A Finite-Field Calculation of the Dipole Hyperpolarizability of Ammonia

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Z. Naturforsch. **46a**, 363–366 (1991); received December 6, 1990

The first (β) and second (γ) electric dipole hyperpolarizabilities are calculated for the ground state of ammonia. All independent components of $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are obtained from the energies of the molecule perturbed by a homogeneous electric field. The values of γ_{xxxx}, γ_{xxxz}, γ_{xxzz} and γ_{zzzz} are 1232, -106, 1077 and $4319\, e^4 a_0^4 E_h^{-3}$, respectively.

Key words: NH_3, Dipole polarizability, Dipole hyperpolarizability.

1. Introduction

Electric polarizabilities and hyperpolarizabilities are of central importance in studies of an impressive range of phenomena, from intermolecular forces to nonlinear optical processes [1–3]. The dipole moment and polarizability, first and second dipole hyperpolarizability of ammonia have been the object of many experimental [4–7] and theoretical [8–15] investigations.

In the work we report a theoretical investigation of the dipole hyperpolarizability of ammonia. All properties are obtained from self-consistent field (SCF) calculations of the energy of the molecule perturbed by a homogeneous electric field, a method applied successfully to similar calculations for ethyne [16], carbon dioxide [17] and water [18]. Our aim is to obtain reliable SCF values, close to the respective Hartree-Fock limits. The available SCF values of the dipole hyperpolarizability are in clear disagreement, and the absence of stability is also present in the SCF values of the dipole polarizability. Hartree-Fock values of molecular properties are true reference results as their knowledge is indispensable to the correct estimate of the respective electron correlation effects.

Atomic units are used throughout this paper although bond lengths are given in the unit used in the original references, usually in Ångströms. The conversion factors from atomic to SI units are:

$1\, a_0 \simeq 0.529177249 \times 10^{-10}$ m,
$1\, e a_0 \simeq 8.478358 \times 10^{-30}$ C m,
$1\, e^2 a_0^2 E_h^{-1} \simeq 1.648778 \times 10^{-41}\, C^2 m^2 J^{-1}$,
$1\, e^3 a_0^3 E_h^{-2} \simeq 3.206361 \times 10^{-53}\, C^3 m^3 J^{-2}$ and
$1\, e^4 a_0^4 E_h^{-3} \simeq 6.235378 \times 10^{-65}\, C^4 m^4 J^{-3}$.

2. Theory

The energy of a molecule in a weak, homogeneous electric field can be written as [3, 19]

$$E = E^0 - \mu_\alpha F_\alpha - (1/2)\, \alpha_{\alpha\beta} F_\alpha F_\beta - (1/6)\, \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/24)\, \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta$$

where F_α is the field at the origin, E^0 and μ_α the energy and permanent dipole moment of the free molecule, and $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ the dipole polarizability, first and second dipole hyperpolarizability. The greek suffixes denote Cartesian components and a repeated suffix implies summation over x, y, and z.

For a molecule of C_{3v} symmetry, like NH_3, μ_α has one independent component, $\alpha_{\alpha\beta}$ has two, $\beta_{\alpha\beta\gamma}$ three and $\gamma_{\alpha\beta\gamma\delta}$ four. With z as the C_3 axis, xz as a symmetry plane and the N atom on the positive z axis with the centre of mass at the origin, we specify the dipole moment tensor by μ_z, the dipole polarizability by α_{xx} and α_{zz}, the first dipole hyperpolarizability by β_{xxx}, β_{zxx} and β_{zzz} and the second dipole hyperpolarizability by γ_{xxxx}, γ_{xxxz}, γ_{xxzz}, and γ_{zzzz}. This choice is, obviously, not unique [1].

The calculation of the molecular properties from (1) is straightforward. Let $E(F_x, F_y, F_z)$ denote the energy of the molecule in the presence of a homogeneous electric field and

$$S_x(F) = E(F, 0, 0) + E(-F, 0, 0) - 2E^0, \tag{2}$$

$$S_z(F) = E(0, 0, F) + E(0, 0, -F) - 2E^0, \tag{3}$$

$$D_x(F) = E(-F, 0, 0) - E(F, 0, 0), \tag{4}$$

$$D_z(F) = E(0, 0, -F) - E(0, 0, F), \tag{5}$$

$$C(F, 0, F) = E(F, 0, F) - E(F, 0, 0) - E(0, 0, F) + E^0. \tag{6}$$

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It follows from (1)–(6) that

$$\mu_z \quad = (8\,D_z(F) - D_z(2\,F))/(12\,F), \tag{7}$$

$$\alpha_{xx} \quad = (S_x(2\,F) - 16\,S_x(F))/(12\,F^2), \tag{8}$$

$$\alpha_{zz} \quad = (S_z(2\,F) - 16\,S_z(F))/(12\,F^2), \tag{9}$$

$$\beta_{xxx} = (D_x(2\,F) - 2\,D_x(F))/(2\,F^3), \tag{10}$$

$$\beta_{zxx} = (C(F, 0, -F) - C(-F, 0, F))/F^3, \tag{11}$$

$$\beta_{zzz} = (D_z(2\,F) - 2\,D_z(F))/(2\,F^3), \tag{12}$$

$$\gamma_{xxxx} = (4\,S_x(F) - S_x(2\,F))/F^4, \tag{13}$$

$$\gamma_{xxxz} = 3(C(-F, 0, F) - C(F, 0, F))/F^4, \tag{14}$$

$$\gamma_{xxzz} = -2(C(F, 0, F) + C(F, 0, -F))/F^4, \tag{15}$$

$$\gamma_{zzzz} = (4\,S_z(F) - S_z(2\,F))/F^4. \tag{16}$$

We compute also isotropic and anisotropic components for the dipole polarizability and the hyperpolarizabilities as [1]

$$\bar{\alpha} \quad = (\alpha_{zz} + 2\,\alpha_{xx})/3, \tag{17}$$

$$\Delta\alpha = \alpha_{zz} - \alpha_{xx}, \tag{18}$$

$$\bar{\beta} \quad = (3/5)\,(\beta_{zzz} + 2\,\beta_{zxx}), \tag{19}$$

$$\Delta\beta = \beta_{zzz} - 3\,\beta_{zxx}, \tag{20}$$

$$\bar{\gamma} \quad = (3\,\gamma_{zzzz} + 8\,\gamma_{xxxx} + 12\,\gamma_{xxzz})/15\,. \tag{21}$$

3. Basis Set Construction and Computational Details

Relying on previous experience [17–19, 21–23], we used a (11s 7p 3d 1f/6s 2p 1d) [6s 4p 3d 1f/4s 2p 1d] basis set consisting of 114 primitive gaussian type functions (GTF) or 94 contracted GTF. This set was built upon a (9s 5p/4s) [4s 2p/2s] substrate [24] and augmented to [6s 4p/4s] by diffuse s- and p-GTF on nitrogen (exponents 0.064996, 0.019805 and 0.051481, 0.016024, respectively, in units of a_0^{-2}) and diffuse s-GTF on hydrogen (exponents 0.048273 and 0.013121). Next, a p-GTF and a d-GTF were added on hydrogen and nitrogen, respectively. Their exponents, 0.900 and 0.740, were chosen to minimize the energy E^0. In a further step, the basis set was augmented to [6s 4p 2d/4s 2p] by a diffuse p-GTF on hydrogen and a diffuse d-GTF on nitrogen. The exponents, 0.158 and 0.134, were chosen to maximize the isotropic component of the dipole polarizability $\bar{\alpha}$. The addition of a f-GTF on nitrogen and a d-GTF on hydrogen led to [6s 4p 2d 1f/4s 2p 1d]. The exponents were 0.147 and 0.081, respectively, and were chosen as follows: for each symmetry we located the values that maximize α_{xx} and those that minimize the anisotropy $\Delta\alpha$. The final value of the exponent was the mean of the aforementioned ones. The final, (11s 7p 3d 1f/6s 2p 1d) [6s 4p 3d 1f/4s 2p 1d] basis set, was obtained with the addition of a tight d-GTF on nitrogen with exponent 0.740 $(0.740/0.134)^{1/2}$ or 1.738982.

All calculations in this work were performed at the experimental molecular geometry as specified by $R_{\mathrm{NH}} = 1.012$ Å and $\widehat{\mathrm{HNH}} = 106.7°$. The Cartesian coordinates of the four nuclei are, in a_0, N (0, 0, 0.127860215), H (1.771674, 0, −0.592178202), and H (−0.885837, ±1.534314692, −0.592178202).

Weak fields were used in this work. The magnitude of the homogeneous field in (7)–(16) was $F = 0.001\ e^{-1}\,a_0^{-1}\,E_{\mathrm{h}}$.

All calculations were performed with Gaussian 86 [24].

4. Results and Discussion

The calculated molecular properties are shown in Tables 1, 2 and 3, along with a selection of SCF values obtained by other authors.

Dipole Moment

Our value for the dipole moment of NH_3 is $-0.6406\,e\,a_0$, in very good agreement with the $-0.635\,e\,a_0$ reported by Werner and Meyer [8], the $-0.6377\,e\,a_0$ by Lazzeretti and Zanasi [9], the $-0.6353\,e\,a_0$ by Amos et al. [10], the $-0.6370\,e\,a_0$ by Diercksen and Sadlej [11] and the $-0.642\,e\,a_0$ by Liu and Dykstra [12]. The value of $-0.6359\,e\,a_0$ obtained by Feller, Boyle and Davidson [25] with a [10s 8p 4d 1f/6s 4p 1d] basis set of 130 CGTF is, quite probably, the most accurate one and should be close to the Hartree-Fock limit for this property.

Dipole Polarizability

We have calculated the values of 13.2725 and 12.7489 $e^2\,a_0^2\,E_{\mathrm{h}}^{-1}$ for α_{zz} and α_{xx}, respectively. Our values are in very good agreement with the more accurate values listed in Table 1. Agreement is considerably better than 1% with the best results of Lazzeretti and Zanasi [9] and Diercksen and Sadlej [11]. The values of 13.98 and 13.03 $e^2\,a_0^2\,E_{\mathrm{h}}^{-1}$ reported by

Table 1. SCF dipole moment and polarizability of NH_3.

Reference	μ_z	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$
WM [a]	−0.627	13.43	12.71	12.95	0.72
	−0.635	13.98	13.03	13.35	0.95
LZ [b]	−0.6367	12.856	12.541	12.646	0.315
	−0.6490	12.885	12.585	12.685	0.300
	−0.6377	13.244	12.733	12.903	0.511
AHKRS [c]	−0.6353	12.960	12.583	12.709	0.377
DS [d]	−0.6370	13.32	12.76	12.95	0.56
	−0.6419	12.74	12.37	12.49	0.37
LD [e]	−0.642	13.19	12.64	12.82	0.55
HA [f]	−0.612	12.86	12.06	12.33	−0.80
	−0.687	10.28	10.15	10.19	0.13
	−0.623	12.51	11.90	12.10	0.61
S [g]	−0.756	5.76	9.45	8.22	−3.69
	−0.721	12.12	12.39	12.30	−0.27
	−0.737	12.54	12.48	12.50	0.05
RW [h]		13.24	12.52	12.76	0.72
M [i]	−0.6406	13.2725	12.7489	12.9234	0.5236

[a] Basis sets A and B respectively in [8]. Molecular geometry specified by $R_{NH}=1.9132\,a_0$ and $\widehat{HNH}=106.67°$.
[b] Basis sets (11s 7p 3d/5s 2p) [8s 5p 3d/3s 2p], (11s 7p 3d/5s 2p) [8s 5p 3d/3s 2p] (same as the first but with more tight d-GTF on nitrogen) and (14s 8p 3d 1f/10s 2p 1d) [9s 6p 3d 1f/6s 2p 1d] [9].
[c] Basis set (13s 8p 3d 1f/10s 2p) [7s 5p 3d 1f/5s 2p] at $R_{NH}=1.012$ Å and $\widehat{HNH}=106.7°$ [10].
[d] Basis sets (12s 8p 3d 1f/7s 2p 1d) [8s 5p 3d 1f/4s 2p 1d] and (11s 7p 2d/6s 2p) [9s 6p 2d/5s 2p], respectively at $R_{NH}=1.9132\,a_0$ and $\widehat{HNH}=106.67°$ [11].
[e] Basis set (11s 8p 3d/6s 2p) [7s 5p 3d/4s 2p] at $R_{NH}=1.012$ Å and $\widehat{HNH}=106.7°$ [12].
[f] Basis sets 6-311++G(3df, 3pd), DZP and DZP+. Calculations with each basis set are performed at the respective theoretical geometry [13].
[g] Basis sets 6-31 G**, 6-31 G(+d+p) and 6-31 G(+sd+sp) at $R_{NH}=1.012$ Å and $\widehat{HNH}=106.1°$ [14].
[h] Basis set (12s 8p 2d 1f/7s 2p 1d) [8s 5p 2d 1f/4s 2p 1d] at $R_{NH}=1.9132\,a_0$ and $\widehat{HNH}=106.67°$ [15].
[i] Present investigation, basis set (11s 7p 3d 1f/6s 2p 1d) [6s 4p 3d 1f/4s 2p 1d] at $R_{NH}=1.9124027\,a_0$ and $\widehat{HNH}=106.7°$.

Table 2. SCF first dipole hyperpolarizability of NH_3.

Ref.	β_{xxx}	β_{zxx}	β_{zzz}	$\bar{\beta}$	$\Delta\beta$
LZ [a]	−9.238	3.876	2.821	6.344	−8.807
	−8.374	5.705	4.003	8.648	−11.612
	−8.930	6.840	7.758	12.863	−12.762
LD [b]	−9.788	7.802	9.126	14.838	−14.280
M [c]	−8.77	7.21	11.71	15.68	−9.92

[a] See footnote b, Table 1.
[b] See footnote e, Table 1.
[c] See footnote i, Table 1. Present investigation.

Table 3. SCF second dipole hyperpolarizability of NH_3.

Ref.	γ_{xxxx}	γ_{xxxz}	γ_{xxzz}	γ_{zzzz}	$\bar{\gamma}$
LD [a]	1070	−119.9	1055	4261	2267
M [b]	1232	−106	1077	4319	2383

[a] See footnote e, Table 1.
[b] See footnote i, Table 1. Present investigation.

Werner and Meyer [8] are a few per cent higher than both the aforementioned ones and ours. Consequently, the $\bar{\alpha}$ and $\Delta\alpha$ obtained by those authors are higher than all the other values in Table 1. The anisotropy of the dipole polarizability shows strong dependence on the basis set. Further investigations are needed to obtain reliable estimates of the dipole polarizability close to the Hartree-Fock limit.

First Dipole Hyperpolarizability

Our values for β_{xxx}, β_{zxx} and β_{zzz} are −8.77, 7.21 and 11.71 $e^3 a_0^3 E_h^{-2}$, respectively. The values reported by Lazzeretti and Zanasi [9] show that with the notable exception of β_{xxx}, the components of the first dipole polarizability tensor depend quite strongly on the quality of the basis set employed in the calculation. The best results of Lazzeretti and Zanasi were presumably obtained with their large [9s 6p 3d 1f/6s 2p 1d] basis set (NH_3-III in their paper, see Table I) comprising 109 CGTF. The value of $\bar{\beta}$ calculated with the aforementioned basis set is 12.863 $e^3 a_0^3 E_h^{-2}$, rather low compared to the 14.838 and 15.68 $e^3 a_0^3 E_h^{-2}$ reported by Liu and Dykstra [12] and us, respectively. Thus, in comparison to the present values of β_{xxx}, β_{zxx} and β_{zzz}, the best values of Lazzeretti and Zanasi show an agreement of 1.8, −5.1 and −33.7% and those of Liu and Dykstra 11.6, 8.2 and −22.1%.

Second Dipole Hyperpolarizability

We have obtained 1232, −106, 1077, 4319 and 2383 $e^4 a_0^4 E_h^{-3}$ for γ_{xxxx}, γ_{xxxz}, γ_{xxzz}, γ_{zzzz}, and $\bar{\gamma}$, respectively. Our values are in remarkably good agreement with those reported by Liu and Dykstra [12]. Their $\bar{\gamma}$ is less than 5% lower than ours. The γ_{zzzz} value reported of Liu and Dykstra is 4261 $e^4 a_0^4 E_h^{-3}$, 1.3% lower than ours. The pattern observed in the case of β, where β_{xxx} is more stable than the other components, is now reversed, as γ_{zzzz} is practically the same while the γ_{xxxx} of Liu and Dykstra is 13.1% lower than ours. It should be noted that their basis set has no f-GTF on nitrogen or d-GTF on hydrogen. One should expect the Hartree-Fock limit for γ to be easier to estimate than that for β.

Comparison with Experiment

Although our results are not directly comparable to experimental values, as this would necessitate at least averaging over the ground vibrational state of the molecule, we include here a brief discussion of the available experimental data. A recent determination of the dipole moment in the ground vibrational state by CO_2 laser-microwave double resonance spectroscopy [4] led to a value of $-0.5791\, e a_0$. A semi-empirical estimate of the static $\bar{\alpha}$ based on dipole oscillator strength distributions (DOSD) [5] gave $14.56\, e^2 a_0^2 E_h^{-1}$. A value of $1.944\, e^2 a_0^2 E_h^{-1}$ for $\Delta\alpha$ has been obtained from measurements of the Rayleigh depolarization ratio at 632.8 nm combined with refractivity data from the literature [6]. Last, $\bar{\beta}$ and $\bar{\gamma}$ have been estimated at an optical frequency from dc-electric-field induced second harmonic generation (ESHG) measurements [8], and their magnitude is 48.4 ± 1.2 $e^3 a_0^3 E_h^{-2}$ and $6087 \pm 107\, e^4 a_0^4 E_h^{-3}$, respectively. Comparing the experimental values to the present results we are led to the conclusion that electron correlation would change significantly the SCF values.

5. Conclusions

We have reported SCF calculations of the dipole moment, dipole polarizability, first and second dipole hyperpolarizability of NH_3. Our values of β and γ should be the most accurate currently available ones. Further calculations are needed to obtain estimates of these properties close to the Hartree-Fock limit. Electron correlation effects are expected to be important for both hyperpolarizabilities.

Acknowledgements

The generous hospitality of the Computer Centre of the Computer Technology Institute of Patras is gratefully acknowledged. Thanks are also due to Ioannis Malekos and Panaghiotis Ktoridis for expert technical assistance and to Dr. Petros Koutsoukos for moral support.

[1] A. D. Buckingham and B. J. Orr, Quart. Rev. London **21,** 195 (1967).
[2] M. P. Bogaard and B. J. Orr, Int. Rev. Sci., Phys. Chem. Series 2, vol. 2 (A. D. Buckingham, ed.), p. 149 (1975).
[3] A. D. Buckingham, Adv. Chem. Phys. **12,** 107 (1967).
[4] K. Tanaka, H. Ito, and T. Tanaka, J. Chem. Phys. **87,** 1557 (1987).
[5] G. D. Zeiss and W. J. Meath, Mol. Phys. **33,** 1155 (1977).
[6] N. J. Bridge and A. D. Buckingham, Proc. Roy. Soc. London Ser. A **295,** 334 (1966).
[7] J. F. Ward and C. K. Miller, Phys. Rev. A **19,** 826 (1979).
[8] H. J. Werner and W. Meyer, Mol. Phys. **31,** 855 (1976).
[9] P. Lazzeretti and R. Zanasi, J. Chem. Phys. **74,** 5216 (1981).
[10] R. D. Amos, N. C. Handy, P. J. Knowles, J. E. Rice, and A. J. Stone, J. Phys. Chem. **89,** 2186 (1985).
[11] G. H. F. Diercksen and A. J. Sadlej, Mol. Phys. **57,** 509 (1986).
[12] S. Y. Liu and C. E. Dykstra, J. Phys. Chem. **91,** 1749 (1987).
[13] T. Helgaker and J. Almlöf, J. Chem. Phys. **89,** 4889 (1988).
[14] M. A. Spackman, J. Phys. Chem. **93,** 7594 (1989).
[15] W. Rijks and P. E. S. Wormer, J. Chem. Phys. **90,** 6507 (1989).
[16] G. Maroulis and A. J. Thakkar, J. Chem. Phys. **93,** 652 (1990).
[17] G. Maroulis and A. J. Thakkar, J. Chem. Phys. **93,** 4164 (1990).
[18] G. Maroulis, J. Chem. Phys. **94,** 1182 (1991).
[19] A. D. McLean and M. Yoshimine, J. Chem. Phys. **47,** 1927 (1967).
[20] D. M. Bishop and G. Maroulis, J. Chem. Phys. **82,** 2380 (1985).
[21] G. Maroulis and A. J. Thakkar, J. Chem. Phys. **88,** 7623 (1988).
[22] G. Maroulis and A. J. Thakkar, J. Chem. Phys. **90,** 366 (1989).
[23] T. H. Dunning, Jr., J. Chem. Phys. **53,** 2383 (1970).
[24] Gaussian 86, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA, 1984.
[25] D. Feller, C. M. Boyle, and E. R. Davidson, J. Chem. Phys. **86,** 3424 (1987).