad (9)$$

There are two different limiting situations to this expression for the Stark effect, $W^{(2)}$. These are

$$E_{0-} - E_{0+} \gg |E_J - E_{J'}| \quad (10)$$

$$|E_J - E_{J'}| \gg E_{0-} - E_{0+}. \quad (11)$$

In the MH_3 series (NH_3 , PH_3 , AsH_3 , SbH_3) the rotational constant, B , is on the order of $B \sim 10 \text{ cm}^{-1}$, and the ground state inversion splitting ($E_{0-} - E_{0+}$) has a maximum value of $.7 \text{ cm}^{-1}$ for NH_3 . Thus for the MH_3 molecules the second limiting case (11) is seen to apply. We will see later that

for the MX_7 molecules and XeF_6 the first limit (10) applies because the rotational constants are much smaller due to larger moments of inertia, and the pseudorotational spacings are larger than the ground state MH_3 inversion doublets. We consider both limits for the MX_3 system.

If we assume the first limit (10) to apply, then Eq. (9) simplifies approximately to

$$W^{(2)} = \frac{\mu_{\text{eff}}^2}{E_{0-} - E_{0+}} \sum_{J'} \langle \text{JKM} | \cos \beta | \text{J'KM} \rangle \langle \text{J'KM} | \cos \beta | \text{JKM} \rangle. \quad (12)$$

If we sum over a complete $| \text{J'K'M'} \rangle$ basis, and use the identity

$$\sum_{\text{all states}} | \text{J'K'M'} \rangle \langle \text{J'K'M'} | = 1 \quad (13)$$

then Eq. (12) becomes

$$W^{(2)} = \mu_{\text{eff}}^2 \langle \text{JKM} | \cos^2 \beta | \text{JKM} \rangle / (E_{0-} - E_{0+}) \quad (14)$$

If the second limiting situation, Eq. (11), is applicable, Eq. (9) becomes

$$\begin{aligned} W^{(2)} &= \mu_{\text{eff}}^2 | \langle \text{JKM} | \cos \beta | \text{JKM} \rangle |^2 / (E_{0-} - E_{0+}) \\ &= \mu_{\text{eff}}^2 K^2 M^2 / J^2 (J+1)^2 (E_{0-} - E_{0+}) \end{aligned} \quad (15)$$

where the $J = J'$ rotational state is the major contribution in this limit, and the known values of the matrix elements are substituted in the second line.

Both limiting expressions, Equations (14) and (15), have been written in terms of the inversion state which can focus,

$|0-\rangle$. If the molecule were in the lower ground state inversion doublet, $|0+\rangle$, the denominator would be negative. The resulting negative $W^{(2)}$ indicates a state which cannot focus.

Equation (15) is well-known. The factor $K^2 M^2 / J^2 (J+1)^2$ ranges in value from zero to nearly unity. It is important to note that the proportion of states with substantial values of this factor does not diminish as J increases.

The matrix elements $\langle JKM | \cos^2 \beta | JKM \rangle$ in Eq. (14) also range in value from zero to unity with the proportion having substantial values remaining about the same as J increases.

Since Eq. (15) applies to the case of NH_3 used by Falconer, et al., in calibration, we may now interpret their value of $0.01 \text{ D}^2/\text{cm}^{-1}$ as the minimum value of $(\mu_{\text{eff}}^2 / (E_{0-} - E_{0+}))$ to yield focusing provided the distribution of values of $W^{(2)}$ is similar to that of Eq. (15), and the distribution of translational velocities is also similar to that for NH_3 .

MX_7 Molecules

The molecules IF_7^2 and ReF_7^3 are thought to be distorted somewhat from the pentagonal bipyramial structure. We shall discuss the structure of these molecules in greater detail elsewhere. We assume that the distortion comprises a puckering of the equatorial ring of five atoms which is coupled to a bending motion of the axial atoms off of the principal axis. Such a motion can generate a dipole moment perpendicular to the principal axis. This coupling is complicated, however, in

that the phase angle of axial-atom motion completes two revolutions for one revolution of the equatorial puckering. The resulting problem in molecular dynamics is very complex, and we pretend only to offer an approximate solution even for the case of free pseudorotation. More rigorous analysis would be desirable.

The wave functions, in terms of the angle ϕ defined for pseudorotation of equatorial atoms, are

$$\begin{aligned}\psi_{\text{pse}} &= R_n(\rho) e^{i2m\phi} = |n, m\rangle \\ n &= 0, 1, 2, \dots \\ m &= 0, \pm 1, \pm 2, \dots\end{aligned}\tag{16}$$

where the factor of two in the exponent for the angular function arises from the boundary condition, $\psi(0) = \psi(\pi)$, for a pseudorotation.⁴ The energy of the pseudorotational mode is

$$E_{nm} = (n + \frac{1}{2}) h\nu_\rho + m^2 B_\phi\tag{17}$$

where ν_ρ is the frequency of the radial motion or amplitude of distortion (ρ) and B_ϕ is the effective rotational constant associated with the pseudorotation.

When the over-all rotation is included one has the usual expression for the energy levels of a symmetric top together with various terms related to the coupling of internal and external motions. Among the latter we estimate that the most important is the coupling which arises from the angular momentum of pseudorotation arising primarily from the motion of the axial atoms. If this coupling (or coriolis) constant is ζ , the full

energy expression becomes

$$\epsilon = (n + \frac{1}{2}) h\nu_{\rho} + m^2 B_{\phi} + BJ(J+1) + K^2(A-B) + \zeta AKm. \quad (18)$$

Here A and B are the usual constants for over-all rotation; each is near 0.6 cm^{-1} for IF_7 or ReF_4 .⁵ The pseudorotational constant is approximately $B_{\phi} = 5 \text{ cm}^{-1}$ for either molecule.^{2,3} The coupling constant ζ is harder to estimate, but its value appears to be approximately 0.5.

The dipole moment will have the form

$$\mu = \mu_{\text{eff}}[\cos 4\phi \underline{i} + \sin 4\phi \underline{j}] \quad (19)$$

where the magnitude of μ_{eff} and the 4ϕ dependence on the pseudorotational phase angle are both determined by the coupling between the pseudorotation and the bending of the axial atoms, and $\underline{i}, \underline{j}$ are molecule fixed axes in the equatorial plane. The dipole field interaction is

$$\epsilon = E \mu_{\text{eff}}[\cos 4\phi \sin \beta \cos \gamma - \sin 4\phi \sin \beta \sin \gamma] \quad (20)$$

The Euler angles⁶ relating the molecule fixed axes to the space fixed z axis of the field are α, β, γ but α does not affect the energy.

Because of the 4ϕ dependence of ϵ , a given state with pseudorotational quantum number m is connected to states with $m \pm 2$. If we omit states with $m = \pm 1$, the treatment is straightforward with the limiting situation of Eq. (10) since $B_{\phi} \gg B$. The second order Stark effect will have the form

$$W^{(2)} = \mu_{\text{eff}}^2 \langle JKM | \sin^2 \beta | JKM \rangle / 8B_{\phi} (m^2 - 1) \quad (21)$$

$$m \neq \pm 1.$$

This demonstrates that the pseudorotational ground state, $m = 0$, will not focus ($W^{(2)}$ is negative) while all the states with $|m| \geq 2$ are focusable ($W^{(2)}$ is positive).

In the special case of $m = \pm 1$, however, the electric field operator connects one of these states with the other. Were it not for the coupling constant with over-all rotation, this would yield a first order Stark effect. In fact it yields for the dominant term

$$W^{(2)} = \frac{\mu_{\text{eff}}^2}{2A\zeta K} |\langle J, K, M, 1 | \sin \beta (\cos 4\phi \cos \gamma - \sin 4\phi \sin \gamma) | J, K, M-1, -1 \rangle|^2 \quad (22)$$

provided $|M-1| \leq J$ and $K \neq 0$. The matrix element involving $\sin \beta$ is zero for states with $K = 0$. Thus there will be a limited number of states satisfying all these conditions and with (ζK) positive which will focus more strongly than those with $|m| \geq 2$.

The beam deflection experiments of Kaiser, et al.,⁷ for IF_7 and ReF_7 were made at temperatures from 150 to 300°K. In this range about 20% of the molecules are in states with $m = \pm 1$. The maximum value of the factor involving angular functions in Eq. (22) is one quarter as compared to unity for the corresponding factor in Eq. (15) while the distributions of values below the maxima may be similar. The mean value of $|K|$ at 150°K is about 7 while at 300°K it is about 10.

It is impossible to make a precise comparison of IF_7 and ReF_7 with the calibrating case of NH_3 because of the differences in translational velocity and in distributions of $W^{(2)}$. One possibility is a comparison of the $W^{(2)}$ value for just the most focusable MX_7 molecules, i.e., some of those with $|m| = 1$, $|K| = 1$, with that for the NH_3 molecules used in calibration. On this basis one obtains a threshold value of $\mu_{\text{eff}} = 0.15 \text{ D}$ for detectable focusing. Also there should be no significant temperature effect since it is only the population of these most-focusable molecules that changes and not their $W^{(2)}$ values.

In view of the strong temperature dependence observed⁷ for ReF_7 and the extremely small proportion of MX_7 molecules considered in the above comparison, we offer, as a more realistic alternative, a comparison of the $W^{(2)}$ value for $|m| = 1$ and the median value of $|K|$ at the temperature where focusing is just detected (150°K for IF_7 and 300°K for ReF_7). The resulting μ_{eff} values are 0.4D for IF_7 and 0.5D for ReF_7 .

It is interesting to substitute these values of μ_{eff} into Eq. (21) with $m = \pm 2$ to determine whether those states contribute to the focusing. The resulting maximum for $W^{(2)}$ is 0.002 for ReF_7 ; hence the states with $|m| \geq 2$ do not contribute appreciably to the focusing portion of the beam.

While our more realistic comparison correctly predicts a decrease in focusability with rise in temperature for these molecules, it does not predict the very sharp change observed⁷ for ReF_7 between 200 and 300°K . It seems impractical

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to probe this matter further, however, without more information about the exact trajectories and other details of the beam experiments as well as a more rigorous theoretical treatment for these molecules.

XeF₆ Assuming Free Pseudorotation

Most evidence indicates that the molecule XeF₆ is distorted from a simple octahedral structure, but the exact nature of the distortion remains to be determined. In another paper we shall discuss this problem in relation to various experimental data. The failure of XeF₆ to focus in beam deflection experiments¹ has been cited, however, as an argument against a distorted structure. We shall consider two models for XeF₆ and derive their second order Stark coefficients. First we assume that the distortion from octahedral symmetry can rotate freely in two dimensions.

The plausible distortion of XeF₆ was discussed very well by Bartell and Gavin⁸ who showed that it could be described by a vector $\underline{r}$ whose magnitude gave the amount of distortion and whose direction gave the direction of distortion. This may be modeled by the equations for a rotating-vibrating diatomic molecule. The wave functions for this free pseudorotation model are

$$\psi_{\text{pse}} = R_n(r) P_l^{|m|}(\cos\theta) e^{im\phi} = |n\ell m\rangle$$

$$m = 0, \pm 1, \pm 2 \dots$$

$$\ell = |m|, |m| + 1, \dots, 0$$

$$n = 0, 1, 2, \dots$$

(23)

The energy levels are

$$E_{n\ell} = (n + \frac{1}{2}) h\nu_r + B_{\theta,\phi} \ell(\ell+1) \quad (24)$$

where ν_r is the frequency of the radial motion, r , and $B_{\theta,\phi}$ is the effective pseudorotational constant.

In terms of this coordinate system we can write the dipole moment as

$$\mu = cr(\sin\theta\cos\phi\hat{i} + \sin\theta\sin\phi\hat{j} + \cos\theta\hat{k}) \quad (25)$$

where $\hat{i}$, $\hat{j}$, $\hat{k}$ are unit vectors along the molecule fixed axes. The dipole-field interaction has the form

$$\epsilon = cEr(\sin\theta\cos\phi\sin\beta\cos\gamma - \sin\theta\sin\phi\sin\beta\sin\gamma - \cos\theta\cos\beta) \quad (26)$$

where β , γ are Euler angles as before. For XeF_6 , we estimate $B_{\theta\phi} = 3.4 \text{ cm}^{-1}$ and the overall rotational constant to be similar to the MX_7 case, which means XeF_6 can also be handled in the limit $B_{\theta\phi} \gg B$, Eq. (10). The second order Stark coefficient for this model of XeF_6 is

$$\begin{aligned} W^{(2)} = & (\mu_{\text{eff}}^2/B_{\theta\phi}) \sum_{\ell'=\ell\pm 1} \{ \langle \text{JKM} | \sin^2\beta | \text{JKM} \rangle [\langle \ell, m | \sin\theta\cos\phi | \ell', m+1 \rangle^2 \\ & + \langle \ell, m | \sin\theta\cos\phi | \ell', m-1 \rangle^2] + \langle \text{JKM} | \cos^2\beta | \text{JKM} \rangle \times \\ & \langle \ell, m | \cos\theta | \ell', m \rangle^2 \} / [\ell(\ell+1) - \ell'(\ell'+1)]. \end{aligned} \quad (27)$$

The increased complication of this expression (compared to those for MX_7 and MX_3) arises because the dipole moment is not restricted to any particular direction or plane with respect

to the molecule fixed frame. Consequently both a $\sin^2\beta$, and a $\cos^2\beta$ term are present in Eq. (27).

All of the terms are present in Eq. (27) provided $\ell \geq 2$ and $|m| \leq \ell-2$; otherwise some of the terms are missing for $\ell' = \ell-1$ but not for $\ell' = \ell + 1$. The effect of these missing terms is to decrease $W^{(2)}$ and make it negative in many cases. Since we are interested in the largest positive values of $W^{(2)}$, we consider cases where all terms are present, and, by substitution of known values for the matrix elements in θ and ϕ , obtain

$$W^{(2)} = (\mu_{\text{eff}}^2/B_{\theta\phi}) [2(2\ell-1)(2\ell+3)]^{-1} \times \\ \{ \langle \text{JKM} | \sin^2\beta | \text{JKM} \rangle [(2\ell+5)/2(2\ell+1) + 3m^2/2\ell(\ell+1)] \\ + \langle \text{JKM} | \cos^2\beta | \text{JKM} \rangle [1 - 3m^2/\ell(\ell+1)] \}. \quad (28)$$

The terms within the braces involve the matrix elements for over-all rotation, which range in value up to one, multiplied by factors of the order unity; hence, this entire quantity will be of order unity. The remaining expression will serve as an approximation to $W^{(2)}$

$$W^{(2)} = (\mu_{\text{eff}}^2/B_{\theta\phi}) [2(2\ell-1)(2\ell+3)]^{-1} \quad (29)$$

The most focusable molecules for most, if not all, over-all rotational states will be those with $\ell=2$, $m=0$. If we apply the limiting condition based upon NH_3 to these molecules, the result is that μ_{eff} could be as large as 1.2D and still not show focusing.

XeF₆ Assuming Restricted Rotation

Earlier studies⁸ of XeF₆ and our own work indicate that the lowest energy conformation of XeF₆ has symmetry C_{3v} and that a plausible potential function is

$$V(\theta, \phi) = -c[\sin^2\theta + \sin^4\theta(\frac{1}{4}\sin^2 2\phi - 1)] \quad (30)$$

This function has octahedral symmetry and yields eight potential minima of symmetry C_{3v} with six potential maxima of height c/3 at points of symmetry C_{4v} and twelve saddle points of height c/12 at points of symmetry C_{2v}. A three-dimensional potential including dependence on the amplitude of distortion r would be slightly more realistic, but the difference would not be significant for the present purpose.

This quantum mechanical problem was solved in 1936 by Devonshire⁹ whose numerical results are quite adequate for low barriers. With present computers it is straightforward to extend reasonably accurate energy level calculations to higher barriers and this was done with a Y_{ℓm}(θ, φ) basis including all functions through ℓ = 15, |m| = 15. The values of the potential energy matrix elements were determined using the usual 3-j symbols. The results are given in Table 1 as energy differences (in cm⁻¹) above the lowest state. Also given are the barrier heights for C_{2v} and C_{4v} as well as the symmetries of the states which also indicate their degeneracies. The states for zero barrier are given on the left and the correlation of these states can be noted from

Table 1

Energy levels (cm^{-1}) for restricted pseudorotation in XeF_6 .

The symmetry symbols also indicate the degeneracies.

$V(C_{2v}) - V(C_{3v})$	0	48.06	120.14	192.22	
$V(C_{4v}) - V(C_{3v})$	0	192.22	480.55	768.89	
<hr/>					
	Sym. Free rot.	Restricted rotation			Sym.
A_{1g}	0	0	0	0	A_{1g}
T_{1u}	6.79	4.33	2.02	0.92	T_{1u}
$T_{2g} + E_g$	20.37	9.83	4.27	1.90	T_{2g}
$A_{2u} + T_{1u} + T_{2u}$	40.75	17.79	6.81	2.90	A_{2u}
		46.06	76.46	107.51	E_g
		48.59	76.91	107.68	T_{2u}
$A_{1g} + E_g + T_{1g} + T_{2g}$	67.92	63.46	85.99	114.23	T_{2g}
		69.81	95.54	121.61	T_{1u}
		89.77	113.07	132.99	T_{1g}
$E_u + 2T_{1u} + T_{2u}$	101.88	100.29	114.90	133.45	E_u
		107.13	137.74	175.26	A_{1g}
		105.67	170.24	217.43	E_g
		112.44	155.19	221.66	T_{1u}

the symmetry symbols. These calculations assume $r = 0.870 \text{ \AA}$ and a reduced mass 6.56 amu which yield $B_{\theta,\phi} = 3.396 \text{ cm}^{-1}$.

For the lowest four of these states for restricted pseudorotation the Stark coefficients are

$$W^{(2)}(A_{1g}) = \mu_{\text{eff}}^2 \langle A_{1g} | \sin\theta \cos\phi | T_{1ux} \rangle^2 [E(A_{1g}) - E(T_{1u})]^{-1} \quad (31A)$$

$$\begin{aligned} W^{(2)}(T_{1u}) = & \mu_{\text{eff}}^2 \{ \langle JKM | \sin^2\beta \cos^2\gamma | JKM \rangle \\ & \langle T_{1ux} | \sin\theta \cos\phi | A_{1g} \rangle^2 [E(T_{1u}) - E(A_{1g})]^{-1} \\ & + [\langle JKM | \sin^2\beta \sin^2\gamma | JKM \rangle \langle T_{1ux} | \sin\theta \sin\phi | T_{2gxy} \rangle^2 \\ & + \langle JKM | \cos^2\beta | JKM \rangle \langle T_{1ux} | \cos\theta | T_{2gxz} \rangle^2] \\ & \times [E(T_{1u}) - E(T_{2g})]^{-1} \} \end{aligned} \quad (31B)$$

$$\begin{aligned} W^{(2)}(T_{2g}) = & \mu_{\text{eff}}^2 \{ [\langle JKM | \sin^2\beta \cos^2\gamma | JKM \rangle \\ & \times \langle T_{2gxz} | \sin\theta \cos\phi | T_{1uz} \rangle^2 + \langle JKM | \cos^2\beta | JKM \rangle \\ & \times \langle T_{2gxz} | \cos\theta | T_{1ux} \rangle^2] [E(T_{2g}) - E(T_{1u})]^{-1} \\ & + \langle JKM | \sin^2\beta \sin^2\gamma | JKM \rangle \langle T_{2gxz} | \sin\theta \sin\phi | A_{2u} \rangle^2 \\ & \times [E(T_{2g}) - E(A_{2u})]^{-1} \} \end{aligned} \quad (31C)$$

$$W^{(2)}(A_{2u}) = \mu_{\text{eff}}^2 \langle A_{2u} | \cos\theta | T_{2gxy} \rangle^2 [E(A_{2u}) - E(T_{2g})]^{-1}. \quad (31D)$$

Only terms involving the energy levels through the lowest A_{2u} state are included in the above expressions. For high barriers, this is a good approximation since the additional terms would involve much larger energy differences in their denominators. For low barriers, however, the additional terms would not be negligible and would decrease $W^{(2)}$ especially for the A_{2u} state.

From the signs of the energy differences it is clear that $W^{(2)}(A_{1g})$ is negative; also, since two of the three terms are negative for $W^{(2)}(T_{1u})$, molecules in this state will not focus strongly if at all. With two of three terms positive, $W^{(2)}(T_{2g})$ will be positive for most over-all rotational states. For high barriers, the largest positive value is found for $W^{(2)}(A_{2u})$.

The square of the angular matrix element for the lowest A_{2u} state, Eq. (31D), ranges from 1/3 for very high barriers to 1/7 for free rotation. If we use this largest $W^{(2)}$ value in the calibration relationship discussed above, the upper limit for the effective dipole moment of XeF_6 ranges from 0.2D for the highest barrier in Table 1 to 0.3D for the intermediate barrier and 0.6D for the low barrier. Our earlier estimate for zero barrier was 1.2D.

Discussion

It is clear from the example of XeF_6 that the electric field deflection method is enormously less sensitive to electrical polarity for a pseudorotating molecule as compared

to one with strongly localized distortion even if inversion is still allowed.

We have little independent evidence for the expected magnitude of the effective dipole moment μ_{eff} for a distorted XeF_6 . The unshared electron pair moves in one direction and the fluorines, also negative, move in the opposite direction. Thus the moment expected from one may largely cancel the other. Thus there is certainly no contradiction between the beam deflection results and the distorted geometry for XeF_6 given by electron diffraction and other measurements. The results of the previous sections do give a limit for μ_{eff} as a function of the potential restricting pseudorotation, but it is a high-enough limit to accommodate most reasonable models.

The interesting situation in MF_7 molecules arising from the coupling of rotation of distortion of axial atoms with the pseudorotation of the equatorial atoms was considered only approximately and deserves more rigorous treatment. Again we see no major contradiction between the beam deflection results and other data, but the temperature coefficient of the focused beam intensity seems surprisingly large.

Acknowledgements

We thank Miss Janice Kim for making the new calculations reported in Table 1. This research was sponsored by the U. S. Atomic Energy Commission. It was also aided by a Procter and Gamble fellowship held by L.S.B.

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