

The Evaluation of Molecular Dipole Moments from the Data of Electrical Stern Gerlach Experiments

R. G. J. Fraser and J. V. Hughes

Citation: [The Journal of Chemical Physics](#) **4**, 730 (1936); doi: 10.1063/1.1749777

View online: <http://dx.doi.org/10.1063/1.1749777>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Quantum measurement theory and the Stern–Gerlach experiment](#)

Am. J. Phys. **66**, 377 (1998); 10.1119/1.18876

[A modern analysis of the Stern–Gerlach experiment](#)

Am. J. Phys. **60**, 306 (1992); 10.1119/1.17136

[Comment on “Paradox in the classical treatment of the Stern–Gerlach experiment”](#)

Am. J. Phys. **52**, 274 (1984); 10.1119/1.13710

[Paradox in the classical treatment of the Stern–Gerlach experiment](#)

Am. J. Phys. **50**, 697 (1982); 10.1119/1.12732

[Generalized Stern–Gerlach experiments and the observability of arbitrary spin operators](#)

J. Math. Phys. **21**, 77 (1980); 10.1063/1.524312



1.10^{-3} , while the second term is of the order of 5.10^{-7} and hence is negligible.

The process of equating the expressions on the right sides of Eqs. (4) and (6) neglects the negative absorption, and is equivalent to omitting from the left side of Eq. (7) a factor $(1 - g_i N_i / g_k N_k)$. Under experimental conditions, light absorption is the only important mechanism responsible for the formation of excited molecules, so that the proportion of excited molecules in the film N_i / N_k is of the order of 10^{-12} .

The coherent scattering in the film can be calculated by regarding the molecules as Hertzian oscillators. With an unpolarized normally incident beam of intensity J_{inc} , the order of the intensity $J_{r\theta}$ scattered by a molecule at a distance r of the order of the molecular radius a in a direction making an angle θ with the normal is, on the assumption that the molecular polarizability is of the order of a^3 , given by the expression

$$J_{r\theta} / J_{inc} = (a^6 / r^4) (2\pi / \lambda)^2 ((1 + \cos^2 \theta) / 2). \quad (12)$$

Only the immediately adjacent molecules can have an appreciable effect, and even at $r = 2a$, for $\lambda = 2400\text{\AA}$, $J_{r\theta} / J_{inc}$ is of the order of 10^{-6} . For large r , $J_{r\theta} / J_{inc}$ is of the order of $a^6 / r^2 \lambda^4$ which cannot be greater than 10^{-18} . Thus it is certain that coherent scattering can never be of importance in photochemical processes in monolayers.

It is not evident *a priori* that a film molecule can be adequately represented by an electric dipole and absorption by an electric quadrupole molecule will now be considered.²⁶ The Einstein probability coefficient B_{ki} , for absorption of radiation of frequency ν_{ik} by a quadrupole is easily found to be

$$B_{ki} = (g_i / g_k) (4/5) (\pi^5 \nu_{ik}^2 / c^2 h^2) |Q_{ik}|^2 \quad (13)$$

in the usual notation, where Q_{ik} , the matrix component of the quadrupole moment is defined by

$$Q_{ik} = -e \int \psi_i^* (\sum_n r_n^2) \psi_k dx_1 \cdots dx_n dy_1 \cdots dy_n dz_1 \cdots dz_n. \quad (14)$$

By induction from Eqs. (7) and (8), it can be seen that the molecular extinction coefficient in a film of quadrupoles is of the order of $15 \sin^4 \theta / 8$ that in solution, where θ is the angle between the quadrupole axis and the direction of the incident beam. However, for $\lambda = 2400\text{\AA}$ and $r = 3A$, B_{ki} (quadrupole) / B_{ki} (dipole) is of the order of 10^{-5} , so that no photochemical reaction due to quadrupole absorption could possibly be detected.

I wish to thank Professor E. K. Rideal for his stimulating criticism and continued help throughout this investigation.

²⁶ Rubinowicz, *Physik. Zeits.* **19**, 440 (1918).

The Evaluation of Molecular Dipole Moments from the Data of Electrical Stern-Gerlach Experiments

R. G. J. FRASER, *Imperial Chemical Industries Limited,*

AND

J. V. HUGHES, *St. John's College, Cambridge, England*

(Received August 21, 1936)

RODEBUSH, Murray, and Bixler¹ report measurements of the electrical dipole moments of the alkali halides by the molecular beam method, which gave values for KCl and KI much

greater than those obtained by Scheffers,² also by a beam method. Scheffers used a wire and concentric cylinder to obtain the necessary inhomogeneous electric field, whereas Rodebush Murray, and Bixler used the Rabi type of field (parallel plate condenser), and they suggest that

¹ W. H. Rodebush, L. A. Murray, and M. E. Bixler, *J. Chem. Phys.* **4**, 372 (1936). See also W. H. Rodebush, *ibid.* p. 536.

² H. Scheffers, *Physik. Zeits.* **35**, 425 (1934).

one cause of the discrepancy between their values and those of Scheffers might lie in a possible error in Fraser's calculation³ of the effective mean square $(E^2)_{av}$ of the electric field in terms of the field E_c between the plates of the condenser. We have therefore reviewed the calculations on which Fraser's quoted value $(E^2)_{av} = k \cdot E_c^2$, $k = 0.6$ is based, with the following results.

1. The value $k = 0.6$, obtained by a process of quadrature, is a particular value, appropriate to the geometry used by Estermann and Fraser,⁴ and is not generally applicable. Unfortunately this is by no means clear from Fraser's text.

2. The effective mean square $(E^2)_{av}$ is determined by evaluating the integral

$$\frac{1}{l} \int_0^l E^2 \cdot dl,$$

where l is the distance between the image slit ($E_0 = 0$) and the detector slit. Thus the value of $(E^2)_{av}$ depends on the geometry of the apparatus, and it is more convenient to have a general expression for $(E^2)_{av}/E_c^2$, soluble directly on insertion of the numerical values appropriate to a given experiment, than to use as hitherto graphical methods of evaluation. Such an expression has been obtained by one of us (J. V. H.), as follows.

Let the x axis be identified with the edge of the condenser, considered infinitely extended in that direction; let $2h$ (z direction) be the width of the gap; and let the positive direction of y lie within the condenser. Then, if y_1, y_2 are the y coordinates of image slit and detector slit, respectively, the above integral is identical with

$$\frac{1}{y_2 - y_1} \cdot \int_{y_1}^{y_2} E^2 \cdot dy.$$

Now E and y can both be expressed as functions of a single parameter⁵ U ; and we may write

³ R. G. J. Fraser, *Molecular Rays* (Cambridge, 1931), p. 171.

⁴ I. Estermann and R. G. J. Fraser, *J. Chem. Phys.* **1**, 390 (1933).

⁵ Cf. Jeans, *Electricity and Magnetism*, fifth edition, (Cambridge, 1927), p. 271.

$$(E^2)_{av} = \frac{\int_{U_1}^{U_2} E^2 \cdot \frac{dy}{dU} \cdot dU}{\int_{U_1}^{U_2} \frac{dy}{dU} \cdot dU},$$

whence

$$\frac{(E^2)_{av}}{E_c^2} = \frac{U_1 - U_2 - \log(e^{U_1} + 1) + \log(e^{U_2} + 1)}{U_1 - U_2 + e^{U_1} - e^{U_2}},$$

where U_1, U_2 are obtained from y_1, y_2 by numerical solution of the equation

$$(y/h) \cdot \pi + 1 = -(e^U + U).$$

3. These formulae, applied to the experimental arrangement of Rodebush, Murray, and Bixler, give $k = 0.85$. Now $\mu: 1/k^{\frac{1}{2}}$, hence their values are to be multiplied by the factor $(0.6/0.85)^{\frac{1}{2}} = 0.84$. Thus $\mu(\text{KCl})$ becomes, in Debye units, 8.00, $\mu(\text{KI})$ becomes 9.24, as compared with the corresponding values 6.3 and 6.8, respectively, obtained by Scheffers.

4. The two sets of results still differ considerably, but Professor Rodebush is of the opinion that the discrepancy between his values as here revised and those of Scheffers is covered by a probable experimental error.⁶ Nevertheless it may possibly be significant that Estermann and Fraser obtained a high value for $\mu(\text{HCl})$ using essentially the same method. Errors, arising from an application of Rabi's formulae in cases where the angle between the incident beam and the field plates is small, lead, however, rather to too small values of the moment;⁷ although it should be observed that Wohlwill's low value for the moment of paranitraniline is irrelevant,⁸ since he evaluated his results by applying the theory of the linear rotator to a polyatomic molecule. A careful re-examination of the theory of the Rabi field has not revealed any unsuspected source of error.

⁶ Private communication.

⁷ H. Scheffers, *Physik. Zeits.* **34**, 245 (1933).

⁸ Cf. H. Scheffers, *Physik. Zeits.* **35**, 425 (1934).