Frequency- and Temperature-Dependence of Second Refractivity Virial Coefficients

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Z. Naturforsch. **48a,** 505–513 (1993); received December 14, 1992

A reasonable heuristic extrapolation of a theory given by Buckingham is used to estimate the frequency- and temperature-dependence of the second refractivity virial coefficient. The calculations are carried out for the atoms He, Ne, Ar, Kr, Xe and the small molecules H_2, N_2, O_2, HCl, CO_2, N_2O, NH_3, CH_4, C_2H_4, and SF_6. In some cases the frequency-dependence of $B_R(\omega, T)$ is compared with experimental values, showing sometimes considerable deviations between experiment and the heuristic approach used in this work.

Key words: Refractive index, Refractive index virial coefficient, Polarizability

1. Introduction

In studies of the optical properties of imperfect gases the so-called refractivity virial coefficients $A_R(\omega, T)$, $B_R(\omega, T)$, $C_R(\omega, T)$, ... play an important role, as they describe the refractive index of fluids through an expansion in powers of the density of the well-known Lorentz-Lorenz function [1]. As for $A_R(\omega, T)$, which describes the optical properties of a free, non-interacting species, extensive research has been done both theoretically (e.g. [2–4]) and experimentally [5–8]. Therefore the temperature and especially the frequency dependence of $A_R(\omega, T)$ is now well understood. However, there is a great lack of information about the higher refractivity virial coefficients [1, 9]. Even nowadays, experiments to determine $B_R(\omega, T)$ are extremely difficult to carry out (e.g. [10–13]) and therefore are often performed at one temperature and with one frequency of the measuring light only. Systematic investigations, both theoretical and experimental of the ω- and T-dependence of the refractivity virial coefficients are scarce [11, 14], and due to the quite large error bounds of the experimental data only of limited value. Also, these experimental investigations cover small temperature and wavelength ranges (mostly near room-temperature and at wavelengths of 400–600 nm). These limitations are not present in theoretical calculations of $B_R(\omega, T)$, but in the case of the frequency-dependence of $B_R(\omega, T)$ a consistent theoretical treatment is at present not available [15, 16], although a lot of work has been done for the static case ($\omega = 0$) [17–22]. So it seems worth to estimate the temperature- and wavelength-dependence of the second refractivity virial coefficient on the basis of the first treatment given by Buckingham [1] for atoms and small molecules.

2. The Dipole-Induced-Dipole-Theory

Usually, the refractivity virial coefficients are introduced by expanding the ordinary Lorentz-Lorenz equation in powers of the molar density ϱ [1]:

$$\frac{n^2(\omega, T, \varrho) - 1}{n^2(\omega, T, \varrho) + 2}\frac{1}{\varrho} = A_R(\omega, T) + B_R(\omega, T)\,\varrho + C_R(\omega, T)\,\varrho^2 + \dots \quad (1)$$

with $n(\omega, T, \varrho)$ the real part of the refractive index, ω the frequency of the measuring light and T the temperature. In the static case ($\omega = 0$) and with $n^2 = \varepsilon$, (1) is the well-known Clausius-Mossotti-function [23]. In this case, the expansion coefficients are known as dielectric virial coefficients $A_\varepsilon(T)$, $B_\varepsilon(T)$, $C_\varepsilon(T)$....

In (1) there is

$$A_R(\omega, T) = \frac{N_A\,\alpha_0(\omega, T)}{3\,\varepsilon_0}, \quad (2)$$

where the mean dipole polarizability of the free molecule $\alpha_0(\omega, T)$ is one third of the trace of the dipole polarizability tensor $\hat{\alpha}_0$ and N_A is Avogadros constant.

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As the series expansion (1) is assumed to converge rapidly, only the second refractivity virial coefficient is considered in the following.

$B_R(\omega, T)$ is connected with the intermolecular interaction potential $U(\tau)$ (τ = relative orientation of the two molecules) and the (mean) pair polarizability $\alpha_{12} = \mathrm{Tr}(\hat{\alpha}_{12})/3$ via [1]

$$B_R(\omega, T) = \frac{N_A^2}{3\Omega\varepsilon_0}\int_0^\infty \{\tfrac{1}{2}\alpha_{12}(\omega) - \alpha_0(\omega)\} \cdot \exp[-U(\tau)/kT]\,d\tau \quad (3)$$

with $\Omega = \varrho \int d\tau$. $B_R(\omega, T)$ is connected with the second dielectric virial coefficient B_ε via [1, 24]

$$B_\varepsilon = B_{Or} + B_R = B_{Or} + B_{Ind}, \quad (4)$$

where the orientational part B_{Or} results from permanent multipole moments and the induced part $B_R = B_{Ind}$ from induced multipole moments. Only the latter one will be considered throughout this paper. The contribution of B_{Or} at low frequencies is not considered in this work but can be calculated in principle using FIR-absorption-data [24, 26]. Formula (3) is assumed to be valid for frequencies far away from the first electronic absorption frequency ω_{01} [25], although obviously a rigorous proof of this statement has not been given yet. Provided the intermolecular pair-potential $U(\tau)$ is known with sufficient accuracy, a suitable way to obtain $B_R(\omega, T)$ seems to calculate the frequency dependence of the pair polarizability tensor $\hat{\alpha}_{12}$ for various intermolecular configurations. For the static case this has been done in a systematic way by Dacre [17–20] with ab initio SCF-CI calculations. These calculations support a relationship already found before for spherical species in the framework of dielectric virial coefficients [26] as well as collision induced absorption (CIA)-spectra [15, 27], namely

$$\Delta\alpha \equiv \tfrac{1}{2}\alpha_{12} - \alpha_0 = \tfrac{1}{3}\{\tfrac{1}{2}\mathrm{Tr}(\hat{\alpha}_{12}) - \mathrm{Tr}(\hat{\alpha}_0)\} = [A_6/r^6 - \lambda_t \exp(-r/r_t)]/2 \quad (5)$$

with λ_t and r_t as two fit parameters and A_6 as given in Appendix A 2. Especially in the case of He, there are some further calculations concerning $B_R(\omega, T)$, where Mazur and Mandel [28, 29] were the first to incorporate its frequency-dependence. Obviously only Arrighini et al. [30] have calculated the frequency dependence of the pair polarizability components $\alpha_{12}^{\perp}(\omega)$ and $\alpha_{12}^{\parallel}(\omega)$ of Helium in the random phase approximation for several interatomic separations, followed by a Cauchy-like expansion of the second refractivity virial coefficient. Alternatively, $\Delta\alpha$ and $U_{12}(\tau)$ may be expressed in terms of multipole moments and linear and nonlinear polarizabilities of the isolated atom or molecule [11]. Although correct, this treatment is only valid for large intermolecular separations and cannot account for the observed negative values of $B_R(\omega, T)$ of helium and neon [17, 18, 24, 26], which clearly result from quantum mechanical charge overlap effects at small separations.

The inclusion of field gradient effects at long range results in properties which are hardly available at present. Namely the important C-tensor [31, 32], describing the excess field at molecule 1 due to a quadrupole induced on 2 by the field gradient of a dipole induced on 1 by the light wave, is only known for some species, and its wavelength-dependence is completely unknown. A quite similar way to obtain the long range part of α_{12} is a statistical mechanical treatment first given by Buckingham [1, 33] on the basis of the dipole-induced-dipole (DID) model of Silberstein. As this model is used in this work it will be considered in some detail now, refering to the work of Buckingham [1, 33]. Neglecting field gradient effects and using a Stockmayer-type intermolecular potential (see Appendix A 1), B_R may be obtained by the sum

$$B_R(T) = \sum_{l=1}^{7} f_l(T, P) + f_{ov}, \quad (6)$$

where P denotes one or more molecular properties and f_{ov} the quantum mechanical charge overlap contribution. The full formulae have been evaluated in [1, 33], but for the sake of clearness they are also given in Appendix A 1. In detail, there is the well-known Kirkwood fluctuation contribution

$$f_1 = f_1(\alpha_0) \quad (7)$$

and the influence of high intermolecular field-strengths due to a dispersion like interaction via the second hyperpolarizability γ:

$$f_2 = f_2(\alpha_0, \gamma). \quad (8)$$

Beside these two always existing contributions, there are three further contributions for molecules with permanent dipole moment μ_0:

$$f_3 = f_3(\mu_0, \beta), \quad (9)$$

$$f_4 = f_4(\mu_0, \gamma), \quad (10)$$

$$f_5 = f_5(\mu_0, \varkappa), \quad (11)$$

β being the first hyperpolarizability and $\varkappa$ is the anisotropy of the polarizability for an axially symmetric molecule defined as $\varkappa = (\alpha_\parallel - \alpha_\perp)/3\,\alpha_0$. To this extend of approximation, two extra contributions do arise through an influence of permanent quadrupole moments θ, namely

$$f_6 = f_6(\varkappa, \theta) \tag{12}$$

and

$$f_7 = f_7(\gamma, \theta)\,. \tag{13}$$

3. Modelling of $B_\mathrm{R}(\omega, T)$

The frequency-dependence of B_R is introduced by the frequency dependences of α_0, $\varkappa$, β, and γ. The frequency-dependence of α_0^η, where η defines the isotropic (ι), parallel ($\parallel$), and perpendicular ($\perp$) component, respectively, is obtained via

$$\alpha_0^\eta(\omega) = (4\pi\varepsilon_0)\,a_0^3\,(S_{-2}^\eta + S_{-4}^\eta\,\omega^2 + S_{-6}^\eta\,\omega^4)\,. \tag{14}$$

For axially symmetric molecules the isotropic values are given as

$$S_{-2k}^\iota = \tfrac{1}{3}(S_{-2k}^\parallel + 2\,S_{-2k}^\perp)\,, \tag{15}$$

where the S_{-2k}^η are known as dipole oscillator strength sums [34], given in a.u.. ω is the frequency in a.u. ($\omega/\mathrm{s}^{-1} = 4.13416 \cdot 10^{16}\,\omega/\mathrm{a.u.}$) and $(4\pi\varepsilon_0)\,a_0^3$ is the atomic unit of the polarizability ($1\,\mathrm{a.u.} = 1.6487775 \cdot 10^{-41}\,\mathrm{C^2\,m^2\,J^{-1}}$). $\alpha_0(0) = (4\pi\varepsilon_0)\,a_0^3\,S_{-2}^\iota$, therefore, is the static mean dipole polarizability. The S_{-2k}^ι are known for many gases with high precision and are taken from [35–38]. Much less is known about the frequency-dependence of $\varkappa$, although some measurements for a limited frequency range exist [39]. The oscillator strength sums $S_{-2k}^\perp$ and $S_{-2k}^\parallel$ are only known for hydrogen and nitrogen [40], which are used in the calculations, of course. In all other cases, for the calculations presented here, $\varkappa$ is assumed to be independent of ω and is taken from [41]. Obviously, no experimental data are known for the frequency dependence of $\beta(\omega)$, and only some experiments concerning $\gamma(\omega)$ have been performed [42–44] for the molecules considered in this work. These are experiments of electric field induced second harmonic generation (ESHG), but it seems to be questionable whether this process corresponds to the field-strength effect considered in the framework of the second refractivity virial coefficients. Therefore, as a rule of thumb, the ω-dependences of β and γ are approximated by

$$\beta(\omega) = \beta(0)\left[1 + 2\left(\frac{\alpha(\omega)}{\alpha(0)} - 1\right)\right] = \beta(0)\left(2\frac{\alpha(\omega)}{\alpha(0)} - 1\right) \tag{16}$$

and

$$\gamma(\omega) = \gamma(0)\left[1 + 3\left(\frac{\alpha(\omega)}{\alpha(0)} - 1\right)\right] = \gamma(0)\left(3\frac{\alpha(\omega)}{\alpha(0)} - 2\right), \tag{17}$$

which clearly seems to be a lower estimate of the frequency-dependence of the second hyperpolarizability γ [44]. On account of insufficient data, the temperature-dependence of $B_\mathrm{R}(\omega, T)$, beside the exponential term in (3), is introduced solely through the T-dependence of α_0 via

$$\alpha_0(\omega, T) = \alpha_0(\omega)\,(1 + b\,T + c\,T^2)\,, \tag{18}$$

where b and c are only known for some gases and are taken from [7]. The very small T-dependence of α_0 of the noble gases [5] is neglected. Also, $\varkappa$ is assumed to be independent of temperature. Although there should be a T-dependence of β and γ, it is neglected because no data are known about this phenomenon. Perhaps, it might be of the same order as the T-dependence of α, but this is only a very rough assumption. Therefore, at present the neglect of the temperature-dependence of β and γ seems to introduce smaller errors than a wrong estimate will do.

As is well known, a critical part in calculating B_R is the correct evaluation of the quantum-mechanical-term f_ov in (6). In many cases [15, 17–20] it can be approximated by

$$f_\mathrm{ov} = -\frac{2\pi N_\mathrm{A}^2}{3\,\varepsilon_0}\int_0^\infty \lambda_\mathrm{t}\exp(-r/r_\mathrm{t})\exp(-U(r)/k\,T)\,r^2\,\mathrm{d}r\,, \tag{19}$$

($\lambda_\mathrm{t} > 0$). In this case, f_ov is assumed to be independent of the shape, although a possible anisotropic behaviour might be introduced via a shape factor. Using ab initio calculations as well as a fit to CIA-spectra and second dielectric virial coefficients, it has been shown that r_t is in the order of $4 \cdot 10^{-11}\,\mathrm{m}$ [15, 27]. λ_t is usually obtained through fitting to existing experimental and/or theoretical data, which is also used in the present work. Additionally, a frequency dependence of λ_t is introduced via

$$\lambda_\mathrm{t}(\omega) = \lambda_\mathrm{t}(0)\,A_6(\omega)/A_6(0)\,, \tag{20}$$

where $A_6(\omega)$ is found in Appendix A 2. This behaviour of $\lambda_t(\omega)$ is confirmed for He by quantum-mechanical-ab initio calculations [30, 45]. All atomic and molecular parameters used for the present calculations can be found in Table 1.

4. Results and Discussion

4.1. $B_R(\omega, T)$-*Surfaces*

For a general survey some characteristic $B_R(\omega, T)$-surfaces are shown in the following, since obviously never before a general discussion of the ω- and T-dependence has been given. In this context, absolute $B_R(\omega, T)$-values do not play a dominant role, since all calculated data are fitted to one experimental point, which, of course, may change in future through improved measuring techniques. All surfaces are calculated in the frequency range $0 \leqq \omega \leqq 0.1822$ a.u. (wavelength $\lambda = 250$ nm). Again it is important to mention that at $\omega = 0$ only the induced part B_{Ind} has been calculated. The temperature ranges are chosen individually because of the various temperatures of decomposition. The general features are discussed for all species, but will be shown only for Xe, N_2, and SF_6, respectively.

$B_R(\omega, T)$ of He and Ne is always negative ($20\,\mathrm{K} < T < 2000\,\mathrm{K}$) and decreases with increasing temperature. Due to the frequency-dependence of f_{ov}, there is also a decrease of $B_R(\omega, T)$ with increasing frequency. The calculated ω-dependence is very small and perhaps at present not detectable by experiment. However it is worth to mention that the frequency-dependence of He is in the same order as predicted by quantum-mechanical *ab initio* calculations [30].

The second refractivity virial coefficient-surface of Xe, shown in Fig. 1, shows a considerable increase of $B_R(\omega, T)$ with increasing frequency, as predicted before by consideration of the DID-model alone [11]. Additionally, the (usual) decrease with increasing temperature can be seen up to the highest temperature of 2000 K. This behaviour is also obtained for Ar, Kr, H_2, O_2, HCl, CO_2, and C_2H_4.

A very interesting behaviour of $B_R(\omega, T)$ is seen in Fig. 2 for N_2. As usual, a decrease of $B_R(\omega, T)$ with increasing temperature is observed but, additionally, the second refractivity virial coefficient changes sign in the vicinity of 1100 K. This means that the quantum mechanical overlap term f_{ov} exceeds the other contributions given in (6). Furthermore, below 1100 K $B_R(\omega, T)$ increases with increasing frequency, but above 1100 K a decrease is calculated with increasing ω. This behaviour is observed for none of the other gases considered here.

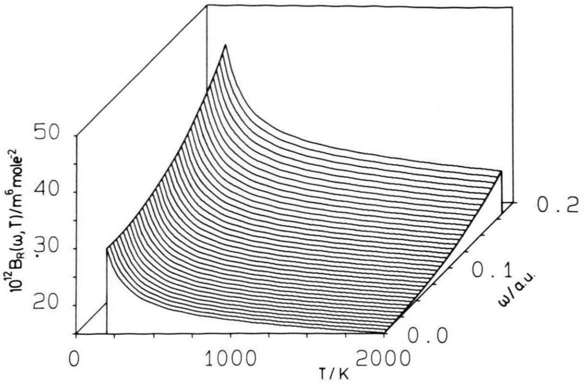

Fig. 1. Second refractivity virial coefficient – surface of Xe.

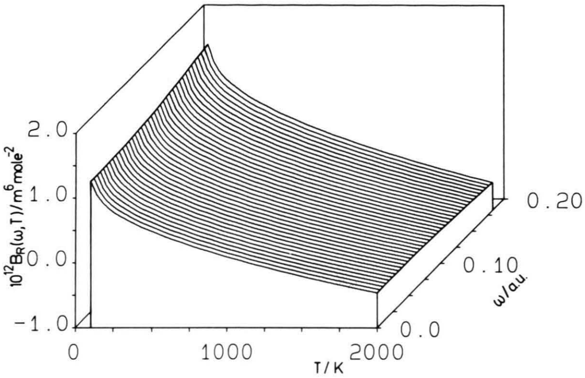

Fig. 2. Second refractivity virial coefficient – surface of N_2.

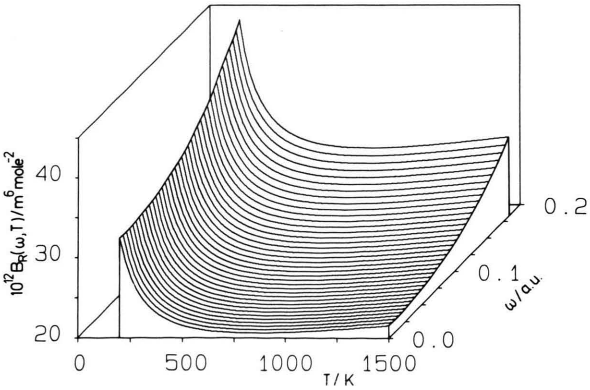

Fig. 3. Second refractivity virial coefficient – surface of SF_6.

In the cases of NH_3, N_2O and CH_4 a large ω-dependence of $B_R(\omega, T)$ can be seen, where an increase with increasing frequency is obtained. However, the

Table 1. Atomic and molecular parameters used to calculate $B_R(\omega, T)$.

	He	Ne	Ar	Kr	Xe	H_2	N_2
$\varepsilon/k/\mathrm{K}$ [a]	10.8	35.7	124.0	164.0	229.0	33.3	91.5
$10^{10}\,r_0/\mathrm{m}$ [a]	2.57	2.789	3.418	3.610	4.055	2.97	3.68
S'_{-2}/a.u. [b]	1.38315	2.669	11.08	16.79	27.16	5.433	11.74
S'_{-4}/a.u. [b]	1.5419	2.886	27.91	56.32	129.6	19.98	29.77
S'_{-6}/a.u. [b]	2.0400	5.063	95.06	256.7	824.7	82.24	98.31
$\varkappa$ [c]	0.0	0.0	0.0	0.0	0.0	0.1253	0.1303
$10^6\,a/\mathrm{K}^{-1}$ [d]	0.0	0.0	0.0	0.0	0.0	5.87	1.8
$10^9\,b/\mathrm{K}^{-2}$ [d]	0.0	0.0	0.0	0.0	0.0	7.54	0.0
$10^{30}\,\mu/\mathrm{C\,m}$ [e]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$10^{52}\,\beta/\mathrm{C^3\,m^3\,J^{-2}}$ [f]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$10^{60}\,\gamma/\mathrm{C^4\,m^4\,J^{-3}}$ [g]	0.0026903	0.0067	0.07275	0.1621	0.4295	0.0428	0.05720
$10^{39}\,\Theta/\mathrm{C\,m^2}$ [h]	0.0	0.0	0.0	0.0	0.0	0.2125	0.5
$10^{40}\,\lambda_t/\mathrm{C^2\,m^2\,J^{-1}}$ [i]	3.894	6.231	153.0	840.0	3471	17.58	264.8
$10^{10}\,r_t/\mathrm{m}$ [j]	0.3333	0.3968	0.4048	0.3968	0.3968	0.4	0.4
T_s/K [k]	323	300	300	300	300	323	300
$10^{12}\,B_R/\mathrm{m^6\,mole^{-2}}$ [k]	−0.0068	−0.14	1.57	6.23	25.5	0.13	0.74

	O_2	HCl	CO_2	N_2O	NH_3	CH_4	C_2H_4	SF_6
$\varepsilon/k/\mathrm{K}$ [a]	128.8	191.4	190.0	220.0	220.5	184.5	244.3	259.0
$10^{10}\,r_0/\mathrm{m}$ [a]	3.362	3.641	4.00	3.879	3.40	3.62	4.071	5.005
S'_{-2}/a.u. [b]	10.59	17.39	17.51	19.70	14.56	17.27	27.70	30.04
S'_{-4}/a.u. [b]	34.75	67.12	50.99	72.11	71.44	62.41	143.5	88.59
S'_{-6}/a.u. [b]	237.1	389.3	211.4	410.7	684.0	298.3	1202	982.1
$\varkappa$ [c]	0.229	0.040	0.270	0.102	0.043	0.0	0.143	0.0
$10^6\,a/\mathrm{K}^{-1}$ [d]	−2.37	1	10.6	1	10	−1.64	10	40
$10^9\,b/\mathrm{K}^{-2}$ [d]	8.69	0.0	0.0	0.0	0.0	13.05	0.0	0.0
$10^{30}\,\mu/\mathrm{C\,m}$ [e]	0.0	3.646	0.0	0.537	4.90	0.0	0.0	0.0
$10^{52}\,\beta/\mathrm{C^3\,m^3\,J^{-2}}$ [f]	0.0	2.34	0.0	−5.1	−5.1	0.0	0.0	0.0
$10^{60}\,\gamma/\mathrm{C^4\,m^4\,J^{-3}}$ [g]	0.06003	0.1939	0.0715	0.215	0.2409	0.1615	0.4219	0.0891
$10^{39}\,\Theta/\mathrm{C\,m^2}$ [h]	0.1334	1.3	1.5	1.168	0.767	0.0	1.11	0.0
$10^{40}\,\lambda_t/\mathrm{C^2\,m^2\,J^{-1}}$ [i]	165.8	500.7	1140	166.9	0.0	500.7	4595	0.0
$10^{10}\,r_t/\mathrm{m}$ [j]	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
T_s/K [k]	–	–	300	–	n.s.p.	300	373	n.s.p.
$10^{12}\,B_R/\mathrm{m^6\,mole^{-2}}$ [k]	–	–	4.75	–	n.s.p.	7.76	19.5	n.s.p.

[a] [11], except for C_2H_4 [49], H_2 [50], O_2 [51], NH_3 [57]. [b] [35–38]. [c] [41], except for H_2 and N_2 [40]. [d] [7], except for HCl, N_2O, NH_3, C_2H_4, SF_6: estimated. [e] [41]. [f] HCl [11], NH_3 [52], N_2O estimated. [g] [53], except for Ne [43], NH_3 [52], C_2H_4, and HCl [54]. [h] [41], except for C_2H_4 [55]. [i] Scaled according to B_R given at the end of this table. [j] [15], except He [17]. [k] Experimental values at $\omega = 0.071976$ a.u., for which λ_t is scaled. All data [11], except for He, H_2 and C_2H_4 [12]. – means no precise experimental B_R available, n.s.p. means no scaling possible, in order to obtain the experimental value.

temperature dependence is somewhat unusual, because there is a sharp decrease between 200 K and 450 K followed by a nearly constant $B_R(\omega, T)$ up to 1500 K.

A very interesting phenomenon is observed for SF_6, Fig. 3, where a large curvature can be seen over the whole range of calculation. Although, as in the most other cases, $B_R(\omega, T)$ increases with increasing frequency, a marked difference can be seen in the temperature dependence, because a minimum of $B_R(\omega, T)$ occurs in the vicinity of 850 K, followed by an increase with increasing temperature up to 1500 K. This effect clearly results from the assumed large temperature dependence of α_0, and obviously compensates the "normal" decrease observed in the other cases. Perhaps, this increase may be even more pronounced if the temperature dependence of the hyperpolarizability is also taken into account.

4.2. *The Frequency-Dependence of* $B_R(\omega, T)$

For all species and at all temperatures examined, the frequency-dependence of $B_R(\omega, T)$ can be expressed with very high accuracy by a Cauchy-like expansion in the range $0 \leqq \omega \leqq 0.2$ a.u.:

$$B_R(\omega, T) = B_R^{(0)}(T)(1 + B_R^{(1)}(T)\,\omega^2 + B_R^{(2)}(T)\,\omega^4). \quad (21)$$

The expansion coefficients $B_R^{(l)}(T)$ are given in Table 2, calculated for $T = 300$ K. Although not shown in detail, it is worth mentioning that the expansion coefficients $B_R^{(l>0)}(T)$ change only slightly with temperature in the ranges examined (except of N_2 by up to $\approx 25\%$). In Fig. 4 the calculated curves are shown in a reduced form for some gases. In general, the ω-dependence of $B_R(\omega, T)$ is high, if there is a large frequency-dependence of the polarizability, described by the Cauchy-coefficients S^{η}_{-4} and S^{η}_{-6} (see Table 1).

In Table 2, the results for He are compared with the only available quantum mechanical *ab initio* calculations of Arrighini et al. [30], showing good agreement between the calculated Cauchy-coefficients. Although comparison with experiment is possible for a limited number of gases [8, 11, 14], only some results will be compared here, because the frequency-dependent measurements are at present not precise enough to make a decision whether the present estimates are reasonable or not. In Fig. 5 the calculations (solid curve) are compared with experiments [8, 11] for CH_4 and C_2H_4. In the case of methane, a quite good agreement between experiment and calculation can be seen, although the measured data sets show a considerable scatter around the calculated curve. In the case of ethene, the measured $B_R(\omega, T)$-values show a much larger frequency-dependence than the calculated ones. Although the error bars of the measured points seem to be realistic, the ω-dependence may be too large perhaps on account of (at present) undetected experimental inaccuracies, which possibly are present in the novel technique of measurement [14]. Nevertheless, in the case of N_2O [46] the experiments are fitted nearly perfectly by the calculated curve, which can be seen in Figure 6. It is worth mentioning that in this case the calculated curve as well as the experimental data points can be shifted all by the same amount on account of the special calculation used (remember that f_{ov} is chosen as a fit parameter), and on account of the special measuring technique, which determines $B_R(\omega, T)$ relative to a given fixed value $B_R(\omega, T)_{(0)}$ [14].

Table 2. Frequency-dependence of $B_R(\omega, T) = B_R^{(0)}(T)(1 + B_R^{(1)}(T)\,\omega^2 + B_R^{(2)}(T)\,\omega^4)$, calculated at $T = 300$ K ($0 < \omega/\text{a.u.} < 0.2$). ΔB_R is the rms-error of the fit.

Gas	$10^{12}\,B_R^{(0)}(T)/$ $m^6\,mole^{-2}$	$B_R^{(1)}(T)$	$B_R^{(2)}(T)$	$10^{16}\,\Delta B_R/$ $m^6\,mole^{-2}$
He	−0.066	2.51	2.43	0.001
He[a]	−0.040	4.27	14.6	–
Ne	−0.138	2.51	3.97	0.001
Ar	1.53	6.15	24.6	0.6
Kr	5.96	8.08	43.1	5.0
Xe	23.75	11.65	105.2	90.0
H_2	0.127	8.93	44.58	0.1
N_2	0.721	5.80	28.45	0.4
O_2	0.782	8.01	65.74	1.0
HCl	11.37	9.37	67.92	20.0
CO_2	4.55	6.82	40.90	4.0
N_2O	21.42	8.69	58.63	30.0
NH_3	16.11	10.97	80.94	9.0
CH_4	7.43	8.96	58.46	10.0
C_2H_4	20.06	12.50	151.6	100.0
SF_6	24.96	7.59	114.4	90.0

[a] Ab-initio calculations at $T = 322$ K [30].

In the case of NH_3, which is not shown as a separate figure, the frequency-dependence of $B_R(\omega, T)$ given by Beaume et al. [47] cannot be reproduced by the present calculations and seems to be rather questionable, as stated before by Sutter [25]. The experimental value $\Delta B_R(\omega, T)/\Delta\omega = +2.7 \cdot 10^{-8}\,m^6\,mole^{-2}$ [47] is about 800 times the calculated one of $\Delta B_R(\omega, T)/\Delta\omega = +3.4 \cdot 10^{-11}\,m^6\,mole^{-2}$ in the range between $\omega = 0.068$ a.u. and $\omega = 0.10$ a.u.

4.3. *The Temperature-Dependence of* $B_R(\omega, T)$

As stated in 4.2., only little is known about the frequency-dependence of $B_R(\omega, T)$. But obviously even less seems to be known about the temperature-dependence of $B_R(\omega, T)$, which should not be confused with the temperature-dependence of $B_\varepsilon(T)$. For most molecules, the latter might have a completely different T-dependence on account of interactions between permanent multipole moments [24]. As mentioned before, most of the experimental data are determined in the vicinity of room-temperature, because unavoidable experimental difficulties arise at other temperatures. Additionally, the very large scattering in the measured data-sets [12] make a direct comparison with the calculated values worthless. So only some results concerning calculated values for SF_6 will be compared

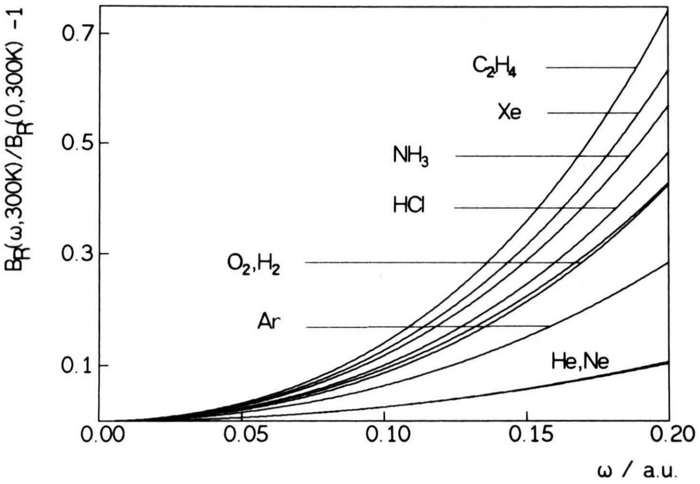

Fig. 4. Relative dispersion of second refractivity virial coefficient $B_R(\omega, T)$ calculated for various gases at $T = 300$ K. Notice that only the induced part $B_{Ind} = B_R$ is calculated.

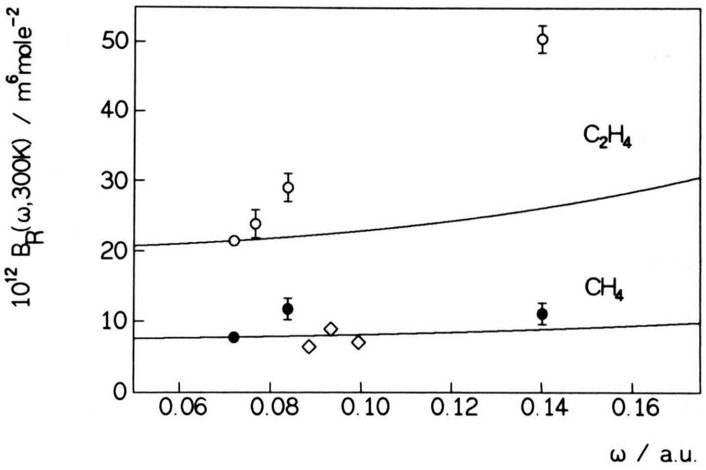

Fig. 5. Dispersion of $B_R(\omega, T)$ of CH_4 (lower part) and C_2H_4 (upper part). ——: calculated this work, ○, ● [8], ◇ [11], (error-bars smaller than symbols used).

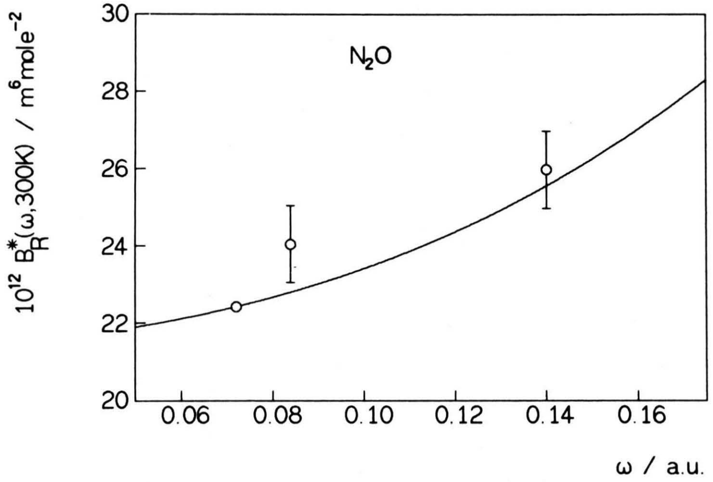

Fig. 6. Dispersion of $B_R^*(\omega, T)$ of N_2O. ——: calculated, this work, ○ [46], both scaled to the same $B_R(\omega = 0.07198$ a.u., $T = 300$ K), see text.

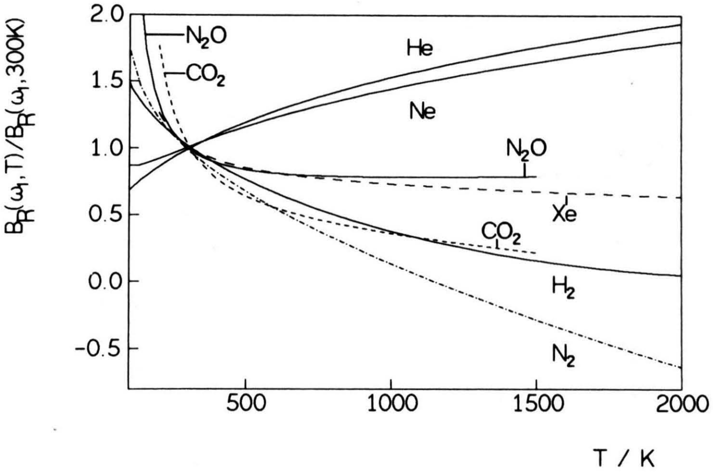

Fig. 7. Calculated temperature dependence of $B_R(\omega, T)$ in reduced form for $\omega = 0.07198$ a.u. ($\lambda = 632.99$ nm).

with results given in the literature [48]. Artym et al. [48] have calculated $b_R = B_R/A_R$ on the basis of a Woolley-potential and obtained $\Delta b_R/\Delta T = -3.0 \cdot 10^{-10}$ $\mathrm{m^3\,mole^{-1}\,K^{-1}}$, which compares reasonably with the present value of $\Delta b_R/\Delta T = -3.7 \cdot 10^{-10}\,\mathrm{m^3}$ $\mathrm{mole^{-1}\,K^{-1}}$, obtained at $\omega = 0.07198$ a.u. and between 300 K and 1400 K.

In Fig. 7 the temperature dependence of $B_R(\omega, T)$ is shown in reduced form $B_R(\omega_1, T)/B_R(\omega_1, 300\,\mathrm{K})$ at $\omega_1 = 0.07198$ a.u. (corresponding to a wavelength of 633 nm) for various gases, showing a very individual behaviour for the species considered here.

For molecules a very interesting contribution will occur at high temperatures, which was first discussed by Buckingham [56]. Due to the high kinetic energy of the species, a change in the equilibrium-geometry of the molecule might occur during a collision, which gives a considerable contribution to the pair-polarizability and therefore to $B_R(\omega, T)$. Up to now, this contribution is completely neglected in all other studies of $B_R(\omega, T)$ at high temperatures.

Although not rigorously correct, the present heuristic extrapolations might give hints to the individual and sometimes rather complex behaviour of the T- and ω-dependence of the second refractivity virial coefficients of the various species. Perhaps, on the basis of these estimates, some species like Xe or SF_6 will be selected for a more detailed and precise experimental study of the temperature- and frequency-dependence of the second refractivity virial coefficient $B_R(\omega, T)$.

Acknowledgement

Financial support of the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie are gratefully acknowledged.

Appendix

A) 1

All calculations are performed with a central-force Lennard-Jones (12:6) potential u_{12} augmented with a dipolar $u_{12\mu}$ and quadrupolar $u_{12\Theta}$ energy term. In the case of axial symmetry and defining Θ_1 and Θ_2 as the angles between the molecular axes and the line of centres, and ϕ as the angle between the planes formed by the axes with the line of centres these contributions read [1, 31]

$$u_{12} = 4\varepsilon\left\{\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right\}, \tag{22}$$

$$u_{12\mu} = \frac{\mu_0^2}{r^3(4\pi\varepsilon_0)}(2\cos\Theta_1\cos\Theta_2 + \sin\Theta_1\sin\Theta_2\cos\phi) \tag{23}$$

and

$$\begin{aligned} u_{12\Theta} = \frac{3\Theta^2}{4r^5(4\pi\varepsilon_0)}(1 &- 5\cos^2\Theta_1 - 5\cos^2\Theta_2 \\ &+ 17\cos^2\Theta_1\cos^2\Theta_2 \\ &+ 16\sin\Theta_1\cos\Theta_1\sin\Theta_2\cos\Theta_2\cos\phi \\ &+ 2\sin^2\Theta_1\sin^2\Theta_2\cos^2\phi)\,. \end{aligned} \tag{24}$$

Introducing the dimensionless quantities τ, y, and φ via (all quantities in S.I. units)

$$y = 2(\varepsilon/kT)^{1/2}, \tag{25}$$

$$\tau = \frac{\mu_0^2}{\varepsilon r_0^3(4\pi\varepsilon_0)}, \tag{26}$$

$$\varphi = \frac{\theta^2}{\varepsilon r_0^5(4\pi\varepsilon_0)} \tag{27}$$

with ε_0 = permittivity of free space, r_0 = distance, for which $u_{12}(r_0) = 0$, and ε = minimum energy of intermolecular potential. Defining now

$$H_n(y) = 12\,y^4 r_0^{n-3}\int_0^\infty r^{2-n} \cdot \exp\left\{-y^2\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]\right\}dr, \tag{28}$$

the individual contributions f_i, (7)–(13), are given by

$$f_1 = \frac{C_1}{(4\pi\varepsilon_0)^3}\frac{\alpha_0^3}{r_0^3}\left\{\frac{H_6(y)}{y^4} + \frac{\tau^2 H_{12}(y)}{48} + \frac{y^4\tau^4 H_{18}(y)}{6400} + \frac{29\,y^8\tau^6 H_{24}(y)}{45\,158\,400} + \ldots\right\}, \tag{29}$$

$$f_2 = C_1\frac{5}{9}\frac{\gamma\varepsilon r_0^3}{\alpha_0\,y(4\pi\varepsilon_0)}H_6(y), \tag{30}$$

$$f_3 = C_1\frac{\mu_0\beta}{(4\pi\varepsilon_0)^2}\left\{\frac{\tau H_6(y)}{36\,y^2} + \frac{y^2\tau^3 H_{12}(y)}{2400} + \frac{29\,y^6\tau^5 H_{18}(y)}{11\,289\,600} + \ldots\right\}, \tag{31}$$

$$f_4 = C_1\frac{\gamma\mu_0^2}{r_0^3(4\pi\varepsilon_0)^3}\left\{\frac{5H_6(y)}{18\,y^4} + \frac{\tau^2 H_{12}(y)}{2400} + \frac{29\,y^4\tau^4 H_{18}(y)}{483\,840} + \ldots\right\}, \tag{32}$$

$$\begin{aligned} f_5 = C_1 \frac{3\varkappa\alpha_0^2}{8(4\pi\varepsilon_0)^2}\Bigg\{&(1-\varkappa)\left[\frac{\tau^2 H_9(y)}{45} + \frac{y^4\tau^4 H_{15}(y)}{3150} + \frac{y^8\tau^6 H_{21}(y)}{564\,480} + \dots\right] \\ &+ \varkappa\left[\frac{\tau^2 H_9(y)}{50} + \frac{y^4\tau^4 H_{15}(y)}{2940} + \frac{y^8\tau^6 H_{21}(y)}{483\,840} + \dots\right]\Bigg\}, \end{aligned} \quad (33)$$

$$f_6 = C_1(224-23\varkappa)\varkappa\alpha_0^2\varphi^2 H_{13}(y)/[6272(4\pi\varepsilon_0)^2], \quad (34)$$

$$f_7 = C_1 \frac{5\gamma\theta^2}{12y^4 r_0^5(4\pi\varepsilon_0)^3} H_8(y) \quad (35)$$

and

$$C_1 = 8\pi^2 N_A^2/9. \quad (36)$$

A) 2

The A_6-term of the long-range contribution to $\Delta\alpha_{12}$ can be formulated as

$$A_6 = \frac{4\alpha_0^3}{(4\pi\varepsilon_0)^2} + \frac{20}{9}\frac{\gamma\varepsilon r_0^6}{\alpha_0}. \quad (37)$$

The ω-dependence is introduced by the ω-dependence of α_0 and γ, the T-dependence solely through the T-dependence of α_0.

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