The Influence of Matter and Black-Body Radiation Photons on the Dipole Polarizabilities α and γ of Atoms

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The influence of the surroundings on the linear dipole polarizability α and second hyperpolarizability γ is discussed in terms of the density ϱ_M of isotropically distributed matter as well as the density ϱ_P of thermal black-body radiation photons. α and γ of the rare gas atoms are studied as examples. At standard conditions, both effects are of comparable size for the rare gases. Possible consequences for ion-molecule reaction rate constants in astronomical environments are suggested.

Apart from a few exceptions theoretical calculations of molecular properties Φ pertain to single, non-interacting particles (see e. g. [1]). In experiments, however, the properties of single particles are more or less influenced by interaction with the surrounding matter and black-body radiation photons [2 - 6]. This is the case even for gases at ambient temperature and pressure.

Concerning the dipole polarizabilities α and γ, the first effect is well-known. Perturbation of α and γ by electric fields produced by the surrounding isotropically distributed matter is usually formulated in a virial expansion of these properties in powers of the molar density $\varrho_M = (N/V)_M/N_A$ of the matter,

$$\Phi(\varrho_M) = \Phi(0)(1 + B_\Phi \varrho_M + C_\Phi \varrho_M^2 + \ldots). \quad (1)$$

In the case of the static linear dipole polarizability $\Phi \equiv \alpha$, (1) is obtained from the Clausius-Mossotti-function [7]. In this case the expansion coefficients B_α and C_α are related to the dielectric virial coefficients via $B_\epsilon = \alpha(0)B_\alpha N_A/(3\varepsilon_0)$ and $C_\epsilon = \alpha(0)C_\alpha N_A/(3\varepsilon_0)$. B_ϵ is known from experiment to within a few percent for a limited number of atoms and small molecules. Concerning the second hyperpolarizability $\Phi \equiv \gamma$ of the rare gases, there are only a few sets of experiments which confirm the density dependence of this property unambiguously [8, 9]. The experimental results are also expressed in a virial expansion similar to (1). In both cases, α and γ, B_Φ is directly related to the radial pair distribution function $g(R)$ and the collision induced incremental pair polarizability $\Delta\Phi = \Phi_{12} - 2\Phi$, where Φ_{12} is the polarizability of a colliding pair.

In what follows it is helpful to remember the frequency dependence of α and γ outside absorbtion bands. $\alpha(-\omega;\omega)$ is usually represented by

$$\alpha(-\omega;\omega) = \alpha(0;0)(1 + a_{1,\alpha}\omega^2 + a_{2,\alpha}\omega^4 + \ldots). \quad (2)$$

The expansion coefficients are related to the well-known dipole sums $S(k)$ via $\alpha(0;0) \equiv 4\pi\varepsilon_0 a_0^3 S(-2)$, $a_{1,\alpha} = S(-4)/S(-2)$ and $a_{2,\alpha} = S(-6)/S(-2)$, where $4\pi\epsilon_0 a_0^3 = 1.648 \times 10^{-41} C^2m^2J^{-1}$ is the atomic unit of the dipole polarizability. These coefficients are precisely known for about 50 atoms and small molecules (see the work of Meath and co-workers, e. g. [10, 11]). In the case of γ, the situation becomes somewhat more complicated because the frequency dependence of γ depends on the type of the non-linear process considered. However, Shelton has shown [12 - 14] that an expansion similar to (2) can be used to describe the frequency dependence of γ as

$$\gamma(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \gamma(0;0,0,0)(1 + a_{1,\gamma}\omega_L^2 + a_{2,\gamma}\omega_L^4 + \ldots) \quad (3)$$

with

$$\omega_\sigma = \omega_1 + \omega_2 + \omega_3 \quad \text{and}$$
$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2 \geq 2\omega_k^2, \quad (4)$$

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Table 1. Comparison of the influence of black-body radiation photons and matter on the dipole polarizabilities α and γ of the rare gases calculated at T = 298.15K and $p = 1 \times 10^5$Pa.

Gas	$a_{1,\alpha}$/au[a]	$a_{1,\gamma}$/au[b]	$10^6 \times B_\alpha/\mathrm{m^3mol^{-1}}$[c]	$10^6 \times B_\gamma/\mathrm{m^3mol^{-1}}$[d]	$10^5 \times \Delta_P^\alpha$	$10^5 \times \Delta_M^\alpha$	$10^5 \times \Delta_P^\gamma$[e]	$10^5 \times \Delta_M^\gamma$
Helium	1.115	2.19	–0.11	0.15	1.87	–0.46	5.03	0.59
Neon	1.081	2.47	–0.12	—	1.81	–0.49	5.67	—
Argon	2.519	5.14	0.30	89	4.23	1.19	11.81	359
Krypton	3.354	6.69	0.69	—	5.64	2.76	15.37	—
Xenon	4.772	7.22	3.15	—	7.99	12.7	16.58	—
Radon	5.585	—	—	—	9.37	—	—	—

[a] $a_{1,\alpha} \equiv S(-4)/S(-2)$ from [11] except for He [25] and Rn [26]; [b] $a_{1,\gamma}$ from [14] except for Ne [12]; [c] B_α from [29] except for He [30]; [d] B_γ of He from [8], calculated result; B_γ of Ar from [9], measured with dc Kerr effect; [e] Δ_P^γ is a lower bound for the black-body radiation effect;

where ω_k is the largest non-zero frequency occuring in (3). The expansion coefficients $a_{1,\gamma}$ and $a_{2,\gamma}$ have been determined for a few atoms and small molecules [12, 14].

Based on experimental results of the temperature dependence of the linear dipole plarizability α of xenon and on theoretical considerations mainly presented by Farley and Wing [3] and Zapryagaev and Zon [5], we have proposed in a previous paper [15] that the temperature dependence of α due to the presence of black-body radiation photons can be described by weighting $\alpha(-\omega;\omega)$ with the Planck distribution $u(\omega,T)$ of the thermal photons. This formula can be obtained by considering the energy-shift $\Delta\varepsilon = -\alpha < E^2(T) >_\omega /2$ of the atomic energy levels in the presence of black-body radiation with a squared mean electric field $< E^2(T) >_\omega \sim u(\omega,T)$. Now we extend this consideration to the non-linear dipole polarizability γ. In this case the energy shift is given by $\Delta\varepsilon = -\gamma < E^4(T) >_\omega /24$. In general, the effect of the black-body radiation photons on α and γ can be described via

$$\Phi(T) = \int u^n(\omega,T)\Phi(\omega)\,\mathrm{d}\omega \Big/ \int u^n(\omega,T)\,\mathrm{d}\omega\,, \quad (5)$$

where we have to use $n = 1$ for α and $n = 2$ in the case of γ. Using (2) and (3), (5) can be solved analytically in terms of the Riemann zeta function $\zeta(z)$ and the factorial gamma function $\Gamma(x)$ [16] to give the final form of the temperature dependence of α and γ:

$$\Phi(T) = \Phi(0)(1 + X_\Phi A_{1,\Phi}T^2 + Y_\Phi A_{2,\Phi}T^4 + \ldots) \quad (6)$$

with $X_\alpha = 40(\pi k_B/E_h)^2/21 = 1.885 \times 10^{-10}\mathrm{K}^{-2}$, $Y_\alpha = (21X_\alpha/10)^2/2 = 7.838 \times 10^{-20}\mathrm{K}^{-4}$, $X_\gamma = 124(\pi k_\mathrm{B}/E_h)^2/95 = 1.292 \times 10^{-10}\mathrm{K}^{-2}$, and $Y_\gamma = (7X_\gamma)^2/29 = 2.820 \times 10^{-20}\mathrm{K}^{-4}$ ($E_h = 4.3597 \times 10^{-18}$J is the atomic unit of energy). For the linear dipole polarizability α, $A_{1,\alpha} \equiv a_{1,\alpha} = S(-4)/S(-2)$ and $A_{2,\alpha} \equiv a_{2,\alpha} = S(-6)/S(-2)$. In the case of the second hyperpolarizability γ, the inequalities $A_{1,\gamma} \geq 2a_{1,\gamma}$ and $A_{2,\gamma} \geq 4a_{2,\gamma}$ are obtained from the special form of the frequency dependence of γ and the inequality given in (4). In thermal equilibrium, the squared temperature, T^2, is directly related to the number density, $(N/V)_\mathrm{P} = N_\mathrm{A}\varrho_\mathrm{P}$, of the black-body radiation photons via [17]

$$T^2 = 2.56\left(\frac{\hbar c}{k_\mathrm{B}}\right)^2\left(\frac{N}{V}\right)_\mathrm{P}^{2/3}\,. \quad (7)$$

According to this relation, Φ in (6) can also be interpreted as a perturbed quantity, now influenced by the density ϱ_P of the surrounding black-body radiation photons. This is directly comparable to (1), where the perturbation due to the surrounding matter is described. Additionally, the explanation of this effect can be given in analogy to the results of Bulanin [18], who has discussed the interaction induced change in $\alpha(\varrho_\mathrm{M})$ in connection with the shift and asymmetrical broadening of spectral lines. Cooke and Gallagher [19] have - on grounds of experimental results - stated explicitely that black-body radiation photons appear to behave like foreign gas atoms in both the shifts and broadenings they produce especially in Rydberg atoms.

The black-body radiation effect has been detected experimentally in 1994 [15]. Hitherto it was assumed to be negligible [5]. However, since B_ε and especially $S(-2)$ and $S(-4)$ are known for the rare gases, the resulting effect of the surroundings on the linear polarizability $\alpha(0)$ of the non-interacting particle can be calculated. Additionally, some estimates can also be given concerning $\gamma(0)$. Neglect of $C_\Phi\varrho_\mathrm{M}^2$ in

(1) and $Y_\Phi A_{2,\Phi} T^4$ in (6) as well as use of the approximation $\varrho_M = p/(RT)$ are fully justified in the context of this work. In Table 1 the relative deviations $\Delta_J^\Phi \equiv [\Phi(\varrho_J) - \Phi(0)]/\Phi(0)$, calculated at standard ambient temperature and pressure, T = 298.15K and $p = 1 \times 10^5$Pa, are presented, where ϱ_J is either the density of matter (ϱ_M) or of photons (ϱ_P).

First we compare the influence of matter and black-body radiation photons on α. It can be recognized that $\Delta_P^\alpha > 0$ for all rare gases, which means that the influence of black-body radiation photons increases the polarizability of these systems. However, in the case of helium and neon $\Delta_M^\alpha < 0$, whereas for argon, krypton and xenon $\Delta_M^\alpha > 0$. This demonstrates that Δ_M^α depends on the nature of the intermolecular forces. The varying sign of Δ_M^α reflects that, depending on the experimental conditions, the influence of short range overlap effects ($\Delta_M^\alpha < 0$) as well as long-range effects ($\Delta_M^\alpha > 0$) may dominate. At present, radon must be excluded from this discussion because B_ε is not known for the heaviest of the rare gases. Δ_M^α and Δ_P^α, respectively, have nearly the same value for helium and neon. In both atomes we have $10^5 \times \Delta_P^\alpha \approx 1.85$ and $10^5 \times \Delta_M^\alpha \approx -0.48$ at the values of p and T given above. The most interesting feature is that, except for xenon, the influence of the photon gas on α is larger than the interaction with gaseous matter, leading to $|\Delta_P^\alpha| > |\Delta_M^\alpha|$. This means that the dominating effect of the surroundings on the polarizability has not been considered at standard conditions up to now. Of course, both effects are almost completely negligible at ambient temperature and pressure as can be seen in Table 1. Δ_M^α increases significantly at high gas densities ϱ_M. This well-known behaviour of the Clausius-Mossotti function and the related Lorentz-Lorenz function must be taken into account e. g. in interferometric measurements of gas densities at high pressures [20, 21].

On the other hand, the effect of the black-body radiation on α may become important in astrochemistry and astrophysics. According to the Hertzsprung-Russell diagram, the surface temperature of stars varies between 3000K and 25000K. This means they are extremely hot radiation sources with nearly black-body radiation characteristics. Besides ionization processes, this black-body radiation field may have some influence on the rate constant of ion-atom and ion-molecule reactions in the astronomical environments (for a recent review of astrochemistry see [22]). This can be inferred from inspection of the simple, and of course approximate, Langevin reaction rate constant $k_L \sim \sqrt{\alpha}$, which is proportional to the square-root of the mean polarizability of the neutral reactant (see e. g. [23]). According to this simple relation, the effect of black-body radiation photons on k_L is small in the case of reactions with helium (approximately 1% at 10000K), but it may become important in the case of reactions with heavier elements and open shell systems, which tend to have much larger oscillator strengths sum ratios $a_{1,\alpha} = S(-4)/S(-2)$ (e. g. Li:$a_{1,\alpha}$ = 214au [11], Cd:$a_{1,\alpha}$ = 18.9 au [24]).

In the case of the second hyperpolarizability γ, the situation becomes much more uncertain. The experimentally determined density dependence of γ of helium and argon in [8] is contrary to theoretical predictions based on a quantum-mechanically extended DID model. As discussed recently by Shelton and Palubinskas [9], however, the evaluation of the experiments of Donley and Shelton [8] is incomplete. To this end, B_γ obtained from density-dependent dc Kerr effect measurements [9] is at present superior to B_γ determined by electric-field-induced second harmonic generation [8]. No experimental evidence is given so far for the influence of black-body radiation photons on the second hyperpolarizability γ, and we present only a short qualitative discussion of this property. Assuming the validity of (5) for γ, Δ_P^γ is calculated to be larger than Δ_M^γ for He but much smaller in the case of Ar. This behaviour is similar to Δ_M^α for He, but contrary to the results obtained for Ar. On the other hand, $|\Delta_M^\alpha|$ is lower than $|\Delta_M^\gamma|$. This result is not surprising because the relative magnitude of the incremental pair-polarizability $\Delta\alpha$ is lower than the incremental pair hyperpolarizability $\Delta\gamma$ [27]. This means that the non-linear polarizabilities are much more affected by intermolecular interactions than α, which can be simply inferred from comparison of gas-phase and liquid-phase values of these properties [28].

Similarly, Δ_P^γ is larger than Δ_P^α. This seems to be a logic result if black-body radiation photons are considered to behave like foreign gas atoms. This reflects that the hyperpolarizability γ is very sensitive to small variations of the tails of the electronic wavefunctions. γ also shows a high sensitivity to diffuse basis functions in *ab initio* calculations for single atoms and molecules.

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[1] D. M. Bishop, Advan. Quant. Chem. **25**, 1 (1994).
[2] A. D. Buckingham, Pure Appl. Chem. **52**, 2253 (1980).
[3] J. W. Farley and W. H. Wing, Phys. Rev. A **23**, 2397 (1981).
[4] G. Birnbaum ed., Phenomena Induced by Intermolecular Interactions, Plenum Press, New York 1985.
[5] S. A. Zapryagaev and B. A. Zon, Opt. Spectrosc. **59**, 15 (1985).
[6] D. M. Bishop, Int. Rev. Phys. Chem. **13**, 21 (1994).
[7] A. D. Buckingham and J. A. Pople, Trans. Faraday Soc. **51** (1955).
[8] E. A. Donley and D. P. Shelton, Chem. Phys. Letters **215**, 156 (1993); Erratum: Chem. Phys. Letters **228**, 701 (1994).
[9] D. P. Shelton and J. J. Palubinskas, J. Chem. Phys. **104**, 2482 (1996).
[10] A. Kumar and W. J. Meath, Can. J. Chem. **63**, 1616 (1985).
[11] G. D. Zeiss and W. J. Meath, Mol. Phys. **33**, 1155 (1977).
[12] D. P. Shelton and E. A. Donley, Chem. Phys. Letters **195**, 591 (1992).
[13] D. P. Shelton, Phys. Rev. **A36**, 3032 (1987).
[14] D. P. Shelton, Phys. Rev. **A42**, 2578 (1990).
[15] U. Hohm and U. Trümper, Chem. Phys. **189**, 443 (1994).
[16] I. S. Gradshteyn and I. M. Ryzhik, Tables of Integrals, Series and Products, Academic Press, New York 1965.
[17] A. C. Phillips, The Physics of Stars, John Wiley & Sons, Chichester 1994, p. 60.
[18] M. O. Bulanin, Chem. Phys. Letters **217**, 466 (1994).
[19] W. E. Cooke and T. F. Gallagher, Phys. Rev. **A21**, 588 (1980).
[20] H. J. Achtermann, H. D. Baehr, and T. K. Bose, J. Chem. Thermodyn. **21**, 1023 (1989).
[21] H. J. Achtermann, J. Hong, W. Wagner, and A. Pruss, J. Chem. Eng. Data **37**, 414 (1992).
[22] A. Dalgarno and J. L. Fox, in: Unimolecular and Bimolecular Ion-Molecule Reaction Dynamics, eds. C. Y. Ng, T. Baer, and I. Powis, John Wiley & Sons, Chichester 1994, p. 1.
[23] M. A. Smith, in: Unimolecular and Bimolecular Ion-Molecule Reaction Dynamics, eds. C. Y. Ng, T. Baer, and I. Powis, John Wiley & Sons, Chichester 1994, p. 183.
[24] D. Goebel and U. Hohm, Phys. Rev. A **52**, 3691 (1995).
[25] A. Koide, W. J. Meath, and A. R. Allnatt, J. Phys. Chem. **86**, 1222 (1982).
[26] C. Hättig, PhD Thesis, University of Bonn (1995).
[27] A. D. Buckingham, E. P. Concannon, and I. D. Hands, J. Phys. Chem. **98**, 10455 (1994).
[28] M. Stähelin, C. R. Moylan, D. M. Burland, A. Willets, J. E. Rice, D. P. Shelton, and E. A. Donley, J. Chem. Phys. **98**, 5595 (1993).
[29] J. Huot and T. K. Bose, J. Chem. Phys. **95**, 2683 (1991).
[30] S. Kirouac and T. K. Bose, J. Chem. Phys. **64**, 1580 (1976).