The Journal of Physical Chemistry A

© Copyright 1998 by the American Chemical Society VOLUME 102, NUMBER 8, FEBRUARY 19, 1998

LETTERS

Electric Dipole Polarizability of As_4, a Challenging Problem for Both Experiment and Theory

Uwe Hohm*,† **and Dirk Goebel**

Institut für Physikalische und Theoretische Chemie, der TU Braunschweig, Hans-Sommer-Strasse 10, D-38106 Braunschweig, Germany

Panaghiotis Karamanis and George Maroulis*,‡

Department of Chemistry, University of Patras, GR-26500 Patras, Greece

Received: October 28, 1997; In Final Form: December 30, 1997

An experimental value of 116.7 ± 1.1 $e^2a_0^2E_h^{-1}$ for the static dipole polarizability of As_4 is deduced from the analysis of refractivity measurements in arsenic vapor. This is in close agreement with the theoretical result of 119.5 ± 3.6 $e^2a_0^2E_h^{-1}$, obtained from ab initio finite-field many-body perturbation theory and coupled-cluster calculations.

The electric dipole polarizability is a fundamental property of atomic and molecular systems. It is of importance to the rational approach to the interpretation of a wide range of phenomena, from intermolecular interactions[1] and the refractive index[2] to Rayleigh and Raman scattering.[2] The universality of the applications[3,4] has motivated systematic experimental and theoretical efforts in order to obtain reliable values of the dipole polarizability. Excellent reviews on the subject are available.[5–7] The aim of this paper is to report the determination of the polarizability of As_4 from experimental measurements and accurate quantum chemical calculations. Arsenic vapor is an important material in semiconductor technology. Its chemical and physical properties have been studied,[8–10] but very little is known about the electric properties of As_2 and As_4.

The equipment used as well as the high-temperature interferometric experiments have been described in detail in ref 11. To be brief, nonisothermal absolute measurements of the refractivity $[n(\omega) - 1]$ have been carried out at two frequencies of $\omega_1 = 0.071\,981\,2\ E_h\hbar^{-1}$ ($\lambda_1 = 632.99$ nm) and $\omega_2 = 0.083\,830\,7\ E_h\hbar^{-1}$ ($\lambda_2 = 543.516$ nm) at four different number densities C. $(n - 1) = \Delta N\lambda/l$ is determined by counting the interference fringe shift ΔN during complete evaporation of the arsene sample. $(l/2) \approx 50$ cm is the length of the sample cell, which is made from fused silica. The temperature range in which full evaporation was achieved lies between 850 and 880 K, and the maximum C of the As_4 vapor phase amounts to 2.7×10^{24} m^{-3}. Additionally, isothermal asymmetric white-light interferometry was applied after complete evaporation of the sample in the frequency range between 0.05 and 0.091 $E_h\hbar^{-1}$ with a resolution of about 3.5×10^{-5} $E_h\hbar^{-1}$. White-light interferometry yields a quasi-continuous refractive-index spectrum, which is fixed to the two refractivities $[n(\omega) - 1]$ obtained at ω_1 and ω_2.

It is well-established that at our experimental conditions arsene vapor consists mostly of As_4 molecules. However, at higher temperatures an increasing amount of As_2 is produced according to the equilibrium

---

*,† Author for correspondence for the experimental part (U.HOHM@TU-BS.DE).

*,‡ Author for correspondence for the theoretical part (MAROU@UPATRAS.GR).

S1089-5639(97)03469-5 CCC: $15.00

$$\mathrm{As_4} \leftrightarrow 2\mathrm{As_2} \tag{1}$$

We will estimate the influence of As_2 molecules present in the arsene vapor on our result of the dipole polarizability of As_4. We rely on the measurements of the equilibrium constant of Drowart et al.[12] and Herms et al.[13] At the lowest number density C used in our experiments of 6.0×10^{23} m^{-3} at 880 K, the upper limit of the ratio of the partial pressures is $p_{As_2}/p_{As_4} \leq 0.004$. This means that the main component of the arsene vapor is As_4, whereas As_2 can be regarded as an impurity. In the whole temperature and density range covered in our experiments, ideal-gas behavior of the arsene vapor can be assumed. Therefore, the measured refractivity $(n - 1)_A$ of a binary mixture of As_4 and As_2 at low densities can be described by the following mixing rule

$$(n - 1)_A = 2\pi a_0^3 (C_{As_4}\alpha_{As_4} + C_{As_2}\alpha_{As_2}) \tag{2}$$

where C_{As_4} and C_{As_2} are the number densities of As_4 and As_2, respectively, and $C_{As} = 4C_{As_4} + 2C_{As_2}$ is the number density of all arsene atoms present in the sample. a_0 is the atomic unit of length, and α is given in atomic units.[24] If we now introduce the degree of dissociation φ, which can be calculated from the equilibrium constant,[12,13] the dipole polarizability of As_4 is related to

$$\frac{(n - 1)_A}{(2\pi a_0^3)(C_{As}/4)} = \alpha_A = (1 - \varphi)\alpha_{As_4} + 2\varphi\alpha_{As_2} = \alpha_{As_4} + \varphi(2\alpha_{As_2} - \alpha_{As_4}) = \alpha_{As_4} + \varphi\Delta\alpha \tag{3}$$

where α_A is the apparent polarizability of the arsene vapor. In a previous paper[14] one of us has obtained an approximate relationship between the change of the dipole polarizability in the course of a chemical reaction and the bond dissociation energy. Using a dissociation energy of 0.0867 E_h[12] (227.6 kJ mol^{-1}) in eq 1, we yield a difference in the polarizabilities of $\Delta\alpha = 2\alpha_{As_2} - \alpha_{As_4} = -3.1\ e^2a_0^2E_h^{-1}$, which is approximately 2.5% of the polarizability of As_4. The order of magnitude of $\Delta\alpha$ compares favorably well with $\Delta\alpha \approx 4.5\ e^2a_0^2E_h^{-1}$ obtained by quantum chemical calculations (unpublished results on As_2 by G. Maroulis and P. Karamanis). With $\varphi = 0.004$, the correction $|\varphi\Delta\alpha|$ amounts to $\approx 0.02\ e^2a_0^2E_h^{-1}$, which is completely negligible compared to $\alpha_A \approx 125\ e^2a_0^2E_h^{-1}$ and also negligible in view of the accuracy of our measurements, which is on the order of 1%. Therefore, without any significant loss of accuracy, the polarizability of As_4 is related to the measured refractivity $(n - 1)_A$ via the relationship

$$[n(\omega,T) - 1]_A = 2\pi a_0^3 \frac{C_{As}}{4} \alpha(\omega,T) \tag{4}$$

Our experiments yield a thermal average $\langle\alpha(\omega)\rangle_T = \alpha(\omega,T)$ of the dipole polarizability of arsene. At $T = 870$ K the nonisothermal absolute measurements yield the dipole polarizabilities $\langle\alpha(\omega_1)\rangle_T = 122.72 \pm 0.37\ e^2a_0^2E_h^{-1}$ and $\langle\alpha(\omega_2)\rangle_T = 125.00 \pm 0.39\ e^2a_0^2E_h^{-1}$. These values are shown in Figure 1 (full circles) together with the quasi-continuously recorded polarizabilities of our white-light interferometric experiments (full curve). In order to obtain the static dipole polarizability we have fitted the frequency-dependent polarizabilities $\alpha(\omega)$ by a three-term Cauchy formula

$$\langle\alpha(\omega)\rangle_T = S_T(-2) + S_T(-4)\omega^2 + S_T(-6)\omega^4 \tag{5}$$

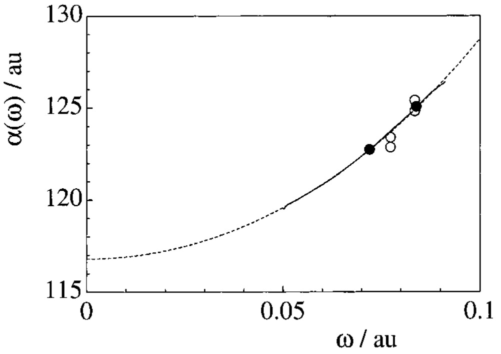

Figure 1. Frequency dependence of the mean dipole polarizability of As_4. ●, Absolute measurements; —, results from white-light interferometry; - - -, fitted curve, according to eq 6 (all this work). ○, measurements by Cuthbertson and Metcalfe (ref 15).

and by a one-term Kramers–Heisenberg dispersion formula

$$\langle\alpha(\omega)\rangle_T = \langle\alpha(0)\rangle_T \frac{\omega_{0T}^2}{\omega_{0T}^2 - \omega^2} \tag{6}$$

In particular we get $S_T(-2) = 116.638 \pm 0.011\ e^2a_0^2E_h^{-1}$, $S_T(-4) = 1149.0 \pm 4.4\ \hbar^2e^2a_0^2E_h^{-3}$, $S_T(-6) = (5.02 \pm 0.41) \times 10^3\ \hbar^4e^2a_0^2E_h^{-5}$, and $\langle\alpha(0)\rangle_T = 116.7966 \pm 0.0034\ e^2a_0^2E_h^{-1}$, $\omega_{0T} = 0.327\,969 \pm 0.000\,089\ E_h\hbar^{-1}$, respectively. In both fits an average deviation of 0.027 $e^2a_0^2E_h^{-1}$ is obtained. From experiment, we advance with a static dipole polarizability of As_4 of $\langle\alpha(0)\rangle_T = 116.7 \pm 1.1\ e^2a_0^2E_h^{-1}$ at $T = 870$ K. In this final result we have included a 1% uncertainty due to our measurements of the refractivity of the arsene vapor.[11] We compare our results with polarizabilities obtained from measurements of the refractive index of arsene vapor reported by Cuthbertson and Metcalfe,[15] who obtained $\langle\alpha(0.077\,316\ E_h\hbar^{-1})\rangle_T = 123.4$ and 122.9 $e^2a_0^2E_h^{-1}$ and $\langle\alpha(0.083\,419\ E_h\hbar^{-1})\rangle_T = 125.4$ and 124.8 $e^2a_0^2E_h^{-1}$, respectively. Figure 1 shows that these polarizabilities are close to ours (open circles). However, the frequency dependence of $a(\omega)$ and especially the static value $a(0)$ can hardly be obtained from these older results. As in the case of many other nonabsorbing substances, the effective transition frequency ω_{0T} of the single-term Kramers–Heisenberg dispersion formula lies in the vicinity of the ionization potential I_P, where the most recent value for As_4 is $I_P = 0.32\,192\ E_h$.[16]

In order to compare the static polarizability obtained in the calculations and in the experiments, it is essential to adapt both results to the same temperature. At moderate temperatures T electronic excitations can be neglected, and α changes due to temperature-dependent vibration–rotation[17] and black-body radiation effects.[18,19] The latter leads to an increase of the measured dipole polarizability $\langle\alpha(0)\rangle_T$ of 0.16 $e^2a_0^2E_h^{-1}$ at 870 K compared to the 0 K value.

We have also determined the dipole polarizability of As_4 relying on finite-field many-body perturbation theory (MP) and coupled-cluster (CC) calculations with carefully optimized basis sets of Gaussian-type functions (GTF). Our first goal was to obtain a reliable estimate of the Hartree–Fock limit of the polarizability. We used three initial basis sets for As. The first (hereafter A0) consists of (12s9p3d) primitive GTF contracted to [4s3p1d].[20] It was augmented to [5s4p1d] by the addition of diffuse 1s1p GTF. A d-GTF was added on [5s4p1d], and its exponent was chosen to maximize the dipole polarizability. The resulting [5s4p2d] (hereafter A1) was augmented further to [5s4p3d] (A2) and [5s4p3d1f] (A3).[21] A second basis set (15s11p5d)[6s4p1d] (hereafter B0),[22] with the addition of 2s2p diffuse GTF, subsequent optimization of a d-GTF (as above), and further addition of more d- and f-GTF gave the series B1−B6. The last basis set was a (17s13p6d)[6s5p2d] (C0) TZV set.[23] Enlarged systematically, as described above, it gave the series C1−C9. In Table 1 we display the dependence of the electric properties[24] of As_4 on basis set size. We have added the electric octopole (Ω) and hexadecapole (Φ) moment as these properties are sensitive measures of the quality of the wave function. All properties pertain to the experimental bond length of R_{As-As} = 2.435 Å.[25] The standard orientation is adopted for this tetrahedral molecule, with the origin at (0, 0, 0) and the four arsenic atoms on the directions defined by the origin and the points (1, 1, 1), (1, −1, −1), (−1, 1, −1), and (−1, −1, 1). The GAUSSIAN 92 set of programs[26] was used in all calculations.

TABLE 1: Dependence of the Electric Octopole (Ω/ea_0^3) and Hexadecapole (Φ/ea_0^4) Moment and Dipole Polarizability ($\alpha/e^2a_0^2E_h^{-1}$) of As_4 on Basis Set Type and Size at the SCF Level of Theory[a]

basis	description	CGTF	Ω	Φ	α
A1	[5s4p2d]	108	9.05	−81.65	110.68
A2	[5s4p3d]	128	6.32	−67.96	111.39
A3	[5s4p3d1f]	156	−1.96	−35.91	114.60
B1	[8s6p2d]	144	−3.22	−41.60	117.52
B2	[8s6p3d]	164	−2.35	−39.89	118.10
B3	[8s6p3d1f]	192	−3.76	−36.87	118.37
B4	[8s6p4d]	184	−2.52	−38.09	118.21
B5	[8s6p4d1f]	212	−3.71	−36.15	118.40
B6	[8s6p4d2f]	240	−3.74	−35.17	118.42
C1	[7s6p3d]	160	−0.98	−53.17	117.94
C2	[7s6p3d1f]	188	−6.75	−19.23	118.61
C3	[7s6p4d]	180	0.01	−49.74	119.10
C4	[7s6p4d1f]	208	−1.64	−43.98	119.29
C5	[7s6p4d2f]	228	−2.52	−41.30	119.46
C6	[7s6p5d2f]	256	−2.51	−40.59	119.51
C7	[7s6p6d]	220	−0.18	−49.56	119.27
C8	[7s6p6d1f]	248	−1.50	−42.85	119.44
C9	[7s6p6d2f]	276	−2.49	−40.79	119.52

[a] Experimental molecular geometry R_{As-As} = 2.435 Å. All properties in atomic units.

It is obvious from Table 1 that the electric properties of As_4 are strongly basis set dependent at the self-consistent field (SCF) level. The presence of f-GTF changes drastically the calculated electric moments. We expect the large B6 [8s6p4d2f] and C9 [7s6p6d2f] basis sets to yield values of Ω and Φ reasonably close to the respective Hartree−Fock limit. Relying on the C9 values, we advance as estimates of this limit $\Omega \approx -2.5 \pm 0.5$ ea_0^3 and $\Phi \approx -40 \pm 8$ ea_0^4. The convergence of the dipole polarizability is more easily evidenced by the contents of Table 1. The large B6 and C9 sets give values of 118.42 and 119.52, respectively, for $\alpha/e^2a_0^2E_h^{-1}$. We expect the value of 119.5 ± 1.2 $e^2a_0^2E_h^{-1}$ to be a reasonable estimate of the Hartree−Fock limit of α.

Electron correlation effects on electric properties are difficult to estimate, even for small systems.[27] We rely on Møller−Plesset perturbation theory [28] and CCSD(T), single- and double-excitation coupled-cluster theory with an estimate of connected triple excitations obtained via a perturbational treatment,[29] in order to obtain an estimate of the electron correlation effects on the polarizability of such a large system as As_4.

Our efforts are summarized by the results displayed in Table 2. The small A1 basis set was used in the CCSD(T) calculations. One should not expect a basis set of this size to yield conclusive evidence about the size of the electron correlation correction for α. Nevertheless, we retain the fact that electron correlation increases the value of α by a few percent, while MP2 gives $\alpha/e^2a_0^2E_h^{-1}$ = 113.35, which is quite close to the CCSD(T) value of 114.27. We used even larger basis sets to calculate MP2 values of the dipole polarizability. The large B3 set gives 118.37 (SCF) and 119.96 (MP2) $e^2a_0^2E_h^{-1}$, an increase of just 1.3%. Next, observe the trends in the values obtained with basis sets C1−C6: from C1 to C2 and from C3 to C6 the increase of the SCF falls to 0.7%. Thus, we gather, as we may, that the electron correlation effects on the dipole polarizability of As_4 do not exceed 1% of the SCF value. Consequently, we propose a theoretical estimate of α = 119.5(3.6) $e^2a_0^2E_h^{-1}$. It is both interesting and instructive to compare this value to the polarizability of four As atoms. With an atom polarizability[30] α_{As} = 29.1 $e^2a_0^2E_h^{-1}$, we obtain $\alpha_{As_4} - 4\alpha_{As}$ = 3.1 $e^2a_0^2E_h^{-1}$, an excess polarizability of no more than 2.6% of the total As_4 value. We note that we have neglected averaging over the ground vibrational state. We have not taken into account the relativistic effects on α, but their inclusion in the case of BrCN[31] was found to change the dipole polarizability by significantly less than 1%.

TABLE 2: Electron Correlation Corrections for the Dipole Polarizability of As_4[a]

basis	description	correlated molecular orbitals	SCF	D2	MP2
A1	[5s4p2d][b]	37−108	110.68	2.67	113.35
B3	[8s6p3d1f]	57−192	118.37	1.59	119.96
C1	[7s6p3d]	37−160	117.95	1.52	119.46
C2	[7s6p3d1f]	37−188	118.61	0.53	119.14
C3	[7s6p4d]	37−180	119.10	−0.23	118.88
C4	[7s6p4d1f]	57−208	119.29	1.23	120.52
C5	[7s6p4d2f]	57−236	119.46	0.83	120.29
C6	[7s6p5d2f]	57−256	119.51	0.83	120.35

[a] All properties in atomic units. [b] Higher levels of theory for A1: MP3 = 112.35, MP4 = 114.92, CCSD = 113.13, and CCSD(T) = 114.27 $e^2a_0^2E_h^{-1}$.

In conclusion, we have determined the static dipole polarizability of As_4 from refractivity measurements and ab initio quantum chemical calculations. Despite the difficulty of the endeavor, the two approaches converge remarkably well: experiment gives 116.7(1.1) $e^2a_0^2E_h^{-1}$, while theory suggests a value of 119.5(3.6) $e^2a_0^2E_h^{-1}$. The study of clusters constitutes a very active field,[32−35] but very little is known about the electric properties of these systems. We hope that this work provides useful insights and valuable information about the possibilities and the perspectives.

References and Notes

(1) Birnbaum, G., Ed.; *Phenomena induced by intermolecular interactions*; Plenum: New York, 1985.

(2) Bogaard, M. P.; Orr B. J. In *Molecular Structure and Properties*; Buckingham, A. D., Ed.; Butterworths: London, 1975; Vol. 2, p 149.

(3) Buckingham, A. D. In *Intermolecular Interactions: From Diatomic to Biopolymers*; Pullman, B., Ed.; Wiley: Chichester, 1978; p 1.

(4) Gray, C. G.; Gubbins, K. E. *Theory of Molecular Fluids*; Clarendon: Oxford, 1984; Vol. 1.

(5) Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1988**, *25*, 37.

(6) Hasanein, A. A. *Adv. Chem. Phys.* **1993**, *85*, 415.

(7) Bonin, K. D.; Kadar-Kallen, M. A. *Int. J. Mod. Phys. B* **1994**, *8*, 3313.

(8) Killen, K. P. *J. Appl. Phys.* **1993**, *73*, 2596.

(9) Leavitt, R. P.; Bradshaw, J. L. *J. Appl. Phys.* **1994**, *76*, 3429.

(10) Smirnov, Y. M. *Phys. Rev. A* **1995**, *51*, 2957.

(11) Goebel, D.; Hohm, U. *J. Phys. D: Appl. Phys.* **1996**, *29*, 3132.

(12) Drowart, J.; Smoes, S.; Vanderauwera-Mahieu, A. *J. Chem. Thermodyn.* **1978**, *10*, 453.

(13) Herms, M.; Wunderwald, U.; Irmer, G. *Cryst. Res. Technol.* **1993**, *28*, 965.

(14) Hohm, U. *J. Chem. Phys.* **1994**, *101*, 6362.

(15) Cuthbertson, C.; Metcalfe, E. P. *Philos. Trans. R. Soc. London* **1907**,

207, 135.

(16) Wang, L. S.; Reutt-Robey, J. E.; Niu, B.; Lee, Y. T.; Shirley, D. A. *J. Electron Spectrosc. Relat. Phenom*. **1990**, *51*, 513.

(17) Hohm, U.; Trümper, U. *J. Raman Spectrosc*. **1995**, *26*, 1059.

(18) Hohm, U.; Trümper, U. *Chem. Phys*. **1994**, *189*, 443.

(19) Hohm, U. *Z. Naturforsch*. **1996**, *48a*, 805.

(20) Poirier, R.; Kari, R.; Csizmadia, I. G. *Handbook of Gaussian basis set*; Elsevier: Amsterdam, 1984; p 615, Table 33.1.1.

(21) Construction details for all basis sets and the values of the optimimal exponents of the polarization GTF are available from the corresponding author.

(22) Binning, R. C.; Curtiss, L. A. *J. Comput. Chem*. **1990**, *11*, 1206.

(23) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys*. **1994**, *100*, 5829.

(24) The first nonvanishing electric moment of a molecule of tetrahedral symmetry is the octopole. Both the octopole and the hexadecapole moment tensor as well as the dipole polarizability tensor have only one independent component; see definitions in: Buckingham, A. D. *Adv. Chem. Phys*. **1967**, *12*, 107. Atomic units are used for all properties. Conversion factors to SI units are length, 1 $a_0 = 0.529\,177\,249 \times 10^{-10}$ m, Ω, 1 $ea_0^3 = 2.374\,182 \times 10^{-50}$ cm^3, Φ, 1 $ea_0^4 = 1.256\,363 \times 10^{-60}$ Cm,^{4} α, 1 $e^2a_0^2E_h^{-1} = 1.648\,778 \times 10^{-41}$ C^2 m^2 J^{-1}.

(25) Morino, Y.; Ukaji, T.; Ito, T. *Bull. Chem. Soc. Jpn.* **1996**, *39*, 64.

(26) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92 (Revision C)*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1992.

(27) Spackman, M. A. *J. Phys. Chem*. **1989**, *93*, 7594.

(28) Urban M.; Cernusak I.; Kellö, V.; Noga, J. *Methods Comput. Chem.* **1987**, *1*, 117.

(29) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(30) *Handbook of Chemistry and Physics,* 77th ed.; CRC Press: Boca Raton, FL, 1996.

(31) Kellö, V.; Sadlej, A. J. *Mol. Phys.* **1992**, *75*, 209.

(32) Schlecht, S.; Schäfer, R.; Woenckhaus, J.; Becker, J. A. *Chem. Phys. Lett.* **1995**, *246*, 315.

(33) Freeman, D. L.; Doll, J. D. *Annu. Rev. Phys. Chem*. **1996**, *47*, 43.

(34) Schäfer, R.; Schlecht, S.; Woenckhaus, J.; Becker, J. A. *Phys. Rev. Lett*. **1996**, *76*, 471.

(35) Vasiliev, I.; Ögüt, S.; Chelikowsky, J. R. *Phys. Rev. Lett*. **1997**, *78*, 4805.