

Dispersion of the refractive index of cadmium vapor and the dipole polarizability of the atomic cadmium 1S_0 state

Dirk Goebel and Uwe Hohm

*Institut für Physikalische und Theoretische Chemie der Technischen Universität Braunschweig, Hans-Sommer-Straße 10,
D-38106 Braunschweig, Federal Republic of Germany*

(Received 15 June 1995)

We report measurements of the frequency dependence of the refractive index and polarizability of cadmium vapor in the frequency range between $\omega=0.045$ and 0.091 a.u. The quasicontinuous refractive index spectra have been measured at $T\approx 1050$ K with a high-temperature Michelson interferometer using the technique of dispersive Fourier-transform spectroscopy. The dispersion of the dipole polarizability $\alpha(\omega)$ of Cd obtained in our experiments can be represented as $\alpha(\omega)=\alpha(0)\omega_0^2/(\omega_0^2-\omega^2)$, with a static polarizability of $\alpha(0)=(49.65\pm 1.46\pm 0.16)$ a.u. and an effective transition frequency of $\omega_0=(0.250\ 61\pm 0.000\ 23)$ a.u. In addition, these measurements yield approximations for the dispersion interaction energy constant $C_6=466$ a.u. and the second hyperpolarizability $\gamma(0)=1.1\times 10^5$ a.u.

PACS number(s): 32.10.Dk, 07.60.Ly, 51.70.+f

INTRODUCTION

The dipole polarizability $\alpha(\omega)$ is one of the most fundamental electro-optical properties of atoms and molecules and it is involved in many basic formulas [1]. However, for many atoms $\alpha(\omega)$ is only known to within 25% [1], which is unacceptable in view of its fundamental importance. Additionally, in most cases $\alpha(\omega)$ is only available at one frequency ω and its frequency dependence turns out to be totally unknown. In order to remove these deficiencies, we have started systematic experimental investigations of the dispersion of the refractive index and dipole polarizability $\alpha(\omega)$ of atomic systems. In the following we will report on our results of atomic cadmium 1S_0 .

In the case of ground-state cadmium the polarizability $\alpha(\omega)$ is a scalar quantity. Outside absorption bands it can be described by the familiar sum-over-states formula [2]

$$\alpha(\omega) = \sum_{n>0} \frac{f_n}{\omega_{0n}^2 - \omega^2} \approx \frac{f}{\omega_0^2 - \omega^2} = \alpha(0) \frac{\omega_0^2}{\omega_0^2 - \omega^2}, \quad (1)$$

where the oscillator strength f_n of the transition $|n\rangle \leftarrow |0\rangle$, as well as the corresponding transition energy ω_{0n} , is given in a.u. The symbol \sum means summation over the discrete part of the spectrum and integration over the continuum. In limited frequency ranges far away from any resonance it is sufficient to use the approximation on the right-hand side of Eq. (1), which is called a one-term Kramers-Heisenberg dispersion formula. In this case f and ω_0 are an effective oscillator strength and an effective transition frequency, respectively.

Series expansion of Eq. (1) yields the Cauchy formula, which is valid up to the first electronic transition frequency ω_{01}

$$\alpha(\omega) = \sum_{k=1}^{\infty} S(-2k) \omega^{2k-2}, \quad (2)$$

in which the dipole oscillator strength sums $S(-2k)$ are defined via [3]

$$S(k) = \sum_{n>0} f_n \omega_{0n}^k. \quad (3)$$

Equations (1) and (2) are not only useful for the description of the frequency dependence of the polarizability, but they can also be used with success to get approximations of other fundamental properties, which are of current interest in experimental and theoretical studies of metal atoms [4–6]. In particular, the dispersion interaction energy coefficient C_6 [7], the static second hyperpolarizability $\gamma(0)$ [8], and the r^{-6} parts of the mean incremental pair polarizability $\Delta\alpha_{12}$ and the incremental pair polarizability anisotropy $\Delta\kappa_{12}$ [9] should be mentioned, which are related to the properties in Eqs. (1) and (2) via

$$C_6 \approx \frac{3}{4} S^2(-2) \omega_0, \quad (4)$$

$$\begin{aligned} \gamma(0) &\approx 27.36 S(-3) S(-4) / S(-2) \\ &\approx 27.36 S(-4) [S(-4) / S(-2)]^{1/2}, \end{aligned} \quad (5)$$

and

$$\begin{aligned} \Delta\alpha_{12} &= f(r) + 4S(-2) [S^2(-2) + 2.85S(-4)] r^{-6}, \\ \Delta\kappa_{12} &= g(r) + 6S(-2) [S^2(-2) + 1.14S(-4)] r^{-6}, \end{aligned} \quad (6)$$

where $f(r)$ and $g(r)$ are functions of the internuclear distance r [10].

EXPERIMENT

Nowadays, a variety of techniques for the measurement of α is available, such as electric-field gradient methods [11–13], light-force technique [14–16], and atomic beam interferometry [17]. However, α can be determined only at one frequency (usually $\omega=0$). Therefore, the important information about the frequency dependence of the polarizability is not obtainable in these measurements and the calculation of

TABLE I. Experimental conditions and measured refractivities $[n(\omega, \rho) - 1]$ of atomic cadmium at different frequencies ω . In all measurements, the volume V of the sample cell is $V = 26.5 \pm 0.2 \text{ cm}^3$.

T (K)	m (10^{-6} kg)	ρ (mol m^{-3})	$\ell(T)$ (m)	$10^5[n(\omega, \rho) - 1]$		
				$[\omega \text{ (a.u.)}] = 0.07198$ $[\lambda \text{ (nm)}] = 632.990$	0.08383 543.516	0.14014 325.130
1043	6.16 ± 0.02	2.0679 ± 0.0082	0.998572 ± 0.000032	6.2964	6.6540 6.6948 6.7220	7.2282
1083	11.03 ± 0.01	3.7028 ± 0.0076	0.999276 ± 0.000030	9.9931 10.4523		
1058	16.28 ± 0.02	5.4652 ± 0.0076	0.999065 ± 0.000038	17.2910		
1003	17.64 ± 0.02	5.9217 ± 0.0076	1.000723 ± 0.000040	18.1536 18.2485 18.2485	18.3575 18.5476 18.9278	23.0999

related properties [see Eqs. (4)–(6)] is not possible.

To overcome these disadvantages we have used the classical technique of measuring the refractive index $n(\omega, \rho)$ dependent on the amount-of-substance density ρ of evaporized cadmium in order to determine $\alpha(\omega)$. The polarizability at the frequency ω is obtained according to the Lorentz-Lorenz relation

$$\frac{n^2(\omega, \rho) - 1}{n^2(\omega, \rho) + 2} = \frac{4}{3} \pi N_A a_0^3 \alpha(\omega) \rho, \quad (7)$$

where $\alpha(\omega)$ is the polarizability in a.u., N_A is Avogadro's constant, and $a_0^3 = 1.481\,847\,4 \times 10^{-31} \text{ m}^3$ is the atomic unit of the polarizability. Additionally dispersive Fourier transform spectroscopy is used in order to obtain the full quasi-continuous refractive index spectrum of cadmium vapor between $10\,000$ and $20\,000 \text{ cm}^{-1}$ [$0.045 < \omega \text{ (a.u.)} < 0.91$], from which the frequency dependence of $\alpha(\omega)$ is calculated [18]. Our apparatus consists mainly of an evacuated high-temperature Michelson twin interferometer with parallel guided beams, which is described in detail in Ref. [19]. Each arm of the interferometer has a length of approximately 250 cm to ensure thermal stability of the end mirrors and of the beam-splitter cube. The interferometer is illuminated with laser radiation sources of $\omega_1 = 0.071\,981\,16 \text{ a.u.}$ ($\lambda_1 = 632.990 \text{ nm}$, HeNe laser), $\omega_2 = 0.083\,830\,75 \text{ a.u.}$ ($\lambda_2 = 543.516 \text{ nm}$, HeNe laser), and $\omega_3 = 0.140\,138\,9 \text{ a.u.}$ ($\lambda_3 = 325.130 \text{ nm}$, HeCd laser), in order to make measurements of the refractivity $[n(\omega, \rho) - 1]$ at discrete frequencies ω dependent on the amount of substance density ρ . Measurements of the dispersive Fourier transform spectra have been carried out using a 100-W halogen lamp as the white-light source. All interferograms were detected with a photomultiplier tube (Hamamatsu R636). The cadmium samples were prepared in a glove box flushed with dry nitrogen. Cadmium (purity 99.999%) of mass m was filled into the sample cell (quartz-glass Suprasil, cylindrical tube with an inner diameter of 8 mm) of volume $V \approx 26.5 \text{ cm}^3$ and length $\ell/2 \approx 50 \text{ cm}$. The cell was evacuated and fused off. It was placed in one arm of the interferometer, while the other arm contains an optically identical evacuated reference cell. Fast heating of the cells to the final temperature T by means of a pipe furnace (maximum temperature $T = 1300 \text{ K}$) leads to

evaporation of the cadmium sample. This increases the optical path difference δ between the two arms of the interferometer. The resulting interference fringe shift ΔN is mainly due to the evaporation of the Cd sample, but is also influenced to a small extent by the thermally induced movement of the interferometer end mirrors. However, evaporation of the cadmium is much faster and both processes occur on two different time scales. Hence ΔN recorded at the wavelength λ is related to the refractivity of the Cd sample via

$$(n - 1) = \frac{\Delta N \lambda}{\ell}. \quad (8)$$

In these high-temperature experiments the uncertainty in ΔN is given by $\Delta(\Delta N) = \pm 2$ and $|\Delta(\Delta N)/\Delta N| \leq 0.02$. This is much larger than the uncertainty in the wavelength $\Delta\lambda/\lambda = \pm 1.6 \times 10^{-5}$ and in the length of the sample cell $\Delta\ell/\ell = \pm 4 \times 10^{-5}$. Therefore, $\Delta(n - 1)/(n - 1) = \pm 0.02$ results. Taking into account the uncertainty of the amount-of-substance density $|\Delta\rho/\rho| \leq 4 \times 10^{-3}$, the polarizability is determined in our experiments with $|\Delta\alpha/\alpha| \leq 3\%$. This is about 50 times the uncertainty that usually results in our measurements of the polarizability of gases [20–22].

All relevant parameters of the absolute measurements of $(n - 1)$ are presented in Table I. Only those measurements in which ΔN could be determined unambiguously have been considered.

If the cadmium sample is completely evaporated and the apparatus is stable with respect to variations in the interference fringe number ($\Delta N \approx 0.1 \text{ h}^{-1}$ at 1050 K), dispersive interferograms $I(\delta)$ are recorded with a halogen lamp. $I(\delta)$ is obtained by changing the optical path difference δ in one of the two arms of the interferometer by moving one end mirror of the Michelson interferometer. The recorded interferogram $I(\delta)$ is Fourier transformed and deconvoluted from the corresponding spectrum of the empty apparatus. This yields the desired refractive index spectrum [18]. At present, the resolution of our dispersive Fourier-transform spectroscopy measurements is given by $4.6 \times 10^{-5} \text{ a.u.}$ (10 cm^{-1}). As dispersive Fourier-transform spectroscopy in the visible is a relative technique, the recorded data are matched to the refractivities $[n(\omega_1, \rho) - 1]$ and $[n(\omega_2, \rho) - 1]$ obtained from the absolute measurements.

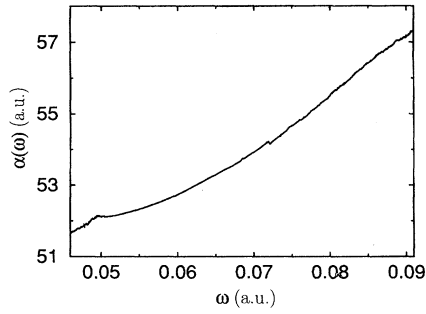


FIG. 1. Frequency dependence of the dynamic dipole polarizability $\alpha(\omega)$ of cadmium.

RESULTS AND DISCUSSION

In order to obtain the polarizabilities of Cd at the discrete frequencies ω_1 , ω_2 , and ω_3 , $[n(\omega, \rho) - 1]$ was fitted vs ρ according to Eq. (7). We have used a constrained fit, which ensures that $n \equiv 1$ at $\rho = 0$. From this fit, the polarizabilities $\alpha(\omega_1) = (54.20 \pm 0.95)$ a.u., $\alpha(\omega_2) = (56.23 \pm 0.38)$ a.u., and $\alpha(\omega_3) = (68.8 \pm 2.3)$ a.u. were obtained. It should be noted that the frequency ω_3 is close to the ${}^3P_1 \leftarrow {}^1S_0$ transition of atomic cadmium located at 0.139 a.u. (326.2 nm) as well as to the $O_u^+ ({}^3\Pi_u) \leftarrow XO_g^+ ({}^1\Sigma_g^+)$ absorption band of the cadmium dimer [23], which is possibly present to a small extent in the evaporized cadmium sample. In Fig. 1 the quasi-continuously recorded frequency dependence of the polarizability of atomic cadmium is shown. The curve is the arithmetic mean of 13 measurements. Beside various calculations

on other metal atoms (see, e.g., [5]), this is the first experimentally determined polarizability curve of a vaporized metal over a large frequency range. Since ground-state cadmium does not show any absorption of electromagnetic radiation at a frequency of 0.05 a.u., the small hump located at this frequency must be regarded as an artifact.

The polarizability curve is fitted to the right-hand side of Eq. (1) and to a Cauchy formula, given by the first two terms of Eq. (2). The resulting fit parameters $\alpha(0) \equiv f/\omega_0^2$, ω_0 , $S(-2)$, and $S(-4)$ are given in Table II. Of course, $\alpha(0) = S(-2)$ should result for the static polarizability. However, since the experimental data have been obtained in a limited frequency range, the fit results in two slightly different values for the static polarizability. From these two values an arithmetic mean of $\alpha(0) = 49.65 \pm 0.16$ a.u. can be calculated. $\omega_0 = 0.25061$ a.u. corresponds to an effective transition energy of $\hbar\omega_0 = 6.8$ eV. This is a reasonable result because ω_0 lies well between the first electronic transition energy $\omega_{01} = 0.139$ a.u. and the ionization threshold $\omega_p = I_p/\hbar = 0.330$ a.u. of cadmium.

Analyses of the experimentally determined refractivities of Cuthbertson and Metcalfe [24], according to (1) and (2), yield $\alpha(0) = 50.0 \pm 2.8$ and $\omega_0 = 0.288 \pm 0.047$, which are in reasonable accordance with our data, although only four refractivities between 0.0694 a.u. (656.2 nm) and 0.0879 a.u. (518.3 nm) have been measured [24]. Note that the uncertainties in $\alpha(0)$ and ω_0 are much larger in those early experiments. Our first experimental determination of the dispersion of the refractive index and the polarizability of cadmium [25] deviates considerably from our present results.

TABLE II. Static polarizabilities $\alpha(0)$, effective eigenfrequencies ω_0 , and Cauchy moments $S(-2)$, $S(-4)$ of atomic cadmium.

Method	$\alpha(0)$ (a.u.)	ω_0 (a.u.)	$S(-2)$ (a.u.)	$S(-4)$ (a.u.)
experimental ^a	50.0 ± 2.8	0.288 ± 0.047	49.7 ± 3.3	1397 ± 515
nonrelativistic multiconfiguration self-consistent field ^b	56.5		56.5	
relativistic self-consistent field ^c	51.8		51.8	
relativistic multiconfiguration self-consistent field ^c	42.5		42.5	
nonrelativistic coupled perturbation theory ^d			75.6	2920
nonrelativistic time-dependent local-density approximation ^e	43.3		43.3	
relativistic time dependent local-density approximation ^e	42.9		42.9	
experimental ^{f,h}	45.31 ± 0.20	0.29077 ± 0.00054		
relativistic linear response ^g	49 ± 12		49 ± 12	
experimental ^h	49.814 ± 0.010	0.25061 ± 0.00023	49.491 ± 0.013	937.3 ± 2.5

^aReference [24].

^bReference [26].

^cReference [27].

^dReference [28].

^eReference [29].

^fReference [25].

^gReference [1].

^hThis work. The uncertainty is the rms error of the fit; note that $|\Delta\alpha(0)/\alpha(0)| \leq 0.03$ due to the experimental uncertainties.

However, the result in [25] is only of limited value because the performance of the measurements has been improved significantly since then.

Except for the results of Bratsev and Khodyreva [28], only $\alpha(0) = S(-2)$ of atomic cadmium 1S_0 has been calculated. These values are given in Table II. It is noteworthy that the recommended value of $\alpha(0) = (49 \pm 12)$ a.u. [1], obtained with a relativistic linear-response method, is very close to the experimentally determined static polarizability $\alpha(0) = (49.65 \pm 1.49 \pm 0.16)$ a.u. of this work. However, the uncertainty has been considerably diminished in the present work. The Cauchy moments $S(-2)$ and $S(-4)$ calculated by Bratsev and Khodyreva [28] are much higher than all other values. It seems that nonrelativistic coupled perturbation theory as used by these authors is not capable of yielding accurate values for the frequency dependence of the polarizability of cadmium. Using the approximation (4) for the dispersion interaction energy constant and (5) for the second hyperpolarizability, we yield $C_6 = 466$ a.u. and $\gamma(0) = 1.1 \times 10^5$ a.u. as the first results for atomic cadmium. These data can be compared with very rough approximations recently given for the higher homolog mercury [6], where $C_6 = 418$ a.u. and $\gamma(0) = 1.6 \times 10^4$ a.u. were obtained. These data have been used in order to reproduce experimentally determined depolarized interaction induced light scattering

(DILS) spectra of mercury. We believe that our experimental results presented for cadmium and the use of more reasonable approximations given by (6) will present a more profound basis for the analyses of DILS spectra of cadmium, which, however, has not been recorded up to now.

CONCLUSIONS

We have shown that high-temperature refractive index measurements are capable of yielding accurate values of the dipole polarizability of vaporized cadmium. The advantage of this technique is that the frequency dependence of the polarizability can be determined quasicontinuously over a wide frequency range. From this, related properties, such as the dispersion interaction energy constant, the second hyperpolarizability, and parts of the incremental pair polarizability tensor, can be approximated. At present, the main drawback is the limited temperature range with a maximum temperature of 1300 K in which our interferometer can operate.

ACKNOWLEDGMENT

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

-
- [1] T.M. Miller, in *Handbook of Chemistry and Physics*, edited by D.R. Lide, 73rd ed. (CRC, Boca Raton, FL, 1992).
- [2] A. Dalgarno, *Adv. Chem. Phys.* **12**, 143 (1967).
- [3] A. Kumar and W.J. Meath, *Can. J. Chem.* **63**, 1616 (1985).
- [4] M. Sampoli, A. Guasti, F. Barocchi, R. Winter, J. Rathenow, and F. Hensel, *Phys. Rev. A* **42**, 6910 (1992).
- [5] M. Marinescu, H.R. Sadeghpour, and A. Dalgarno, *Phys. Rev. A* **49**, 982 (1994).
- [6] F. Barocchi, F. Hensel, and M. Sampoli, *Chem. Phys. Lett.* **232**, 445 (1995).
- [7] O. Goscinski, *Int. J. Quantum Chem.* **2**, 761 (1968).
- [8] U. Hohm, *Chem. Phys. Lett.* **183**, 304 (1991).
- [9] U. Hohm, *Chem. Phys. Lett.* **211**, 498 (1993).
- [10] L. Frommhold, *Advan. Chem. Phys.* **41**, 1 (1981).
- [11] T.M. Miller and B. Bederson, *Adv. At. Mol. Phys.* **13**, 1 (1977).
- [12] T.M. Miller and B. Bederson, *Adv. At. Mol. Phys.* **25**, 37 (1989).
- [13] R. Schäfer, J. Woenckhaus, J.A. Becker, and F. Hensel, *Z. Naturforsch. Teil A* **50**, 445 (1995).
- [14] M.A. Kadar-Kallen and K.D. Bonin, *Phys. Rev. Lett.* **68**, 2015 (1992).
- [15] K.D. Bonin and M.A. Kadar-Kallen, *Phys. Rev. A* **47**, 944 (1993).
- [16] M.A. Kadar-Kallen and K.D. Bonin, *Phys. Rev. Lett.* **72**, 828 (1994).
- [17] C.R. Ekstrom, J. Schmiedmayer, M.S. Chapman, T.D. Hammond, and D.E. Pritchard, *Phys. Rev. A* **51**, 3883 (1995).
- [18] D. Goebel, U. Hohm, K. Kerl, U. Trümper, and G. Maroulis, *J. Phys. Chem.* **98**, 13 123 (1994).
- [19] U. Hohm and K. Kerl, *Meas. Sci. Technol.* **1**, 319 (1990).
- [20] U. Hohm, *Mol. Phys.* **78**, 929 (1993).
- [21] U. Hohm and U. Trümper, *Chem. Phys.* **189**, 443 (1994).
- [22] U. Hohm and U. Trümper, *J. Raman Spectrosc.* (to be published).
- [23] M. Czajkowski, R. Bobkowski, and L. Krause, *Phys. Rev. A* **40**, 4338 (1989).
- [24] C. Cuthbertson and E.P. Metcalfe, *Philos. Trans.* **207**, 135 (1907).
- [25] D. Goebel, U. Hohm, and K. Kerl, *J. Mol. Struct.* **349**, 253 (1995).
- [26] H. Basch, M.D. Newton, J. Jafri, J.W. Moscovitz, and S. Topiol, *J. Chem. Phys.* **68**, 4005 (1978).
- [27] M.E. Rosenkrantz, W.J. Stevens, M. Krauss, and D.D. Konowalow, *J. Chem. Phys.* **72**, 2525 (1980).
- [28] V.F. Bratsev and N.V. Khodyreva, *Opt. Spectrosc.* **54**, 551 (1983).
- [29] F.A. Parpia and W.R. Johnson, *Phys. Lett.* **99A**, 172 (1983).