Angular Dependence of Raman Scattering Intensity

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In order for the ir transition to be active, the product of matrix elements, $\langle g \mid \mu_\lambda \mid e \rangle \langle e \mid (\delta H/\delta Q) \mid g \rangle$ must be nonvanishing. From group theory we know that $\langle g \mid \mu_\lambda \mid e \rangle$ is nonvanishing if Γ_e, the irreducible representation of any excited electronic intermediate state is contained in the direct product of irreducible representations $\Gamma_\lambda \times \Gamma_g$; Γ_λ is the irreducible representation of μ_λ which must transform like one of the principal axes x, y, z where λ is the direction of the polarization of the incident photon beam and Γ_g is the irreducible representation of the ground state of the molecule. Similarly $\Gamma_{H'}$ must be contained in $\Gamma_e \times \Gamma_g$ so that $\Gamma_{H'} = \Gamma_e \times \Gamma_g = \Gamma_\lambda \times \Gamma_g \times \Gamma_g = \Gamma_\lambda$. Consequently, $\Gamma_{H'}$ which is the same as Γ_{Q_a}, the irreducible representation of normal coordinate, must transform like Γ_λ which must be one of the three irreducible representations, Γ_x, Γ_y, or Γ_z.

For Raman scattering we have by similar arguments:

$$\Gamma_{Q_a} = \Gamma_{\lambda_1} \times \Gamma_{\lambda_2}$$

which form the basis of a nine-component tensor ($\Gamma_{xx}\Gamma_{xy}\cdots\Gamma_{zz}$) of which six are independent if the tensor is symmetric.

For hyper-Raman the same arguments apply and

$$\Gamma_Q = \Gamma_{\lambda_1} \times \Gamma_{\lambda_2} \times \Gamma_{\lambda_3}$$

form the bases of a 27-component tensor of which 10 are independent if the tensor is symmetric. Decius et al.[10] have given the selection rules for both Raman and hyper-Raman scattering for various point groups.

ACKNOWLEDGMENT

[10] S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. 43, 4083 (1965).

Angular Dependence of Raman Scattering Intensity

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The angular distribution of the intensity of Raman scattered light from a sample of randomly oriented molecules is calculated for all Raman active vibrational transitions for the common molecular point groups. Experiments of Damen, Leite, and Porto are presented.

I. INTRODUCTION

Recently Damen, Leite, and Porto[1] have suggested that the angular dependence of Raman scattering from a molecular liquid or gas might be useful in the identification of the point group symmetries of molecular vibrational transitions. However, the theory with which they compared their experimental results is an old one due to Placzek[2] which does not discuss molecular symmetries as such but rather divides all types of scattering into three general types which are called "trace scattering," "quadrupole scattering," and "magnetic dipole scattering." As we shall show Placzek's formulas are not generally applicable to all point group symmetries. We give here for the first time the exact expressions for the angular dependence of the intensity of Raman scattering for randomly oriented molecules for all molecular point groups which are isomorphic with one of the crystallographic point groups. The usefulness of

these formulas will be illustrated for the A_{1g} vibrations of benzene which has D_{6h} symmetry.

II. THEORY

The Raman intensity or scattering efficiency is given by[3]

$$I = A\left[\sum_{\lambda,\nu} {}^1e_\lambda R_a^{\lambda\nu2} {}^2e_\nu\right]^2 \qquad \lambda,\nu = X, Y, Z, \qquad (1)$$

where A is a constant, ${}^1e_\lambda$ and ${}^2e_\nu$ are the polarization components of the incident and the scattered photon, respectively, and $R_a^{\lambda\nu}$ is the $\lambda\nu$th component of the Raman tensor associated with the ath normal mode. The magnitude of the element $R_a^{\lambda\nu}$ can be calculated from the equations given in the previous paper.[4] Equation (1) is the basic expression for calculating the angular dependence of the Raman transition probability, and hence the intensity of the scattered radiation, for an oriented molecule or crystal. If, however, we consider a molecular system in which the molecules are randomly oriented, the indices of the Raman tensor will refer to the molecule coordinate axes and the

[1] T. C. Damen, R. C. C. Leite, and S. P. S. Porto, Phys. Rev. Letters, 14, 9 (1965).
[2] G. Placzek, *Handbuch der Radiology* (Akademic Verlagsgesellschaft, Leipzig, Germany, 1934), Vol. 6, Pt. 2, pp. 205–274.

[3] R. Loudon, Advan. Phys. 13, 423 (1964).
[4] W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, J. Chem. Phys. 52, 1576 (1970), preceding paper.

polarization indices will refer to the fixed laboratory axes. In order to generalize Eq. (1) to hold for this situation we must transform $R_a{}^{\lambda\nu}$ as

$$R_a{}^{\lambda\nu} = \sum_{ij} \Phi_{\lambda i}\Phi_{\nu j}R_a{}^{ij} \qquad i,j = x,y,z, \qquad (2)$$

where the summation is taken over the molecular axes $(i,j=x,y,z)$ and $\Phi_{\lambda i}$ and $\Phi_{\nu j}$ are direction cosines between the fixed laboratory axes and the molecular axes.

The scattering efficiency now becomes

$$I = \langle A[\sum_{\lambda,\nu}\sum_{ij} {}^1e_\lambda\Phi_{\lambda i}R_a{}^{ij}\Phi_{\nu j}{}^2e_\nu]^2\rangle_{Av}, \qquad (3)$$

where the average is taken over all molecular orientations relative to a fixed laboratory axis described as follows. First, assume the polarization direction of the incident light to be vertical in the laboratory Z direction, with propagation in the Y direction. The angle of scattering θ is measured from the Y axis and the plane of scattering will be the XY plane. Thus the component of the scattered radiation which is vertically polarized

(perpendciular to the plane of scattering) can be referred to as the "polarized" component, and the component which is horizontally polarized (in the component which is horizontally polarized (in the plane of scattering) as the "depolarized" component. By taking the ratio of the intensity of the depolarized to polarized component of the scattered light, the depolarization ratio for any scattering angle may be formed.

Following the geometry specified above we can write the expression for the intensity of the "polarized" component of the scattered light, I_p, with ${}^1e_\lambda = {}^1e_Z = 1$ and ${}^2e_\nu = {}^2e_Z = 1$, to obtain

$$I_p = I_v{}^v = \langle A[\sum_{ij}\Phi_{Zi}\Phi_{Zj}R_a{}^{ij}]^2\rangle_{Av}. \qquad (4)$$

In Eq. (4) the superscript v refers to vertical polarization of the incident light and the subscript v refers to the vertical polarization of the scattered light. Carrying out the square and noting that the components of the Raman tensor $R_a{}^{ij}$ are constants under the averaging process we obtain

$$I_v{}^v = A\{\sum_i \langle\Phi_{Zi}{}^4\rangle_{Av}(R_a{}^{ii})^2 + \sum_{i\neq j}\langle\Phi_{Zi}{}^2\Phi_{Zj}{}^2\rangle_{Av}[(R_a{}^{ii})(R_a{}^{jj}) + 2(R_a{}^{ij})^2] + 4\sum_{i\neq j}\langle\Phi_{Zi}{}^3\Phi_{Zj}\rangle_{Av}(R_a{}^{ii})(R_a{}^{ij})$$
$$+ \sum_{i\neq j}\langle\Phi_{Zi}{}^2\Phi_{Zj}\Phi_{Zk}\rangle_{Av}[4(R_a{}^{ij})(R_a{}^{ik}) + 2(R_a{}^{ii})(R_a{}^{jk})]\}. \qquad (5)$$

In obtaining Eq. (5) we have assumed that the tensor components $R_a{}^{ij}$ are symmetric, i.e., $R_a{}^{ij} = R_a{}^{ji}$. To evaluate the direction cosine averages we use the fact that[5]

$$\langle\Phi_{\lambda i}{}^4\rangle_{Av} = \tfrac{1}{5} \qquad \langle\Phi_{\lambda i}{}^2\Phi_{\lambda j}{}^2\rangle_{Av} = \tfrac{1}{15} \qquad \langle\Phi_{\lambda i}{}^2\Phi_{\nu i}{}^2\rangle_{Av} = \tfrac{1}{15} \qquad \langle\Phi_{\lambda i}{}^2\Phi_{\nu j}{}^2\rangle_{Av} = \tfrac{2}{15} \qquad \langle\Phi_{\lambda i}\Phi_{\lambda j}\Phi_{\nu i}\Phi_{\nu j}\rangle_{Av} = -\tfrac{1}{30} \qquad (6)$$

are the only nonvanishing averages of direction cosines to the total power of four. Thus,

$$I_v{}^v = A[\tfrac{1}{5}\sum_i (R_a{}^{ii})^2 + \tfrac{1}{15}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{2}{15}\sum_{i\neq j}(R_a{}^{ij})^2] \qquad (7)$$

is the final averaged expression for the transition probability for any angle of scattering of the polarized component.

We now proceed to derive a similar expression for the depolarized component or in-plane scattering I_d,

$$I_d = I_h{}^v = \langle A(\sum_{ij}\Phi_{Zi}\Phi_{Xj}R_a{}^{ij}\cos\theta + \sum_{ij}\Phi_{Zi}\Phi_{Yj}R_a{}^{ij}\sin\theta)^2\rangle_{Av}. \qquad (8)$$

Completing the square and evaluating the direction cosine averages we obtain

$$I_h{}^v = A[\tfrac{1}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{10}\sum_{i\neq j}(R_a{}^{ij})^2] \qquad (9)$$

since the direction cosines of the cross terms vanish and the coefficients of the $\cos^2\theta$ term and $\sin^2\theta$ term are identical Hence, the depolarized component is also independent of scattering angle giving

$$\rho = I_h{}^v/I_v{}^v = [\tfrac{1}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{10}\sum_{i\neq j}(R_a{}^{ij})^2 / \tfrac{1}{5}\sum_i (R_a{}^{ii})^2 + \tfrac{1}{15}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{2}{15}\sum_{i\neq j}(R_a{}^{ij})^2]$$
$$(10)$$

which is the depolarization ratio for any angle of scattering in terms of the components of the Raman tensor, and is clearly independent of the scattering angle. It can be seen that when ath normal vibration is totally nonsymmetric, i.e., the components of its Raman tensor are all nondiagonal, the depolarization ratio reduces to $\rho = \tfrac{3}{4}$ which agrees with the result obtained from semiclassical theory.

Now we consider the case where the incident light is polarized horizontally, i.e., in the XY plane. The intensity of the in-plane (horizontal) polarization will be denoted by $I_h{}^h$ and the out-of-plane (vertical) polarization by $I_v{}^h$.

[5] S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. **43**, 3803 (1965).

Again performing the averages we obtain

$$I_v{}^h = A\left[\tfrac{1}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{10}\sum_{i\neq j}(R_a{}^{ij})^2\right] \qquad (11)$$

and

$$I_h{}^h = \left[\tfrac{1}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{10}\sum_{i\neq j}(R_a{}^{ij})^2\right]\sin^2\theta + \cos^2\theta\left[\tfrac{1}{5}\sum_i (R_a{}^{ii})^2 + \tfrac{1}{15}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj})\right.$$
$$\left. + \tfrac{2}{15}\sum_{i\neq j}(R_a{}^{ij})^2\right]. \qquad (12)$$

We find no angular dependence of Raman intensity if the light is observed with vertical polarization, but there is an important dependence on scattering angle for light observed with horizontal polarization.

If we consider the ratio of the intensity of the scattered light which is polarized horizontally in the XY plane to the intensity of the scattered light which is polarized vertically in the Z direction we can obtain a polarization ratio for this geometry as well; this ratio is a function of the scattering angle θ,

$$\rho_l{}^{(\theta)} = I_h{}^h/I_v{}^h, \qquad (13)$$

$$\rho_l{}^{(\theta)} = \left\{\left[\tfrac{1}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{10}\sum_{i\neq j}(R_a{}^{ij})^2\right]\sin^2\theta + \cos^2\theta\left[\tfrac{1}{5}\sum_i (R_a{}^{ii})^2 + \tfrac{1}{15}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj})\right.\right.$$
$$\left.\left. + \tfrac{2}{15}\sum_{i\neq j}(R_a{}^{ij})^2\right]\right\}/\left[\tfrac{1}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{10}\sum_{i\neq j}(R_a{}^{ij})^2\right]. \qquad (14)$$

If the incident light is unpolarized it may be considered to be a noncoherent mixture of light polarized in the Z direction and in the X direction with no interference in phase. For unpolarized light the ratio of intensity of horizontally to vertically polarized light is given by

$$\rho_n{}^{(\theta)} = (I_h{}^h + I_h{}^v)/(I_v{}^h + I_v{}^v). \qquad (15)$$

Putting Eqs. (7), (9), (11), (12) into Eq. (15) and scattering $\theta = 90°$, we have

$$\rho_n = \left[\tfrac{2}{15}\sum_i (R_a{}^{ii})^2 - \tfrac{1}{15}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{1}{5}\sum_{i\neq j}(R_a{}^{ij})^2\right]/\left[\tfrac{4}{15}\sum_i (R_a{}^{ii})^2 + \tfrac{1}{30}\sum_{i\neq j}(R_a{}^{ii})(R_a{}^{jj}) + \tfrac{7}{30}\sum_{i\neq j}(R_a{}^{ij})^2\right]. \qquad (16)$$

And for a totally nonsymmetric vibration the depolarization ratio reduces $\rho_n = 6/7$ which again agrees with the semiclassical treatment.

III. COMPARISON WITH EXPERIMENT

The angular dependence of the Raman intensity may be used to identify the symmetry of the normal mode involved. For example, the angular dependence of the intensity of the scattered light from various vibrational modes of benzene has been determined experimentally by Damen et al.[1] For the e_{2g} 1585–1606 cm^{-1} doublet they observed that the intensities were independent of angle when the incidence polarization was perpendicular to the plane of scattering and a $(1 + \cos^2\theta/6)$ dependence when the incident polarization was in the plane of scattering. These results were obtained theoretically by Placzek[2] for a quadrupole type scatterer.

The angular dependence may be obtained directly from our results by adding the in-plane and out-of-plane scattering intensities. For incident polarization perpendicular to the scattering plane there is no angular dependence. However, when the incident polarization lies in the scattering plane the total scattering intensity is given by

$$I_T = I_v{}^h + I_h{}^h. \qquad (17)$$

Using the expressions given by Eqs. (11)–(12) and

the Raman scattering matrix for an e_{2g} mode in the D_{6h} point group[3]

$$\begin{pmatrix} d & d & 0 \\ d & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

we obtain $C(1 + \cos^2\theta/6)$ in agreement with both the experimental results and the earlier calculations of Placzek.

However our results are of more general validity than Placzek's since by use of the Raman tensor for any vibrational mode one can obtain the dependence immediately from the use of Eqs. (11), (12), and (17). For convenience we have calculated the angular dependence of the intensity of Raman scattered light for randomly oriented molecules of various point groups, and the results are given in Table I. In this table the quantities a, b, c, etc., are the Raman tensor elements taken from the review article by Loudon.[3] Thus we see how by measurements even on randomly oriented molecules it may be possible to obtain some knowledge of the value of the elements of the Raman scattering tensor.

To illustrate this last point let us consider the A_{1g} vibration (again the D_{6h} point group). The Raman

TABLE I. Angular dependence of Raman scattering intensity for various molecular point groups.

Group					Scattering probabilities	
C_2	C_s	C_{2h}			$I_v{}^h$	$I_h{}^h$
A	A'	A_g			$(1/15)(a^2+b^2+c^2+3d^2-ab-ac-bc)$	$(1/15)(a^2+b^2+c^2+3d^2-ac-ab-bc)(1+\{[2(a^2+b^2+c^2)+d^2+3(ab+bc+ac)][a^2+b^2+c^2+3d^2-ac-ab-bc]^{-1}\}\cos^2\phi)$
B	A''	B_g			$(1/5)(e^2+f^2)$	$(1/5)(e^2+f^2)(1+\cos^2\phi/3)$
D_2	C_{2v}	D_{2h}				
A	A_1	A_g			$(1/15)(a^2+b^2+c^2-ab-ac-bc)$	$(1/15)(a^2+b^2+c^2-ab-ac-bc)(1+\{[2(a^2+b^2+c^2)+3(ab+ac+bc)](a^2+b^2+c^2-ab-ac-bc)^{-1}\}\cos^2\phi)$
B_1	A_2	B_{1g}			$(1/5)d^2$	$(1/5)d^2(1+\cos^2\phi/3)$
B_2	B_1	B_{2g}			$(1/5)e^2$	$(1/5)e^2(1+\cos^2\phi/3)$
B_3	B_2	B_{3g}			$(1/5)f^2$	$(1/5)f^2(1+\cos^2\phi/3)$
C_3	C_{3i}					
A	A_g				$(1/15)(a-b)^2$	$(1/15)(a-b)^2\{1+[(7a^2+6ab+2b^2)(a-b)^{-2}]\cos^2\phi\}$
E	E_g				$(2/5)(c^2+d^2+e^2+f^2)$	$(2/5)(c^2+d^2+e^2+f^2)(1+\cos^2\phi/3)$
D_3	C_{3v}	D_{3d}				
A_1	A_1	A_{1g}			$(1/15)(a-b)^2$	$(1/15)(a-b)^2\{1+[(7a^2+6ab+2b^2)(a-b)^{-2}]\cos^2\phi\}$
E	E	E_g			$(2/5)(c^2+d^2)$	$(2/5)(c^2+d^2)(1+\cos^2\phi/3)$
C_4	S_4	C_{4h}				
A	A	A_g			$(1/15)(a-b)^2$	$(1/15)(a-b)^2\{1+[(7a^2+6ab+2b^2)(a-b)^{-2}]\cos^2\phi\}$
B	B	B_g			$(1/5)(c^2+d^2)$	$(1/5)(c^2+d^2)(1+\cos^2\phi/3)$
E	E	E_g			$(2/5)(e^2+f^2)$	$(2/5)(e^2+f^2)(1+\cos^2\phi/3)$
C_{4v}	D_4	D_{2d}	D_{4h}			
A_1	A_1	A_1	A_{1g}		$(1/15)(a-b)^2$	$(1/15)(a-b)^2\{1+[(7a^2+6ab+2b^2)(a-b)^{-2}]\cos^2\phi\}$
B_1	B_1	B_1	B_{1g}		$(1/5)c^2$	$(1/5)c^2(1+\cos^2\phi/3)$
B_2	B_2	B_2	B_{2g}		$(1/5)d^2$	$(1/5)d^2(1+\cos^2\phi/3)$
E	E	E	E_g		$(2/5)e^2$	$(2/5)e^2(1+\cos^2\phi/3)$
C_6	C_{3h}	C_{6h}				
A	A'	A_g			$(1/15)(a-b)^2$	$(1/15)(a-b)\{1+[(7a^2+6ab+2b^2)(a-b)^{-2}]\cos^2\phi\}$
E_1	E''	E_{1g}			$(2/5)(c^2+d^2)$	$(2/5)(c^2+d^2)(1+\cos^2\phi/3)$
E_2	E'	E_{2g}			$(2/5)(e^2+f^2)$	$(2/5)(e^2+f^2)(1+\cos^2\phi/3)$
D_6	C_{6v}	D_{3h}	D_{6h}			
A	A_1	A_1'	A_{1g}		$(1/15)(a-b)^2$	$(1/15)(a-b)^2\{1+[(7a^2+6ab+2b^2)(a-b)^{-2}]\cos^2\phi\}$
E_1	E_1	E''	E_{1g}		$(2/5)c^2$	$(2/5)c^2(1+\cos^2\phi/3)$
E_2	E_2	E'	E_{2g}		$(2/5)d^2$	$(2/5)d^2(1+\cos^2\phi/3)$
T	T_h	O	T_d	O_h		
A	A_g	A_1	A_1	A_{1g}	0	$a^2\cos^2\phi$
E	E_g	E	E	E_g	0	$2b^2\cos^2\phi$
F	F_g	F_2	F_2	F_{2g}	$(3/5)d^2$	$(3/5)d^2(1+\cos^2\phi/3)$

tensor is given by

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

and we obtain the scattering efficiency as

$$I_T = I_h{}^h + I_v{}^h = \tfrac{2}{15}(a-b)^2 + \tfrac{1}{15}(7a^2 + 6ab + 2b^2)\cos^2\theta.$$

$$(18)$$

We can distinguish three cases:

$$I_T = (2a^2/15)[1 + 3.5\cos^2\theta] \qquad (b \ll a), \quad (19)$$

$$I_T = (2/15)(a-b)^2 + a^2\cos^2\theta \qquad (b \approx a), \quad (20)$$

$$I_T = (2/15)b^2[1 + \cos^2\theta] \qquad (b \gg a). \quad (21)$$

The experimental data on the angular dependence of intensity of scattering for the A_{1g} mode of benzene[1] follow apprxoimately a $\cos^2\theta$ relation except that a residual scattering is observed at 90° which should vanish according to the Placzek theory.

The most reasonable interpretation of this experimental result seems to be that the residual scattering is due to a finite collection angle and consequently

Placzek's theory is capable of accounting for the observed experimental results. Another possibility is that there is actually a slight difference in a and b and that at least part of the residual 90° scattering is due to the slight difference $2(a-b)^2/15$. Thus we see that with very precise data it may become possible to obtain quantitative information about the magnitudes of the components of the Raman tensor even from a completely disoriented sample.

For benzene the Raman tensor elements a and b are probably very nearly equal since exciting laser line is so far from resonance from the first strongly allowed electronic transition (about 1800 Å) which lies in the xy plane, so that both the polarizability tensor and its derivative for the A_{1g} vibration are characteristic of an isotropic scatterer. However it should be easy to pick conjugated molecules which possess very strongly allowed first transitions near but slightly above the laser frequency (particularly if the argon laser is used) so that in this case the xx and yy and zz Raman tensor elements would be different in magnitude and a different scattering pattern would result. Thus the equations presented here should be of help in obtaining quantitative information concerning the size of the Raman tensor elements for molecular vibrations and also help in the identification of the symmetry of molecular vibrations.

Interaction of Microwave Radiation with a Polar Gas under Conditions of Power Saturation*

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The propagation of microwave radiation through a gas-phase dielectric under conditions of power saturation is considered. It is shown that the nonuniform polarization gives rise to additional modes of electromagnetic oscillation. The amplitudes of the induced electric field are estimated and shown to be small. The results of the calculation substantiate that Harrington's method of averaging the power distribution in determining the power density distinction function $\phi_{w\varrho}$ is correct for application to microwave spectroscopy.

INTRODUCTION

Recently Harrington[1] has shown that useful molecular data can be obtained from gas-phase rotational microwave spectroscopy under conditions of power saturation. He has defined several new experimental parameters which are related to the microwave propagation characteristics of the spectrometer system, intrinsic molecular properties, and intermolecular interactions. Analysis of spectroscopic data in terms of these parameters has proven successful in a number of cases. The essential feature of the Harrington approach is

that intensity measurements can be made under power saturation. In such a case, radiation absorption is much stronger than at power levels where the absorption is strictly proportional to the power density. However, the general property of microwave propagation in a nonuniform dielectric has not been considered.

In this work we examine some of the physical properties of a gas-phase dielectric when it interacts with the microwave radiation field in a waveguide. Of particular interest is the case of power saturation: when the polarization **P** is no longer directly proportional to the electric field **E**. In such a case, the electric susceptibility is a function of the field strength: the electric field varies across the waveguide. One result of the nonuniform dielectric is that other modes of electromagnetic

[1] H. W. Harrington, (a) J. Chem. Phys. **46**, 3698 (1967); (b) *ibid.* **49**, 3023 (1968).