1005. *Absolute Intensities in the Infrared Region for Some Benzene Combination Bands.*

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The absolute infrared intensities have been measured for the combination bands in the region 1500—2000 cm.$^{-1}$ derived from the out-of plane vibrations for benzene and *p*-dideuterobenzene. They are satisfactorily interpreted with the aid of one dipole gradient parameter, $\partial^2\mu/\partial\gamma^2 = \pm 1{\cdot}20$ D, but an improved fit is obtained with two gradient parameters, $\partial^2\mu/\partial\gamma_j^2 = \pm 1{\cdot}10$ D and $\partial^2\mu/\partial\gamma_j\partial\gamma_{j+2} = \pm 0{\cdot}14$ D.

Many absolute intensity measurements have been made [1] on infrared active fundamentals and there has been some work on the overtone bands of X–H stretching vibrations.[2-6] The combination bands of the out-of-plane vibrations of benzene and its derivatives tend to be strong, are in the range 1600—2000 cm.$^{-1}$ which is relatively free from fundamental absorption, and their interpretation is well known.[7-11] From qualitative measurements it has been suggested [8,10] that the important quantity governing the intensity of these bands is a very high value of the second derivative of the dipole moment with respect to the out-of-plane C–H deformation, $\partial^2\mu/\partial\gamma^2$. The present gas-phase measurements on benzene and *p*-dideuterobenzene were undertaken to test whether one such quantity satisfactorily explained the intensities of all the bands and to obtain its numerical value.

Experimental

The intensities were measured on a single-beam grating spectrometer [12] and also on a Perkin–Elmer 21 with a sodium chloride prism used with narrow slits to give an effective slit width of $\leqslant$ 5 cm.$^{-1}$. No appreciable difference of intensity was observed between the two instruments, and the Perkin–Elmer was used for the majority of measurements, especially where atmospheric water vapour interferes with single-beam measurements.

The measurements were made in a 1-metre ($\pm 0{\cdot}25\%$) folded-path cell from the Perkin–Elmer Corporation, and nitrogen to a pressure of 700 mm. was added to give sufficient [12] pressure broadening. Some trouble was experienced with absorption of benzene vapour inside the cell so that the pressure gradually fell after the cell was filled. This trouble was reduced by allowing the cell to come to equilibrium with benzene vapour before a brief pumping and filling to the desired pressure. The pressures thereafter estimated from the absorption intensity at 1038

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[1] Mills, *Ann. Reports*, 1958, **55**, 55.
[2] Wolf and Liddel, *J. Amer. Chem. Soc.*, 1935, **57**, 1464.
[3] Moccia and Thompson, *Proc. Roy. Soc.*, 1957, *A*, **243**, 154.
[4] Russell and Thompson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 318.
[5] Benedict, Herman, Moore, and Silverman, *Canad. J. Phys.*, 1956, **34**, 850.
[6] Benedict, Herman, Moore, and Silverman, *J. Chem. Phys.*, 1957, **26**, 1671.
[7] Young, DuVall, and Wright, *Analyt. Chem.*, 1951, **23**, 709.
[8] Whiffen, *Spectrochimica Acta*, 1957, **7**, 253.
[9] Kakiuti, *J. Chem. Phys.*, 1956, **25**, 777.
[10] Kakiuti, *J. Chem. Soc. Japan*, 1956, **77**, 1839.
[11] Kakiuti, *J. Chem. Soc. Japan*, 1959, **80**, 28.
[12] Spedding and Whiffen, *Proc. Roy. Soc.*, 1956, *A*, **238**, 245.

cm.$^{-1}$ were about 10% lower than those read on a glycol manometer. The absorption of this fundamental band was found to be $0{\cdot}415 \times 10^{-7}$ cm.^{2} molecule^{-1} sec.$^{-1}$ using a 10-cm. glass cell and the Perkin-Elmer spectrometer; this is in good agreement with the earlier[12] value of $0{\cdot}44 \times 10^{-7}$ and with the value obtained at the University of Minnesota[13] of $0{\cdot}42 \times 10^{-7}$. Consequently this value, $0{\cdot}42 \times 10^{-7}$ for the band at 1038 cm.$^{-1}$, was used to evaluate the exact benzene pressure in the cell; the value $0{\cdot}21 \times 10^{-7}$ was used for the corresponding band of *p*-dideuterobenzene at 1034 cm.$^{-1}$. Measurements at five or more pressure were taken for each band and the standard deviation about the mean values was 5% or less for each band. The *p*-dideuterobenzene was that used previously.[12]

THEORY

Assumptions.—A full and exact treatment of the intensities of these combination bands would involve the introduction of a wide variety of cubic potential constants and second derivatives of the dipole moment function. The cubic constants are relatively unimportant in this case and are neglected altogether. The unimportance is due to the facts (i) that none of the combining fundamentals (antisymmetric to the ring plane) can have the same symmetry as the combination level (symmetric to the ring plane). (ii) There are no fundamentals of the correct symmetry in the range 1700—2000 cm.$^{-1}$ which could interact with the combination level (Fermi resonance). This effect may be present below 1700 cm.$^{-1}$.

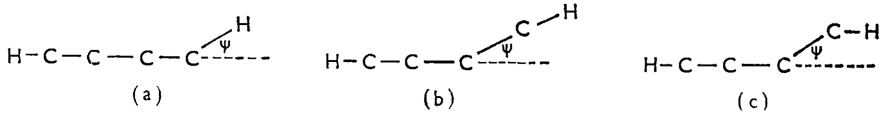
It would also be inappropriate for interpreting results of the present accuracy to retain all seven relevant second derivatives of the dipole-moment function. Those involving explicitly distortion of the carbon skeleton are therefore omitted. This is justified since the absorption above 1500 cm.$^{-1}$ arises predominantly from C–H distortion.

This leaves three terms proportional to the second order of the C–H bendings. These can be chosen in two ways. Either the distortion can be measured from the external bisector of the ring angle, as is usual for the potential energy, in which case, with the usual symbols,[14] the coefficients retained are of the form $\partial^2\mu/\partial\gamma_j\partial\gamma_k$. Alternatively[9] the distortions can be measured from the equilibrium positions in the molecular plane, in which case the coefficients are of the form $\partial^2\mu/\partial\theta_j\partial\theta_k$ with θ defined by

$$r_0\theta_j = (z_j - Z_j)$$

whereas
$$r_0\gamma_j = (z_j - Z_j) + \rho(Z_{j-1} - 2Z_j + Z_{j+1})$$

The difference between the two dominant terms can be seen pictorially in the Figure. Had it not been necessary to ignore the ring-distortion terms the two treatments would necessarily express the same dipole function in different co-ordinates. However, with the incomplete set the two forms predict different relative intensities and can be compared with the experiments.



Dipole moment assumed in treatment I for distortion: (a) $(\psi^2/2)\ (\partial^2\mu/\partial\gamma_j^2)$; (b) 0; (c) $(\psi^2/2)\ (\partial^2\mu/\partial\gamma_j^2)$: *in treatment II* (a) $(\psi^2/2)\ (\partial^2\mu/\partial\theta_j^2)$; (b) $(\psi^2/2)\ (\partial^2\mu/\partial\theta_j^2)$; (c) 0.

All relevant dipole moments lie in the plane of the ring which is seen edge on.

Algebraic formulation. Symmetry requires that the dipole arising from the terms in $\partial^2\mu/\partial\gamma_j\partial\gamma_k$ lies along the bisector of the angle between the *j* and the *k* position and the

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[13] Crawford and Overend, personal communication; Hisatsune and Jayadevappa, *J. Chem. Phys.*, 1960, **32**, 565.

[14] Whiffen, *Phil. Trans.*, 1955, *A*, **248**, 131.

ring centre. Added vectorially, the retained terms contribute to the dipole as in eqns. (1) and (2)

$$\begin{aligned}\mu_x = \ldots &+ 3^{\frac{1}{2}} . 2^{-1}(\gamma_2^{\,2} + \gamma_3^{\,2} - \gamma_5^{\,2} - \gamma_6^{\,2})(2^{-1}\partial^2\mu/\partial\gamma_j^{\,2}) \\ &+ 2^{-1}(\gamma_1\gamma_2 + 2\gamma_2\gamma_3 + \gamma_3\gamma_4 - \gamma_4\gamma_5 - 2\gamma_5\gamma_6 - \gamma_6\gamma_1)(\partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+1}) \\ &+ 3^{\frac{1}{2}} . 2^{-1}(\gamma_1\gamma_3 + \gamma_2\gamma_4 - \gamma_4\gamma_6 - \gamma_5\gamma_1)(\partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+2}) \ldots \quad (1)\end{aligned}$$

$$\begin{aligned}\mu_y = \ldots &\, 2^{-1}(2\gamma_1^{\,2} + \gamma_2^{\,2} - \gamma_3^{\,2} - 2\gamma_4^{\,2} - \gamma_5^{\,2} + \gamma_6^{\,2})(2^{-1}\, \partial^2\mu/\partial\gamma_j^{\,2}) \\ &+ 3^{\frac{1}{2}} . 2^{-1}(\gamma_1\gamma_2 - \gamma_3\gamma_4 - \gamma_4\gamma_5 + \gamma_6\gamma_1)(\partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+1}) \\ &+ 2^{-1}(\gamma_1\gamma_3 - \gamma_2\gamma_4 - 2\gamma_3\gamma_5 - \gamma_4\gamma_6 + \gamma_5\gamma_1 + 2\gamma_6\gamma_2)(\partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+2}) \ldots \quad (2)\end{aligned}$$

For use in computing the transition moments these must be transformed into the symmetry co-ordinates; the expressions are then

$$\begin{aligned}\mu_x = \ldots &(2^{\frac{1}{2}}\, S_{11}\, S_{10a} + 2^{\frac{1}{2}}\, S_5\, S_{17a} + S_{10a}\, S_{17b} + S_{10b}\, S_{17a})(2^{-1}\, r_0^{\,-2}\, \partial^2\mu/\partial\gamma_j^{\,2}) \\ &+ 3^{\frac{1}{2}} . 2^{-\frac{1}{2}}(S_{11}\, S_{10a} - S_5\, S_{17a})(r_0^{\,-2}\, \partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+1}) \\ &+ (2^{-\frac{1}{2}}\, S_{11}\, S_{10a} + 2^{-\frac{1}{2}}\, S_5\, S_{17a} - S_{10a}\, S_{17b} - S_{10b}\, S_{17a})(r_0^{\,-2}\, \partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+1}) \ldots \quad (3)\end{aligned}$$

$$\begin{aligned}\mu_y = \ldots &(-2^{\frac{1}{2}}\, S_{11}\, S_{10b} - 2^{\frac{1}{2}}\, S_5\, S_{17b} + S_{10b}\, S_{17b} - S_{10a}\, S_{17a})(2^{-1}\, r_0^{\,-2}\, \partial^2\mu/\partial\gamma_j^{\,2}) \\ &+ 3^{\frac{1}{2}} . 2^{-\frac{1}{2}}(-S_{11}\, S_{10b} + S_5\, S_{17b})(r_0^{\,-2}\, \partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+1}) \\ &+ (-\, 2^{-\frac{1}{2}}\, S_{11}\, S_{10b} - 2^{-\frac{1}{2}}\, S_5\, S_{17b} - S_{10b}\, S_{17b} + S_{10a}\, S_{17a})(r_0^{\,-2}\, \partial^2\mu/\partial\gamma_j\, \partial\gamma_{j+2}) \ldots \quad (4)\end{aligned}$$

Such quantities as $\partial^2\mu/\partial S_5\, S_{17a}$ are readily obtained from eqn. (3).

In terms of the distortion angle θ, eqns. (1) and (2) remain entirely unchanged in form, γ being replaced by θ throughout. It is convenient to introduce new symmetry co-ordinates $\bar{S}$ which are the same functions of θ as the S are of the γ. Equations (3) and (4) then hold provided S is replaced by $\bar{S}$ and γ by θ throughout. The relations between S and $\bar{S}$ are given by eqns. (5)—(9):

$$\bar{S}_5 = S_5 + 3^{-\frac{1}{2}}\, \rho\, S_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\bar{S}_{11} = S_{11} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$\bar{S}_{17} = S_{17} - 3 . 4^{-1}\, \rho\, S_{16} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$\bar{S}_{10a} = \frac{m_c + m_2(\rho + 1)}{m_c + m_2(\rho + 1)^2}\, S_{10a} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

$$\bar{S}_{10b} = \frac{3m_c + (2m_1 + m_2)(\rho + 1)}{3m_c + (2m_1 + m_2)(\rho + 1)^2}\, S_{10b} + \frac{2^{\frac{1}{2}}(m_1 - m_2)\rho(\rho + 1)}{3m_c + (2m_1 + m_2)(\rho + 1)^2}\, [(\rho + 4^{-1})S_4 + S_5] \quad (9)$$

Equations (8) and (9) apply only to molecules of V_h or D_{6h} symmetry which includes the cases of interest here. The masses enter eqn. (8) and (9) through the condition of no rotation which must be applied since the angles θ, in contrast to γ, are non-zero for pure rotation. m_1, m_2 are the masses of the hydrogen (or deuterium) atoms in the positions indicated and m_c is the mass of a carbon atom.

The normal expression for a transition intensity [15] can be written

$$\text{band area/molecule} = \frac{8\pi^3(\nu_i + \nu_j)}{3ch}\, |\mu_{0,0;\,1,1}|^2$$

where the nomenclature is modified to be appropriate for the 0,0 to 1,1 combination of non-degenerate fundamentals ν_i and ν_j. The relevant term in the dipole-moment expansion is

$$\ldots (\partial^2\mu/\partial Q_i\, \partial Q_j) Q_i\, Q_j \ldots$$

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[15] Wilson, Decius, and Cross, " Molecular Vibrations," McGraw Hill, New York, 1955.

and, provided anharmonicity is neglected so that the combination level can be expressed as a product of harmonic oscillator wave functions of frequencies ν_i and ν_j,

$$|\mu_{0,0;1,1}|^2 = \frac{h^2}{64\pi^4\,\nu_i\nu_j}\,(\partial^2\mu/\partial Q_i\,\partial Q_j)^2$$

$$\text{and band area/molecule} = \frac{h}{24\pi c}\cdot\frac{\nu_i+\nu_j}{\nu_i\nu_j}\,(\partial^2\mu/\partial Q_i\,\partial Q_j)^2.$$

For degenerate vibrations it is simplest to let i and j refer to a particular orthogonal decomposition of the degeneracy and to sum the intensity over all i, j pairs which give the same combination frequency ($\nu_i + \nu_j$). The final expression is equivalent to that given by Kakiuti,[9] it being appreciated that in his convention K_{ij} and K_{ji} are to be added together whereas in the present form $\partial^2\mu/\partial Q_j\,\partial Q_i$ is not to be included as well as $\partial^2\mu/\partial Q_i\,\partial Q_j$.

The form in terms of the normal co-ordinates is readily transformed into one involving the symmetry co-ordinates by means of the usual [15] matrices since

$$\begin{aligned}\partial^2\mu/\partial Q_i\,\partial Q_j &= \sum_{m,n}(\partial^2\mu/\partial S_m\,S_n)(\partial S_m/\partial Q_i)(\partial S_n/\partial Q_j)\\ &= \sum_{m,n} l_{i,m}l_{j,n}(\partial^2\mu/\partial S_m\,\partial S_n).\end{aligned}$$

For the formulation in θ it is convenient to introduce modified l, namely $\bar{l}$, which are the same function of l as $\bar{S}$ are of S. This leaves the form of the equations unchanged.

Force field and normal co-ordinates. The force field and normal co-ordinates obtained previously [14] would be sufficiently accurate, but the occasion has been taken to modify slightly the exact numerical values. The chief adjustment has been in a change of the assumed C–H distance to 1·084 Å and C–C to 1·397 Å as required by the Raman spectra.[16]

TABLE 1.

Benzene		b_{2g}				e_{1g}		a_{2u}		e_{2u}	
ν_{calc}		991	707			851		673		969	406
ν_{obs}		990	707			846		673		967	398
	l_4	$-1·008$	1·727		l_{10}	1·120	l_{11}	1·037	l_{16}	0·650	0·954
	l_5	1·457	$-0·521$						l_{17}	1·364	0·233
Hexadeuterobenzene		b_{2g}				e_{1g}		a_{2u}		e_{2u}	
ν_{calc}		838	591			662		494		798	349
ν_{obs}		829	599			660		496		789	345
	l_4	1·756	0·956		l_{10}	0·871	l_{11}	0·762	l_{16}	0·865	0·764
	l_5	$-1·377$	0·053						l_{17}	1·186	0·108
p-Dideuterobenzene			b_{2g}							b_{3u}	
ν_{calc}		960	744	631				880		596	373
ν_{obs}		957	736	633				873		596	364
	l_4	$-1·041$	1·458	0·888			l_{11}	0·396		0·860	0·115
	l_5	1·355	$-0·624$	$-0·053$			l_{16}	0·688		$-0·427$	0·823
	l_{10b}	0·452	0·626	$-0·542$			l_{17b}	1·212		$-0·306$	0·144

a_u class = a decomposition of e_{2u} for benzene. Also b_{1g} class = a decomposition of e_{1g} class of benzene.

Frequencies in cm.$^{-1}$; l in (a.m.u.)$^{-\frac{1}{2}}$; observed = vapour-state frequencies of Brodersen and Langseth [17, 18] where known, elsewhere liquid frequencies from the same sources.

Also normalisation has been carried out to the more regular $L^+FL = \Lambda$ condition.[15] The revised force constants are $\Phi_1 = 0·510$, $\Phi_2 = 0·412$, $\Phi_3 = 0·340$, $\Phi_4 = 0·248$, $\theta_1 = 0·197$, $\theta_2 = 0·159$, $\eta_1 = 0·240$ and $\eta_2 = -0·158$ mD/Å. The frequencies and co-ordinates are shown in Table 1 and are compared with the experimental frequencies obtained by

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[16] Stoicheff, *Canad. J. Phys.*, 1954, **32**, 339.

[17] Brodersen and Langseth, *Kgl. danske Videnskab. Selskab, Mat.-fys. Skrifter*, 1956, **1**, No. 1.

[18] Brodersen and Langseth, *Kgl. danske Videnskab Selskab, Mat.-fys. Skrifter*, 1959, **1**, No. 7.

Brodersen and Langseth.[17,18] The recommendations of Mulliken [19] have been followed in designating the classes of *p*-dideuterobenzene since the existing literature is not consistent. This differs from that used by Whiffen [8,14] by replacing his subscripts 1, 2, 3 by 3, 1, 2, respectively, and from that of Brodersen and Langseth [18] by interchange of subscripts 2 and 3 on the *b* classes.

Results and Discussion

The observed intensities are quoted in the final column of Table 2. It is clear that for *p*-dideuterobenzene some of the experimental observations relate to two overlapping bands.

TABLE 2.

			Calculated intensity			
Assignment		$\nu_{\text{obs.}}$	I	II	III	obs
Benzene						
$b_{2g} \times e_{2u} = e_{1u}$	990 + 967	1957	0·31	0·25	0·22	0·22
$e_{1g} \times e_{2u} = e_{1u}$	846 + 967	1808	0·20	0·29	0·28	0·29
$b_{2g} \times e_{2u} = e_{1u}$	707 + 967	—	0·05	0·02	0·05	<0·04
$e_{1g} \times a_{2u} = e_{1u}$	846 + 673	1528	0·15	0·41	0·11	0·09
Dideuterobenzene						
$b_{2g} \times a_u = b_{2u}$	957 + 967	1930	0·21	0·18	0·18	0·20
$b_{2g} \times b_{3u} = b_{1u}$	957 + 873	1810	0·09	0·06	0·05	0·12
$b_{1g} \times a_u = b_{1u}$	846 + 967		0·05	0·07	0·07	
$b_{1g} \times b_{3u} = b_{2u}$	846 + 873	1720	0·09	0·14	0·10	0·13
$b_{2g} \times a_u = b_{2u}$	736 + 967		0·00	0·02	0·00	
$b_{2g} \times b_{3u} = b_{1u}$	736 + 873	1600	0·05	0·00	0·05	0·05
$b_{2g} \times a_u = b_{2u}$	633 + 967		0·02	0·00	0·02	

Frequencies in cm.$^{-1}$. All intensities × 10^{-7} *ln* cm.^{2} molecule^{-1} sec.$^{-1}$.

Column I shows the best fit with $\partial^2\mu/\partial\gamma_j^2$ as the only non-zero parameter, and it is clear that this is a fairly successful parameter although the relative intensities of the benzene bands at 1957 and 1808 cm.$^{-1}$ are wrong. The value required is $\partial^2\mu/\partial\gamma_j^2 = \pm 1{\cdot}20$ D.

Column II shows the best fit with $\partial^2\mu/\delta\theta_j^2$ as the only non-zero parameter though the band at 1528 cm.$^{-1}$ is incorrectly predicted to be the strongest, as in the related work of Kakiuti.[9] It is possible that this band has lost intensity by Fermi interaction with the fundamental at 1485 cm.$^{-1}$; but this mechanism is not available for the corresponding hexadeuterobenzene band at 1155 cm.$^{-1}$. Treatment II gives this as decidedly stronger than bands at 1636 and 1458 cm.$^{-1}$ in direct contrast to semiquantitative experiments.[18] Treatment II requires $\partial^2\mu/\delta\theta_j^2 = \pm 2{\cdot}20$ D and this seems extremely high.

Several two-parameter treatments were tried, of which the most successful, III, allowed $\partial^2\mu/\partial\gamma_j\,\partial\gamma_{j+2}$ as well as $\partial^2\mu/\partial\gamma_j^2$ to be non-zero. Quite a small value of this "meta" type coefficient is required: column III of Table 2 shows the calculated values with $\partial^2\mu/\partial\gamma_j^2 = \pm 1{\cdot}10$ D and $\partial^2\mu/\partial\gamma_j\,\partial\gamma_{j+2} = \pm 0{\cdot}14$ D. The relative signs found are such that if γ_j and γ_{j+2} have the same sign the net dipole directed from the centre of the ring to the $(j + 1)$th atom is less than that produced by equal distortion with the hydrogen atoms at positions j and $(j + 2)$ moving to opposite sides of the ring.

In no case is the absolute sign of the dipole produced on distortion obtainable from the present experiments. Both experiment [20] and naive theoretical expectations [12] suggest the hydrogen atom to be at the positive end of the first derivative with respect to out-of-plane bending, in which case it is more likely that it will be at the negative end of the dipole in the plane when this is governed by $\partial^2\mu/\partial\gamma_j^2$. The "effective" dipole moment for the C–H bond would be $-\partial^2\mu/\partial\gamma^2$ and is more likely to be of the same sign for the two cases. That there is not numerical agreement between the two values of

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[19] Mulliken, *J. Chem. Phys.*, 1955, **23**, 1997.

[20] Bell, Thompson, and Vago, *Proc. Roy. Soc.*, 1948, *A*, **129**, 498.

" effective " bond moment, namely 0·61 D from $\partial\mu/\partial\gamma$ [12] and 1·10 D from $\partial^2\mu/\partial\gamma_j^2$, is just another example of the fact that the total dipole moment cannot properly be considered as consisting of a set of fixed bond moments whose direction, but not magnitude, is varied as the bonds are bent. The magnitude of $\partial^2\mu/\partial\gamma_j^2$ is so large that it may prove possible to calculate its sign more reliably than that of $\partial\mu/\partial\gamma$ for which there are two treatments [21,22] which tend to favour the sign contrary to experiment.[20]

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[21] Coulson and Stephen, *Trans. Faraday Soc.*, 1957, **53**, 272.
[22] Eggers, *J. Chem. Phys.*, 1955, **23**, 221.