OCTOPOLE MOMENT OF THE METHANE MOLECULE

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By simple calculations it is shown that available measuring techniques do not allow to determine directly the sign and numerical value of the octopole moment of molecules from the effect of their orientation by the gradient of an external electric field's gradient. Nevertheless, indirect methods involving contemporaneous results on the second virial coefficients of the equation of state for gases or dielectric polarization in gases are shown to lead easily, rapidly and with sufficient accuracy to the octopole moment of tetrahedral molecules. These methods as applied by the author led to an octopole moment of $5-6 \times 10^{-34}$ e.s.u. cm^3, a value that may well correspond to reality.

1. Introduction

We consider a system of electric charges $e_1, e_2 \ldots e_\nu$ in an external electric field given by the potential φ. The position of the ν-th charge e_ν with respect to the origin (chosen within the charge system) of the reference frame x_ν, y_ν, z_ν is given by the vector $\boldsymbol{r}_\nu$. The potential energy of interaction between the charge system and external field, $u = \sum_\nu e_\nu \, \varphi(\boldsymbol{r}_\nu)$, can be expressed quite generally in tensorial notation [1] by the power series

$$u = - \sum_{n=0}^{\infty} \frac{2^n n!}{(2n)!} \, \boldsymbol{M}^{(n)}[n] \boldsymbol{E}^{(n)}, \tag{1}$$

wherein

$$\boldsymbol{E}^{(n)} = -\{\nabla^n \varphi(\boldsymbol{r})\}_0, \tag{2}$$

is the intensity of the electric field of order n at the origin, whereas [2]

$$\boldsymbol{M}^{(n)} = \frac{1}{n!} \sum_\nu e_\nu \left\{ (2n-1)!! \boldsymbol{r}_{\nu 1} \boldsymbol{r}_{\nu 2} \ldots \boldsymbol{r}_{\nu n} - (2n-3)!! r_\nu^2 \sum \boldsymbol{U}_{12} \boldsymbol{r}_{\nu 3} \ldots \boldsymbol{r}_{\nu n} + \right.$$
$$\left. + (2n-5)!! r_\nu^4 \sum \boldsymbol{U}_{12} \boldsymbol{U}_{34} \boldsymbol{r}_{\nu 5} \ldots \boldsymbol{r}_{\nu n} - (2n-7)!! r_\nu^6 \sum \boldsymbol{U}_{12} \boldsymbol{U}_{34} \boldsymbol{U}_{56} \boldsymbol{r}_{\nu 7} \ldots \boldsymbol{r}_{\nu n} + \ldots \right\}, \tag{3}$$

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is a tensor of rank n determining the 2^n-pole electric moment of the system of charges, U_{12} being the unit tensor, ∇ — the differential operator and the symbol $[n]$ in Eq. (1) denoting n-fold contraction of the product of $M^{(n)}$ and $E^{(n)}$.

From Eq. (1) we have, to within the electric field of order three [3],

$$u = -M^{(0)}E^{(0)} - M^{(1)} \cdot E^{(1)} - \frac{1}{3} M^{(2)} : E^{(2)} - \frac{1}{15} M^{(3)} \vdots E^{(3)} - ..., \tag{4}$$

where, by the general definition of Eq. (3), the consecutive (monopole, dipole, quadrupole, octopole) electric moments of the system of charges are expressed as follows:

$$e \equiv M^{(0)} = \sum_{\nu} e_{\nu},$$

$$\boldsymbol{\mu} \equiv M^{(1)} = \sum_{\nu} e_{\nu} r_{\nu},$$

$$\boldsymbol{\Theta} \equiv M^{(2)} = \tfrac{1}{2} \sum_{\nu} e_{\nu}(3 r_{\nu 1} r_{\nu 2} - r_{\nu}^2 \, U_{12}),$$

$$\boldsymbol{\Omega} \equiv M^{(3)} = \tfrac{1}{2} \sum_{\nu} e_{\nu}\{5 r_{\nu 1} r_{\nu 2} r_{\nu 3} - r_{\nu}^2 \, (U_{12} r_{\nu 3} + U_{23} r_{\nu 1} + U_{31} r_{\nu 2})\}. \tag{5}$$

Dealing with a molecule as a system of electric positive and negative charges, we see from the definition (3) and (5) that the higher the order of the electric moment, the greater is the part played by the more subtle details of the molecule's electric structure and type of symmetry. Herein lies the reason for the extensive research work aimed at collecting the greatest possible amount of information on the molecular electric moments of various orders. Since for a molecule $M^{(0)} = \sum_{\nu} e_{\nu} = 0$, the first molecular moment $M^{(1)}$ to become oriented in a first-order electric field $E^{(1)}$ (*i.e.* in a homogeneous field) is its dipole moment. This fact was utilized by Debye [4] for determining the dipole moments of molecules from measurements of the dielectric permittivity of gases, vapours or infinitely dilute solutions. Furthermore, Eq. (4) shows that molecular electric quadrupoles will become oriented in a second-order electric field $E^{(2)}$, or field gradient, only. This led Debye [5] to suggest that molecular quadrupoles could be determined directly by measuring the birefringence induced in a gas by an inhomogeneous electric field or, more strictly, an electric field gradient. The quantitative theory is due to Buckingham [3], and has recently been applied by him and Disch [6] to the experimental determination of the sign and numerical value of the quadrupole moment of the CO_2 molecule. There is also the possibility, as yet restricted to the realm of theory, of determining directly molecular quadrupoles from investigations of the effect of an electric field gradient on the dielectric permittivity of a gas [7] or on Rayleigh light scattering in gases, particularly on the degree of depolarization of the light scattered [8].

In accordance with the form of the fourth term in the expansion (4), electric octopoles are subject to orientation only in an electric field of the third order $E^{(3)}$, *i.e.* they undergo orientation by the gradient of a field gradient. It can thus be reasonably hoped to determine octopole moments by investigating the birefringence induced in gases by the gradient of an electric field's gradient. The present paper is aimed at providing a quantitative analysis of the chances for such an experiment, which, if successful, would yield direct information

as to the sign and value of the octopole moment of molecules not possessing permanent moments of lower order, *i.e.* presenting neither a dipole nor a quadrupole moment. This is the case of *e.g.* molecules having the tetrahedral symmetry, like methane, carbon tetrachloride, and so forth. Their case is all the simpler and more interesting as there the octopole moment tensor $\mathbf{\Omega}$ which in three-dimensional space has in general 27 components presents but six equal components $\Omega_{123} \equiv \Omega$:

$$\mathbf{\Omega} = \Omega\{i_1 j_2 k_3 + i_1 j_3 k_2 + j_1 k_2 i_3 + j_1 k_3 i_2 + k_1 i_2 j_3 + k_1 i_3 j_2\}, \tag{6}$$

with $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ denoting unit vectors directed along the axes $1, 2, 3$ of the molecular coordinate system.

However, the evaluations of this investigation, as performed for methane, show the birefringence induced in a gas by the gradient of an electric field's gradient to be so extremely small as to be inaccessible to quantitative determination by existing measuring techniques. We are thus left with indirect methods based on accessible measurements of effects revealing perceptibly interactions of the octopolar type. Such methods are now being used with success for determining the value of molecular quadrupole moments [9—14]; certain of these will be applied in this paper for determining the numerical value of the octopole moment for the methane molecule. The procedure of calculating molecular multipole moments directly from known wave-functions, though by far the most elegant, comes up against unsurmountable computational difficulties in the case of molecules with more than two atoms, and is thus restricted to diatomic problems such as *e.g.* the hydrogen molecule for which Kołos and Roothaan [15] were able to carry out a complete and exact calculation of the wave-function and the quadrupole moment [1].

2. Direct method

An optically isotropic medium, such as a gas, of volume V containing N molecules, if placed in a strong electric field, becomes anisotropic with the tensor of its electric permittivity $\boldsymbol{\epsilon}$ given by the equation in the dipole polarization approximation

$$(\boldsymbol{\epsilon} - \boldsymbol{U}) \cdot \boldsymbol{E}^{(1)} = 4\pi\varrho\langle\boldsymbol{m}\rangle_\varphi, \tag{7}$$

where $\boldsymbol{m}$ is the total electric dipole moment of the molecule in the presence of the applied electric field, $\varrho = N/V$ — the mean number density of molecules, $\boldsymbol{U}$ — the unit tensor and

$$\langle\boldsymbol{m}\rangle_\varphi = \frac{\displaystyle\int \boldsymbol{m} \exp\left\{-\frac{u(\varphi)}{kT}\right\} d\tau}{\displaystyle\int \exp\left\{-\frac{u(\varphi)}{kT}\right\} d\tau} \tag{8}$$

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[1] Professor Kołos had the kindness of informing me recently that the respective calculations have been greatly improved *i.a.* by the assumption of a more realistic model of the H_2 molecule.

Also, Dr P. Cade kindly let me know that in cooperation with Professor Roothan and others (see *e.g. Technical Report of the University of Chicago*, 1962—63 part two) he obtained very accurate wave-functions for diatomic molecules.

is the statistical mean value in the presence of the external electric field with potential φ when the configuration of a molecule is τ; k is Boltzmann's constant, and T — the absolute temperature.

The potential energy of interaction of the permanent molecular octopole moment $\boldsymbol{\Omega} = \boldsymbol{M}^{(3)}$ and the third-order electric field $\boldsymbol{E}^{(3)}$ is given as by (4),

$$u(\varphi) = -\frac{1}{15}\,\boldsymbol{M}^{(3)} : \boldsymbol{E}^{(3)} = -\frac{1}{15}\,\boldsymbol{\Omega} : \boldsymbol{E}^{(3)}. \tag{9}$$

When immersed in an intense electric field, the dipole moment $\boldsymbol{m}$ of an octopole molecule undergoes a variation given by the following expansion (only terms relevant to our problem are taken into account):

$$\boldsymbol{m} = \boldsymbol{\alpha} \cdot \boldsymbol{E}^{(1)} + \frac{1}{2}\,\boldsymbol{\beta} : \boldsymbol{E}^{(1)}\boldsymbol{E}^{(1)} + \ldots, \tag{10}$$

where $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are, respectively, the tensors of the linear and nonlinear dipole polarizability of the isolated molecule.

Under the effect of strong inhomogeneity of the electric field, a gas with molecules presenting the energy (9) and dipole moment (10) will become birefringent, by Eq. (7), to the amount

$$\varepsilon_{zz} - \varepsilon_{xx} = \frac{2\pi\varrho}{105kT}\,\langle\boldsymbol{\beta} : \boldsymbol{\Omega}\rangle\,(\boldsymbol{zz} - \boldsymbol{xx}) : (\boldsymbol{E}^{(1)} \cdot \boldsymbol{E}^{(3)}). \tag{11}$$

This is the difference between the electric permittivities measured in the direction of the unit vectors $\boldsymbol{z}$ and $\boldsymbol{x}$ along the axes Z and X of the laboratory coordinate system, respectively.

In the case of molecules presenting the tetrahedral symmetry we obtain from (11) by (6)

$$\varepsilon_{zz} - \varepsilon_{xx} = \frac{4\pi\varrho}{35kT}\,\beta\Omega(\boldsymbol{zz} - \boldsymbol{xx}) : (\boldsymbol{E}^{(1)} \cdot \boldsymbol{E}^{(3)}), \tag{12}$$

where we have denoted $\beta \equiv \beta_{123}$ and $\Omega = \Omega_{123}$.

On assuming $\beta = 6\times10^{-30}$ e.s.u., and $\Omega = 5\times10^{-34}$ e.s.u. cm^3 (this is the value which will be derived further on for the CH_4 moleule) we have by (12)

$$\varepsilon_{zz} - \varepsilon_{xx} = 5\times10^{-26}\,pT^{-2}\,(\boldsymbol{zz} - \boldsymbol{xx}) : (\boldsymbol{E}^{(1)} \cdot \boldsymbol{E}^{(3)}), \tag{13}$$

at a gas pressure of p atmospheres and the temperature T. Regrettably, this represents very low anisotropy as compared with the birefringence in Voigt's effect, which is

$$\varepsilon_{zz} - \varepsilon_{xx} = 9\times10^{-14}\,p\,T^{-1}\{(\boldsymbol{E}^{(1)} \cdot \boldsymbol{z})^2 - (\boldsymbol{E}^{(1)} \cdot \boldsymbol{x})^2\}, \tag{14}$$

and consequently is not accessible to experimental detection and measurement by the methods now in use.

3. Indirect methods

Since it is hardly feasible to mount an experiment allowing to measure octopole moments directly, we have to recur to indirect methods of determining Ω. Such methods are provided by effects now measurable in which molecular interactions of the dipole-octopole, quadru-

pole-octopole or octopole-octopole type are sufficiently apparent. Birefringence in a real gas or liquid, if due to the square of the intensity of a homogeneous electric field *i.e.* to the well-known Kerr effect, is also an effect of this kind. In the case of a liquid consisting of tetrahedral molecules, we obtain in sufffficient approximation (the non-relevant term corresponding to Voigt's effect is omitted)

$$\varepsilon_{zz} - \varepsilon_{xx} = \frac{24\pi\varrho^2}{5kT} \left\{ \alpha^4 \left[\langle r^{-6}\rangle + \frac{8\Omega^2}{7kT} \langle r^{-13}\rangle \right] + \right.$$
$$\left. + \frac{16}{7} \beta^2\Omega^2\langle r^{-10}\rangle \right\} \{(E^{(1)}\cdot z)^2 - (E^{(1)}\cdot x)^2\}, \tag{15}$$

with the notation

$$\langle r^{-n}\rangle = \int r^{-n}g\,(r)d\mathbf{r}, \tag{16}$$

$g(r)$ being the well-known radial distribution function of molecules mutually distant by $\mathbf{r}$.

Eq. (15) can be successfully evaluated numerically in the case of a not too strongly condensed gas when the radial function in (16) can be replaced by

$$g(r) = \exp\left\{\frac{4\varepsilon}{kT}\left[\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right]\right\}, \tag{17}$$

ε and σ being the well-known parameters of the Lennard-Jones 6—12 potential. By (17), the mean values of (16) can be expressed directly by means of the functions H_n due to Pople [9]. However, as the relevant measurements of $\varepsilon_{zz} - \varepsilon_{xx}$ are not available, Eq. (15) cannot be used here for evaluating Ω.

Johnston, Oudemans and Cole [16] showed that an effect well adapted to simple determination of the octopole moment of tetrahedral molecules is to be found in the dielectric polarization of real gases given as

$$P_D = A_D + \frac{B_D}{V} + ..., \tag{18}$$

where A_D and B_D are respectively the first and second dielectric virial coefficients. In the zeroth approximation, the contribution to the second dielectric virial coefficient B_D from the dipole moment induced in a molecule of polarizability α by the octopole of another molecule with moment Ω amounts to [16, 17]

$$B_D^{(0)} = \frac{64\pi N^2}{15kT} \alpha^2\Omega^2\langle r^{-10}\rangle. \tag{19a}$$

If in computing B_D we take into consideration the statistical Boltzmann factor containing the potential energy of interaction between the octopole of one molecule and the octopole of the other, we obtain additionally, to a first approximation,

$$B_D^{(1)} = \frac{256\pi N^2}{35k^2T^2} \alpha^2\Omega^4\langle r^{-17}\rangle. \tag{19b}$$

Assuming for methane $\Omega = 6 \times 10^{-34}$ e.s.u. cm^3 and the central forces parameters $\varepsilon/k = 137°K$ and $\sigma = 3.882Å$ from viscosity data [18], we obtain from (19a) and (19b) values of B_D in satisfactory agreement with the experimental results of Johnstone et al. [16], as seen from Table I.

TABLE I

Calculated and experimental values of B_D in cm^6/mol^2 for methane; $\alpha = 2.6 \times 10^{-24}$ cm^3 and $\Omega = 6 \times 10^{-34}$ e.s.u.cm^3

$T°K$	$B_D^{(0)}$	$B_D^{(1)}$	$B_D^{cal} = B_D^{(0)} + B_D^{(1)}$	B_D^{exper}
137	19.4	2.7	22.1	—
242	8.9	0.8	9.7	9.0[16]
315	6.7	0.5	7.2	7.3[16]

Particularly reliable values of the octopole moment of tetrahedral molecules can be derived from investigation of the second virial coefficient $B(T)$ of Kamerlingh Onnes' state equation for real gases. In addition to the contribution B_{centr} due to molecular interaction in accordance with central forces law, total $B(T)$ consists of the contribution [13, 19]

$$B_{ind.dip-octop} = - \frac{24N}{5kT} \alpha\Omega^2 \langle r^{-10} \rangle, \tag{20}$$

due to interaction between a molecule's octopole and the dipole moment induced by it in another molecule, as well as the contribution [19]

$$B_{octop-octop} = - \frac{4752N}{175k^2T^2} \Omega^4 \langle r^{-14} \rangle \tag{21}$$

from octopole-octopole molecular intraction.

Using once again the values of ε/k and σ from viscosity data (the appropriateness of this procedure has been widely proved by Orcut [14] for quadrupole gases) we obtain by (16), (17), (20) and (21) the values of B assembled in Table II, where it is seen that good agreement between the calculated (B_{calc}) and experimental values of Thomaes et al. [20] result if the octopole moment of the CH$_4$ molecule is $\Omega = 5 \times 10^{-34}$ e.s.u. cm^3 (the insignificant divergence between B_{calc} and B_{exper} for low temperatures may be due to our not having taken into account quantum corrections in our computations). It is seen that the contributions to B_{calc} from the existence of non-central interactions of the methane molecules (the figures in the third and fourth columns of Table II) average 15 per cent of the contribution from the central forces alone (column 2 of Table II).

The value $\Omega = 6.5 \times 10^{-34}$ e.s.u. cm^3 calculated theoretically by Paar (as cited from ref. [16]), who used a one-centre wave-function with Slater orbitals, is slightly larger than the values 5 and 6×10^{-34} e.s.u cm^3 determined above from the data for B and B_D which are seen to be quite reasonable.

TABLE II

Calculated and experimental values of the second virial coefficient of methane (in cm³/mol) for $\Omega = 5 \times 10^{-34}$ e.s.u cm³

$T°K$	B_{centr}	$B_{ind. dip-octop}$	$B_{octop-octop}$	B_{calc}	B_{exper}[20]
142.6	−174.8	−3.0	−24.3	−202.1	−205.6
176.7	−119.2	−2.1	−14.7	−136.0	−135.0
239.8	−63.9	−1.5	−7.7	−73.1	−73.0
295.0	−37.9	−1.1	−5.1	−44.1	−44.5

It is also worth mentioning that supplementary and at the same time verifying information on the Ω value of the methane molecule as well as other tetrahedral molecules can be had from investigations of the second virial coefficients of appropriately chosen gas mixtures as discussed elsewhere [13, 17, 19].

In the general case the total second virial coefficient of a gas mixture is given by

$$B_m = \sum_{ij} x_i x_j \{ B_{ij}^{centr} + B_{ij}^{ind} + B_{ij}^{el} \}, \tag{22}$$

where x_i is the mole fraction of the i-th component in the gas mixture. B_{ij}^{centr} describes central interaction between two molecules of species i and j, B_{ij}^{ind} is the first moncentral part of B_m resulting from the inductive tensorial interactions and is of the form [2]

$$B_{ij}^{ind} = -\frac{N}{8kT} \sum_{n=0}^{\infty} \frac{2^n (2n+2)! \, (n!)^2}{(2n)! \, (2n+1)!} \{ \alpha_i (M_j^{(n)}[n]M_j^{(n)}) + (M_i^{(n)}[n]M_i^{(n)})\alpha_j \} \langle r_{ij}^{-2(n+2)} \rangle, \tag{23}$$

whereas

$$B_{ij}^{el} = -\frac{N}{4k^2T^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{2^{n+m}(2n+2m)! \, (n! \, m!)^2}{(2n)! \, (2m)! \, (2n+1)! \, (2m+1)!} \times$$

$$\times (M_i^{(n)}[n]M_i^{(n)}) (M_j^{(m)}[m]M_j^{(m)}) \langle r_{ij}^{-2(n+m+1)} \rangle \tag{24}$$

results from electrostatic multipole interaction; $M_i^{(n)}$ is the n-th rank tensor of the $2n$-pole permanent moment of a molecule of species i defined by (3) and possessing the scalar dipole polarizability α_i.

Since the complete exact calculation of molecular octopole moments from known wave-functions is beset with great difficulties, the indirect, simple ways of determining Ω in tetrahedral molecules as discussed here gain considerable importance and in many cases can yield fully reliable results, especially if satisfactory agreement is achieved for the entire range of temperatures accessible in the experimental investigation of second virial coefficients. Applying this method, Orcutt [14] recently obtained entirely reasonable values for the quadrupole moments of certain axially symmetric molecules.

As seen from Eqs (15) and (18)—(21), which contain even powers of Ω only, the indirect methods are disadvantageous in that they do not allow to determine the sign of the

octopole moment. Solely Eq. (11) or (12) could make this possible, once the value and sign of the non-linear polarizability β were know and, obviously, if the effect as such were accessible to measurement, of which we have no hope at present. Thus, practically, we have as yet no method of direct measurement of octopole moments which might be said to be the counterpart of the Debye-Buckingham method for determining directly molecular quadrupoles, consisting in measuring the optical birefringence induced in gases by an electric field gradient. In the situation when, also, the method of direct calculation of molecular octopole moments from known wave-functions generally presents considerable difficulties, the indirect method of determining molecular octopoles used in the present paper is alone of great convenience in its applications and leads in a simple way to results whose occuracy is in many cases satisfactory and reliable.

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