Dependence of the Molecular Polarization of Carbon Dioxide on Pressure

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(Received June 8, 1954)

One of the present writers[1] has proposed a theoretical formula for the pressure effect on the dielectric constant of gases on the basis of the mutual action of dipoles, namely

$$\left(\frac{\varepsilon-1}{\varepsilon+2}\right)\frac{M}{d}=P=a+\frac{b}{T}+\frac{3ab^2\rho}{8\pi N\beta^3T^{2'}},\qquad(1)$$

where ρ is the concentration of gas molecules in moles per cc or the reciprocal of molecular volume. The symbol β denotes the radius of the action sphere of molecules. All others have their usual significances. This theoretical equation indicates that the molecular polarizations of nonpolar substances are independent of pressure even when raised to a few hundred atmospheric pressures. The constancy of molecular polarization is in agreement with experiments on hydrogen, nitrogen, methane and air. For polar substances, the equation predicts that the molecular polarization at constant temperature increases linearly with the reciprocal of molecular volume. The results of ammonia conform to this relation. The value of molecular radius which is calculated from the pressure dependence of molecular polarization agrees well with those values obtained from the viscosity of the gas or from the constant b in the van der Waals equation of state. Somewhat exceptional behavior is exhibited by carbon dioxide. Although this gas is nonpolar, the molecular polarization increases slightly but definitely with pressure. It was suggested that this behavior might be due to effects other than dipole-dipole interaction, such as quadrupole interactions, which were neglected in the derivation of the aforementioned theoretical equation. Since then knowledge of the electronic structure of carbon dioxide molecule has been extended to such a degree that it is now possible to give a quantitative interpretation of the pressure dependence of the molecular polarization of this gas. In the present paper the results of a theoretical treatment on this problem will be given.

MacCormack and Schneider[2] used experimental second virial coefficient data for carbon dioxide to investigate the intermolecular potential of this molecule on the basis of a Lennard-Jones model. It was found that the derived force constants varied with temperature, the low temperature data yielding higher values of the collision diameter. They interpreted the results in terms of partial binary association and suggested a T-shaped configuration for the resulting dimer having a separation between the centers of monomeric units, viz. C-C distance, equal to 3.91 Å. A conceivable dimer configuration with the two monomeric molecular axes aligned in parallel was proved to be unstable. The suggested dimer formation could explain adequately the increase of collision diameter at lower temperatures and the dimer configuration led to a Coulomb interaction energy to compare favorably with the heat of dimerization obtained from the temperature dependence of the equilibrium constant of dimerization. The equilibrium constant was obtained from the second virial coefficient observed experimentally at lower temperatures and the coefficient calculated for a monomeric gas on the basis of the Lennard-Jones parameters from the high temperature data. The value of the equilibrium constant K_p of dimerization at 100°C. was found to be equal to 4.51×100^{-4} atm^{-1}.

The T-shaped dimer has no center of symmetry and hence should have a finite overall moment μ, which contributes to orientation polarization. If the degree of association is denoted by w, the molecular polarization P of the gas is given by

$$P=(1-w)P_{mono}=(w/2)P_{di}.\qquad(2)$$

Inasmuch as the dimer is a loose complex, it is reasonable to suppose that the electronic polarization is unaffected by dimerization. Therefore

$$P=P^\circ+(w/2)(P_{ort}+\Delta P_A),\qquad(3)$$

where P° ($=P_{mono}$) is the molecular polarization of unassociated carbon dioxide, i,e., the limiting value of molecular polarization at approaching zero pressure and P_{ort} is the orientation polarization of dimers,

$$P_{ort}=\frac{4\pi N}{3}\left(\frac{\mu^2}{3kT}\right).\qquad(4)$$

The quantity ΔP_A is the increase of atomic

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[1] M. Kubo, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **27**, 295 (1935); This Bulletin **13**, 167 (1938). Cf. S. Glasstone, *Ann. Repts. Progr. Chem.*, **33**, 130 (1936); P. W. Bridgman, *Revs. Mod. Phys.*, **18**, 70 (1946).

[2] K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.*, **19**, 849 (1951).

polarization of dimers over twice the atomic polarization of monomers. Since the force field in monomeric units, viz. CO_2 molecules, will not be altered appreciably by the formation of the loose dimer, the assumption may be made that the vibrational modes of monomeric units remain practically unaffected by dimerization. A carbon dioxide molecule has four $(3\times3-5=4)$ normal vibrations, while the T-shaped dimer molecule has twelve $(3\times6-6=12)$ normal modes. Therefore ΔP_A will be the sum of contributions from four $(12-2\times4=4)$ modes of intermonomer vibrations.

By definition, the equilibrium constant is given as

$$K_p=\frac{p[(CO_2)_2]}{p^2(CO_2)}=\frac{(w/2)}{(1-w)^2p}, \tag{5}$$

where p denotes the total pressure. Solving this equation for w and expanding the solution in a power series in K_pp, one obtains

$$w=2K_pp(1-4K_pp+\cdots\cdots). \tag{6}$$

On introducing this in Equation 3, it becomes

$$P=P^\circ+K_pp(1-4K_pp)(P_{ort}+\Delta P_A). \tag{7}$$

The molecular polarization P can be measured as a function of pressure p and the molecular polarization P° at approaching zero pressure has been obtained accurately ($P^\circ=7.35$ cc.).[3] As has already been mentioned, $K_p=4.51\times10^{-4}$ atm^{-1} at 100°C.[2] Therefore Equation 7 contains only one unknown parameter, $P_{ort}+\Delta P_A$, which can be obtained from experimental data. On the other hand, P_{ort} can be calculated if the dipole moment of a dimer can be estimated and ΔP_A will be obtained if the frequencies, the reduced masses and the effective charges of the four intermonomer vibrations mentioned above are evaluated properly. Subsequently the authors give a comparison of the sum of these two calculated quantitise with the experimental value of $P_{ort}+\Delta P_A$.

The dielectric constant of carbon dioxide at high pressures has been measured by many investigators. Inasmuch as one of the present writers reviewed available data on this problem in his previous reports,[1] references to earlier works need not be comprehensive. The measurements of Keyes and Kirkwood[4] and of Uhlig, Kirkwood and Keyes[5] carried out in the Massachusetts Institute of Technology were revised at the same laboratory by Keyes and Oncley[3] using a new cell. The extensive data by Michels and Michels[6] were critically examined by Keyes and Oncley, who corrected them for the "origin failure" ascribed to a variable displacement of the internal parts of the condenser when subjected to stresses induced by the presence of a high pressure gas. The adjusted data were found to be in good agreement with those obtained by themselves.

In Fig. 1. a plot is made of the molecular polarization obtained by Keyes and Oncley against pressure rather than against P°/v as is done in the original report, where v denotes the molecular volume.* To convent molecular volume data to pressure, Michels and Michels' p-v-T data[7] were used. The old density data obtained by Amagat and the new by MacCormack and Schneider[8] gave practically identical results. The full line in Fig. 1. depicts the value of P calculated by Equation (7) with $P_{ort}+\Delta P_A=3.30$ cc. Over the entire pressure range studied, the points lie very close to the parabolic line within experimental errors as is expected from Equation (7). If experimental points lie on a parabola, one can give an empirical equation with three constants capable of fitting the curve to experimental points. It should be noted that in Equation (7) there are only two adjustable parameters, viz., P° and $P_{ort}+\Delta P_A$. This indicates that the explanation of the change of polarization with pressure in terms of partial association is adequate.

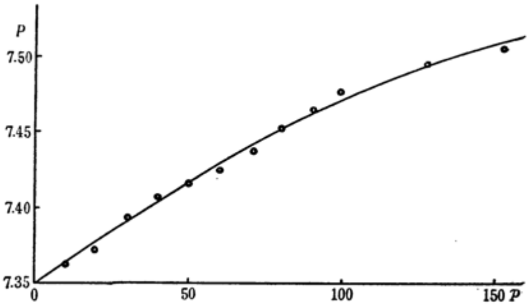

Fig. 1. Dependence of the molecular polarization P(cc.) of carbon dioxide upon pressure p(atm.).

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[3] F. G. Keyes and J. L. Oncley, *Chem. Revs.*, **19**, 195 (1936).

[4] F. G. Keyes and J. G. Kirkwood, *Phys. Rev.*, **36**, 754, 1570 (1930).

[5] H. H. Uhlig, J. G. Kirkwood and F. G. Keyes, *J. Chem. Phys.*, **1**, 155 (1933).

[6] A. Michels and C. Michels, *Phil. Trans. Roy. Soc. London*, **231**, 409 (1933).

* Since P° is equal the real volume per mole of molecules regarded as conducting spheres, P°/v is the ratio of the real volume of molecules to the total volume which they occupy.

[7] A. Michels and C. Michels, *Proc. Roy. Soc. London*, A**153**, 201 (1935); A. Michels, C. Michles and H. Wouters, ibid., **153**, 214 (1935).

[8] K. E. MacCormack and W. G Schneider, *J. Chem. Phys.*, **18**, 1269 (1950).

Estimation of the Dipole Moment of a Dimer

The geometrical configuration of the dimer of carbon dioxide proposed by MacCormack and Schneider2) is given in Fig. 2. As regards the charge distribution in a monomeric unit, it may be assumed that each oxygen atom carries $-\kappa e$, while the carbon atom carries $+2\kappa e$. Here e denotes the absolute value of an electronic charge. In a dimer the electric field of each of the three point charges in a monomeric unit polarizes each of the three atoms of the partner monomer. The vector sum of eighteen ($2\times3\times3=18$) induced moments is equal to the over-all moment μ of a dimer. Straightforward calculations yield that the moment is directed antiparallel to the positive z-axis with the following value:

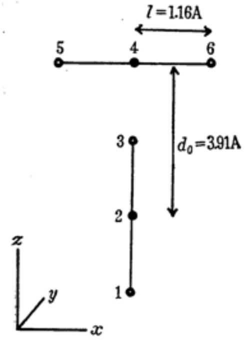

Fig. 2. Geometrical configuration of the dimer of carbon dioxide. Black circles and white circles stand for carbon and oxygen atoms respectively.

$$\mu=(\alpha_C+2\alpha_O)\kappa e\left[\frac{1}{(d_0-l)^2}+\frac{1}{(d_0+l)^2}-\frac{2d_0}{(d_0{}^2+l^2)^{3/2}}\right], \tag{8}$$

$$[\quad]=5.59\times10^{14}\ \mathrm{cm}^{-2}.$$

Here α_C and α_O denote the polarizabilities of carbon and oxygen atoms respectively. In this case $\alpha_C+2\alpha_O$ is equal to the polarizability α of a carbon dioxide molecule. This molecule is fairly anisotropic, the polarizability in the direction parallel to the molecular axis $\alpha_{\parallel}$ ($=4.05\times10^{-24}$cm^3.) being greater than that perpendicular to the axis $\alpha_{\perp}$ ($=1.95\times10^{-24}$ cm^3).* If the relative position of the two monomeric units in a dimer is taken into account, it is reasonable to assume that $\boldsymbol{\alpha}$ in this case is equal to $(\alpha_{\parallel}+\alpha_{\perp})/2$ rather than $(\alpha_{\parallel}+2\alpha_{\perp})/3$. Hence $\boldsymbol{\alpha}=3.00\times10^{-24}$ cm^3.

Carbon dioxide has been treated from the molecular orbital point of view by Mulliken,9) Moffitt,10) Mulligan11) and Shull.12) The last author discussed in detail the off-center electron distribution of a carbon atom, which distribution he stated could hardly be interpreted as an ionic character of a C-O bond. Subtracting the terms due to this off-center distribution, he was left with a net equivalent charge distribution in which each of the oxygen atom carries $-0.40e$, i.e., $\kappa=0.40$.

On introducing the values of $\boldsymbol{\alpha}$ and κ in Equation (8), one obtains $\mu=0.322$ D, which corresponds to the orientation polarization at 100°C. given by

$$P_{ori}=\frac{4\pi N}{3}\left(\frac{\mu^2}{3kT}\right)=1.694\ \text{cc.} \tag{9}$$

Contribution of the Four Intermonomer Normal Vibrations to Atomic Polarization

The dimer molecule has a symmetry C_{2v} with symmetry elements of $C_2(z)$, $\sigma_v(xz)$ and $\sigma_v(yz)$. Normal vibrations can be classified into four symmetry types as shown in Table I. Of the four intermonomer normal vibrations mentioned in the foregoing section, one belongs to type A_1, two to type B_2, and one to type B_2. The four normal vibrations in question are shown in Fig. 3.

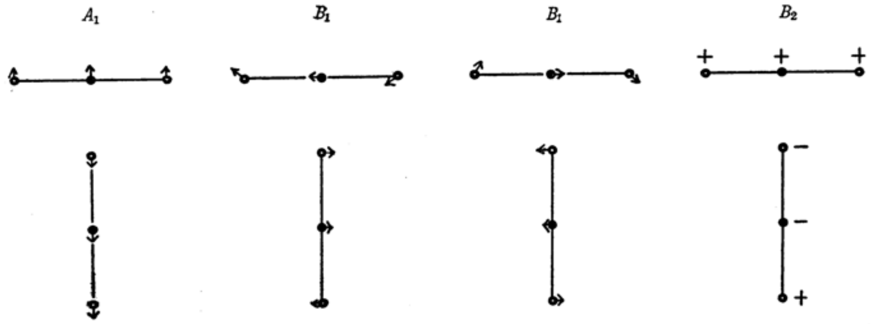

Fig. 3. Intermonomer normal vibrations of the dimer of carbon dioxide.

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* Taken from Landolt-Börnstein, Zahlenwerte und Funktionen, 6th ed. 1951, Band I, 3 Teil, p. 511.

9) R. S. Mulliken, *J. Chem. Phys.*, **3**, 720 (1935); *Revs. Mod. Phys.*, **14**, 204 (1942).

10) W. Moffitt, *Proc. Roy. Soc. London*, A**196**, 524 (1949).

11) J. F. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951).

12) H. Shull, *Proc. Natl. Acad. Sci. U. S.*, **38**, 400 (1952).

TABLE I

CLASSIFICATION OF VARIOUS NORMAL VIBRATIONS OF THE DIMER OF CARBON DIOXIDE INTO SYMMETRY TYPES

Symmetry types	Symmetry coordinates	No. of normal vibr.	Translation and rotation	Genuine normal vibr.	Intra-monomer vibr.	Inter-monomer vibr.
A_1	$z_1,\ z_2,\ z_3,\ z_4,\ x_5+x_6,\ z_5+z_6$	6	T_z	5	4	1
A_2	y_5-y_6	1	R_z	0	0	0
B_1	$x_1,\ x_2,\ x_3,\ x_4,\ x_5-x_6,\ z_5-z_6$	6	$T_x,\ R_y$	4	2	2
B_2	$y_1,\ y_2,\ y_3,\ y_4,\ y_5+y_6$	5	$T_y,\ R_x$	3	2	1
Total number		18	6	12	8	4

The contribution of a normal mode of vibration to the atomic polarization is given by[13]

$$Q=\frac{1}{3}\left(\frac{Ne_{eff}^2}{3\pi M_{eff}\nu^2}\right)=\frac{4\pi Ne_{eff}^2}{9k_0}, \tag{10}$$

in which N is Avogadro's number, e_{eff} is the effective charge, ν is the vibrational frequency, M_{eff} is the effective mass associated with the vibration, and k_0 is the force constant. The factor 1/3 was introduced to take into account all the possible orientation in space of a molecule having a linear oscillator. Therefore if the effective charge and the force constant for a particular normal vibration are known, the contribution of the normal vibration to the atomic polarization can be calculated.

Normal Vibration of Type A$_1$.—Let q denote the increase of C-C distance over its equilibrium value. Apparently q is the normal coordinate of this vibration. The dipole moment which points along the direction of negative y-axis can be calculated in the same manner as in the derivation of Equation (8), even when the vibration is excited. This yields immediately the effective charge given by

$$e_{eff}=\frac{d\mu}{dq}=-2\alpha\kappa e\left[\frac{1}{(d_0-l)^3}+\frac{1}{(d_0+l)^3}-\frac{2d_0^2-l^2}{(d_0^2+l^2)^{5/2}}\right], \tag{11}$$

$$[\quad]=2.99\times10^{22}\ \mathrm{cm}^{-3}.$$

It should be mentioned here that the polarizabilities of carbon and oxygen atoms enter the equation in the form of $\alpha_C+2\alpha_O$ and no assignment to individual atoms is required.

To obtain the force constant of this vibration, the potential function V was constructed out of the attraction term of Coulomb interactions and the repulsion term of the Lennard-Jones potential assumed to be proportional to the inverse twelfth power of the separation d $(=d_0+q)$, viz.

$$V=\sum\frac{E_iE_j}{r_{ij}}+\frac{\lambda}{d^{12}}, \tag{12}$$

where E_i denotes a charge in one of the monomeric units, E_j that in the other, r_{ij} the distance between them to be expressed as a function of l, d_0 and q. The values of E's are $+2\kappa e$ for carbon atoms, and $-\kappa e$ for oxygen atoms.

The constant λ was chosen so as to give a minimum of V at $d=d_0$, namely

$$\lambda=2\kappa^2e^2\left[\frac{1}{(d_0-l)^2}-\frac{d_0-l}{[(d_0-l)+l^2]^{3/2}}-\frac{2}{d_0^2}+\frac{2d_0}{(d_0^2+l^2)^{3/2}}+\frac{1}{(d_0^2+l)^2}-\frac{d_0+l}{[(d_0+l)^2+l^2]^{3/2}}\right]\frac{d_0^{13}}{12}, \tag{13}$$

$$[\quad]=1.60\times10^{14}\ \mathrm{cm}^{-2}.$$

Through cumbersome but straightforward calculations, one obtains the following expression for the force constant:

$$\begin{aligned}k_0=\frac{d^2V}{dq^2}=2\kappa^2e^2\Bigg[&-\frac{2}{(d_0-l)^3}-\frac{1}{[(d_0-l)^2+l^2]^{3/2}}+\frac{3(d_0-l)^2}{[(d_0-l)^2+l^2]^{5/2}}+\frac{4}{d_0^3}+\frac{2}{(d_0^2+1^2)^{3/2}}\\&-\frac{6d_0^2}{(d_0^2+l^2)^{5/2}}-\frac{2}{(d_0+l)^3}-\frac{1}{[(d_0+l)^2+l^2]^{3/2}}+\frac{3(d_0+1)^2}{[(d_0+l)^2+l^2]^{5/2}}\Bigg]+12\times13\frac{\lambda}{d_0^{14}},\end{aligned} \tag{14}$$

$$[\quad]=-2.51\times10^{22}\ \mathrm{cm}^{-3}.$$

In this equation, the right-hand side of Equation (13) was substituted for λ, leading to:

$$k_0=5.62\kappa^2e^2\times10^{22}\ \mathrm{erg/cm^2}. \tag{15}$$

Introducing this value as well as that of effective charge in Equation (10), one obtains the following value for the contribution of this normal vibration to atomic polarization:

$$Q(A_1)=0.482\ \mathrm{cc}. \tag{16}$$

Normal Vibration of Type B$_2$.—The normal coordinate q of this vibration may be taken as one-half of the difference between y-coordinates of the two carbon atoms. One can determine the displacements of atoms from the plane of a dimer molecule in equilibrium under two conditions, that no translation and no rotation of the dimer molecule as a whole take place, and that the configuration of monomeric units remain unchanged. The result are shown in Table II, where ξ denotes

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[13] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford Press, 1932, p. 363.

$Md_0/2ml=4.63$, M and m being the masses of a CO_2 molecule and an O-atom respectively.

TABTE II
DISPLACEMENT OF ATOMS FROM THE PLANE OF A DIMER MOLECULE

O–atom, 1	$(\xi-1)q$
C–atom, 2	$-q$
O–atom, 3	$-(\xi+1)q$
Atoms, 4, 5, 6	$+q$

It is obvious from symmetry considerations that the change of moment takes place in a direction parallel to z-axis. Calculations analogous to the foregoing yield the following result:

$$e_{eff}=\frac{d\mu_y}{dq}=-\alpha\kappa e\left[\frac{2+\xi}{(d^0-l)^3}+\frac{2-\xi}{(d_0+l)^3}-\frac{4}{(d_0^2+l^2)^{3/2}}\right], \tag{17}$$

$$[\quad]=2.40\times10^{23}\ \mathrm{cm}^{-3}.$$

Again the assignment of polarizability to individual atoms is not necessary. In this case, however, α should be equal to $\alpha_\perp$ rather than to $(\alpha_\parallel+\alpha_\perp)/2$, because all the y-components of induced moments are perpendicular to the molecular axes of monomeric units. The electrostatic and repulsive interactions being assumed as in Equation (12), the potential function of this normal vibration is calculated as:

$$V=V_0+\kappa^2e^2\Big[\frac{(2+\xi)^2}{(d_0-l)^3}-\frac{(2+\xi)^2}{[(d_0-l)^2+l^2]^{3/2}}-\frac{8}{d_0^3}+\frac{8}{(d_0^2+l^2)^{3/2}}+\frac{(2-\xi)^2}{(d_0+l)^3}$$
$$-\frac{(2-\xi)^2}{[(d_0+l)^2+l^2]^{3/2}}\Big]q^2-\frac{24\lambda}{d_0^{14}}q^2+\dots, \tag{18}$$

$$[\quad]=4.35\times10^{23}\ \mathrm{cm}^{-3}.$$

Mentioned should be made here that the third term in this equation due to repulsion is less than 4% of the second term due to electrostatic force and hence the assumed functional form of repulsive potential is rather trivial. The force constant is obviously twice the coefficient of q^2 in the right-hand side of Equation 18. The contribution of this normal vibration to atomic polarization can then be evaluated by the use of Equation (10),

$$Q(B_2)=0.212\ \mathrm{cc.} \tag{19}$$

Normal Vibration of Type B.—There are two normal vibrations belonging to the symmetry type of B_1, both of which are infrared active. Unless some assumptions be made for the force field of the dimer molecule, it is difficult to evaluate the effective charges and the force constants of these normal vibrations. Since the contributions of these vibration are rather minor portions of $P_{ort}+\Delta P_A$ compared with the first term, the writers gave up tedious efforts to evaluate the values of Q and simply assumed that every normal vibration contributes nearly the same amount to atomic polarization. This assumption may be justifiable to some extent because each of the vibrations of symmetry types A_1 and B_2 contributes to ΔP_A an amount of the same order of magnitude as that of the other vibration. The sum of P_{ort} (=1.694 cc.), $Q(A_1)$ (=0.482 cc.), $Q(B_2)$ (=0.212 cc.) and $2Q(B_1)$ (=0.694 cc.), i.e., $P_{ort}+\varDelta P_A$ is equal to 3.08 cc. It can be seen that this order of magnitude compares favorably with 3.30 cc. obtained experimentally from the pressure dependence of molecular polarization.

In conclusion, mention should be made of the dielectric constant of ethylene studied by David, Hamann and Pearse.[14] The values of the Clausius-Mosotti function at high pressures were found to exceed the value at the limiting zero pressure. In view of the similarity between the behavior of carbon dioxide and ethylene in this respect, it may be suggested that ethylene also forms a T-shaped dimer molecule which, owing to π-electron transfer, has a finite electric moment.

Summary

The dependence of the molecular polarization of carbon dioxide upon pressure was explained by partial binary association suggested by MacCormack and Schneider on the basis of the second virial coefficient. The theoretical considerations indicate that molecular polarization increases with pressure and that the rate of increase of molecular polarization decrease as the pressure increases. The results of theoretical predictions agree with experiments quantitatively over the entire pressure range if a parameter contained in the theoretical formula is adjusted properly. This parameter can be interpreted as the molecular polarization of dimeric molecules plus the difference between the atomic polarization of dimers and twice the atomic polarization of monomers. The three quantities, the dipole moment of the dimer, the effective charges of four intermonomer normal modes of vibration and the force

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[14] H. G. David, S. D. Hamann and J. F. Pearse, *J. Chem. Phys.*, **19**, 1491 (1951).

constants of the same, were evaluated theoretically. A numerical value of the aforementioned parameter which is calculated from these three quantities compares favorably with that obtained from the dependence of molecular polarization on pressure.

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