PHYSICAL REVIEW A **76**, 052515 (2007)

Polarizabilities of Ba and Ba_2: Comparison of molecular beam experiments with relativistic quantum chemistry

Sascha Schäfer,[*] Max Mehring, and Rolf Schäfer
Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany

Peter Schwerdtfeger
Center of Theoretical Chemistry and Physics, Institute of Advanced Studies and the Institute of Fundamental Science, Massey University (Auckland Campus), Private Bag 102904, North Shore MSC, Auckland, New Zealand

(Received 17 August 2007; published 29 November 2007)

The dielectric response to an inhomogeneous electric field has been investigated for Ba and Ba_2 within a molecular beam experiment. The ratio of the polarizabilities per atom of Ba_2 and Ba is determined to be 1.30 ± 0.13. The experimental result is compared to a high level *ab initio* quantum chemical coupled cluster calculation with an energy-consistent scalar relativistic small-core pseudopotential for Ba. For the barium atom a polarizability of 40.82 $Å^3$ is obtained and the isotropic value of the polarizability calculated for Ba_2 is 97.88 $Å^3$, which is in good agreement with the experimental results, demonstrating that a quantitative understanding of the interaction between two closed-shell heavy element metal atoms has been achieved.

DOI: 10.1103/PhysRevA.76.052515 PACS number(s): 33.15.Kr, 31.25.−v

I. INTRODUCTION

The interaction of closed-shell heavy elements has recently achieved much attention, particularly concerning the metal-to-insulator transition in small metal clusters [1]. However, it remains a challenge for computational chemistry to accurately describe these interesting types of bonding, since an in-depth treatment of both electron correlation and relativistic effects is necessary. Experimentally determined static electric polarizabilities are therefore a valuable tool to check these difficult quantum chemical calculations since the dielectric response to an electric field is a sensitive probe of the electronic structure [2,3]. In the present work we report on the experimental determination of the static polarizability of the barium dimer within a molecular beam electric field deflection experiment [4]. The experimental results are compared to a high level *ab initio* quantum chemical calculation. It is our aim to demonstrate that a quantitative agreement between theory and experiment can be achieved. We have focused on the barium dimer as it is a closed-shell system and therefore reasonably simple to be treated theoretically with high accuracy and also shows a large dielectric response, which leads to a small experimental error. In addition, the polarizability of the barium atom is known to be 39.7 ± 3.2 $Å^3$ [5], in good agreement with quantum chemical calculations [6–8]. It is hence possible to use the barium atom as an internal calibration in the experiment to obtain a reliable absolute value for the static polarizability of the barium dimer. Experimental values of the ground state Ba_2 are only available for the vibrational spectrum [9] and the ionization potential [10]; also, only a few theoretical studies on Ba_2 are published [11–15].

II. EXPERIMENT

The dielectric properties of isolated particles can be measured by deflecting a highly collimated molecular beam in an inhomogeneous electric field [4]. The response of the molecular beam to the electric field depends on the induced dipole moments of the particles. The induced dipole moments are proportional to the electric field strength E. Since the deflection d toward high field is proportional to the strength of the electric field gradient and the induced dipole moments [16,17], d is given by

$$d = \frac{C}{mv^2}(\Delta\phi)^2\frac{\alpha}{N}. \tag{1}$$

The polarizabilities per atom α/N could be obtained from the measured deflection d, if the applied electric potential $\Delta\phi$, the velocity v, and the atomic mass m of the particles and the apparatus function C is known. The apparatus function C depends on the geometry of the electrodes generating the inhomogeneous field and the distance between the electric field and the detection region. A detailed description of this method and its application is given by Miller and Bederson [4].

A schematic overview of the apparatus used in the present investigation is shown in Fig. 1. Barium atoms and clusters are produced by a pulsed laser vaporization source [18]. A barium rod is irradiated with the focused light of a Nd:YAG laser, forming a small amount of metal plasma. The plasma is then cooled down in a flow of helium gas and condenses to form clusters. The pressure of the helium pulse in the cluster source has been measured with an integrated piezoelectric crystal-based pressure sensor to be typically (1–10) mbar [19]. The helium-barium cluster mixture is then expanded through a cylindrical nozzle (length: 20 mm, width: 3 mm) held at room temperature into a high vacuum apparatus, thereby producing a supersonic beam of barium species. The molecular beam becomes narrowed with a double skimmer,

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[*] Corresponding author.

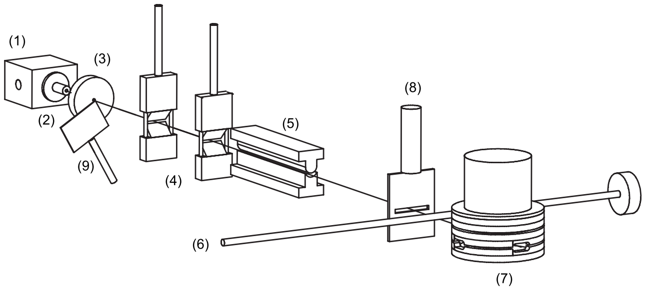

FIG. 1. Experimental setup of the molecular beam experiment. Clusters are generated in a pulsed laser vaporization source (1), expanding through a nozzle (2) into the high vacuum apparatus, skimmed (3), and collimated (4) before they enter the inhomogeneous electric field (5). After a field-free flight path of about 1.2 m the clusters become ionized by a photon with an energy of 7.89 eV from an excimer laser (6). The intensity of the molecular beam is measured with a time-of-flight mass spectrometer (7) in dependence of the slit (8) position. The velocity of the different species in the molecular beam is determined with a shutter (9) based on a hard disk drive.

afterwards passing through a chopper for measuring the velocities of the species in the molecular beam. The chopper unit is based on a hard disk drive voice-coil actuator for fast and easy controllable chopping, as has been suggested in the literature in the case of a laser beam shutter [20]. After passing two collimators the molecular beam reaches the inhomogeneous electric field. The electric field used in the experiment is the electric analog of the so-called "two-wire-magnetic-field" first developed by Rabi and co-workers [21]. The advantage of this field geometry is that the product of the electric field and its gradient is approximately constant over the dimensions of the molecular beam. The experimental setup of the deflection electrodes is similar to the one reported by Bederson *et al.* [22]. The distance between the two electrodes is 1.5 mm and the maximum achievable value of the electric field is 20 kV/mm. About 1200 mm downstream from the deflection unit the clusters are ionized with an excimer laser (7.87 eV) after they have passed a slit having a width of 330 μm. The position of the slit can be varied with an accuracy of 2 μm. Ionized clusters reaching the acceleration zone of the time-of-flight mass spectrometer (TOFMS) are then deflected perpendicular to the molecular beam axis with a strong voltage pulse applied to the meshes of the acceleration unit of the TOFMS and detected by an even cup [17]. The intensity of the ionized clusters is then measured with and without electric field in dependence of the slit position. The spatial separation of the ionization region and the acceleration zone guarantees that mass spectra free of photofragmentation products are obtained. The measured molecular beam profiles without electric field have a full width at half maximum (FWHM) of typically 1.2 mm. The spatial extension of the ionization laser pulse and also the aperture of the acceleration unit is about 10 mm in diameter. This ensures that all clusters passing the collimators could be collected with the TOFMS, because the observed deflections for the highest applied electric potential of 28 kV are about 0.3 mm.

III. THEORY

For the theoretical part we used the recently adjusted energy-consistent scalar relativistic small-core pseudopotentials for Ba [23]. The pseudopotentials are accompanied by a large optimized valence basis set, $(14s12p7d5f3g)$ contracted to $(11s9p7d5f3g)$. It was shown that a smaller version of this basis set already gives accurate results for the static dipole polarizability of neutral Ba. Spin-orbit effects are neglected as they are of second order. Electron correlation was treated by applying second-order Møller-Plesset perturbation theory (MP2) and coupled cluster (CC) with single and double excitations (CCSD) plus perturbative triples [CCSD(T)] [24]. A full active orbital space was used in the pseudopotential MP2 and CC calculations. The polarizabilities were obtained by numerical differentiation of the total energy with respect to the applied field. We applied homogeneous electric fields of 0.0, 5.14, 10.28, and 25.71×10^8 V/m. For the dimer Ba_2 we used the calculated bond distance of 4.881 Å obtained by Spiegelmann and co-workers [11] using relativistic configuration interaction calculations. They also give a slightly larger spin-orbit coupled value of 4.905 Å, but we chose the smaller distance as basis set incompleteness corrections and improvement in the electron correlation procedure would lead to smaller distances. We note that our scalar relativistic CCSD(T) distance obtained for Ba_2 of 5.048 Å is too large mostly due to basis set incompleteness. To obtain an accurate distance to an error less than 0.01 Å would be a formidable task.

IV. EXPERIMENTAL AND THEORETICAL RESULTS

The dielectric response of the Ba atom and dimer has been investigated with a molecular beam experiment. Molecular beam profiles, i.e., the intensities of the different species measured with the TOFMS in dependence of the position of the slit, are shown in Fig. 2. The data has been obtained with and without an applied electric potential of 28 kV keeping the nozzle at room temperature. For the Ba atom and the dimer a deflection toward high field is clearly visible. From the collimator and slit geometry one would expect that the shape of the molecular beam profile is trapezoidal. However, the beam profiles are smeared out because the velocity distribution is not sharp and also the intensity of the ionization laser is not completely homogeneous over the total molecular beam. For simplicity the molecular beam profiles have therefore been analyzed by fitting Gauss functions to the experimental data. The adapted Gaussians are also shown in Fig. 2. From the maxima of the Gaussians obtained for the data sets with and without electric field, the deflection d of the molecular beam could be determined. Alternatively, the deflection is determined by moving the data points with electric field against the data points obtained without electric field until the deviation between both data sets is minimized. Both procedures lead to identical results within the uncertainty of the fit or the minimization routine. Deflections d including the uncertainty are also displayed in Fig. 2 for the Ba atom and dimer.

In order to convert deflections into absolute values of the polarizabilities, the velocities v of Ba and Ba_2 as well as the

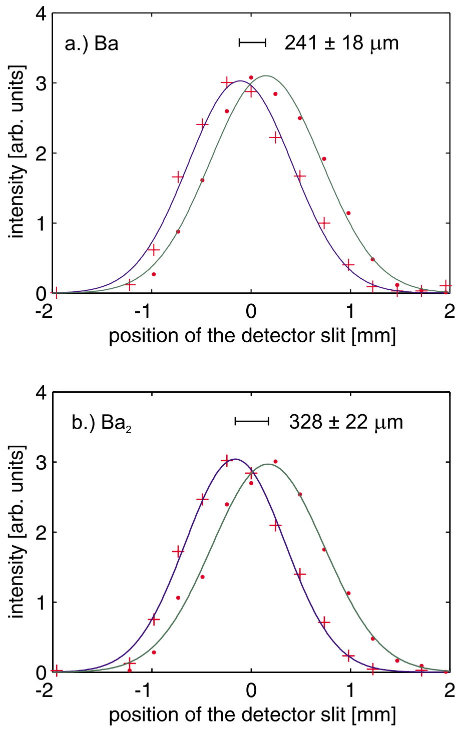

FIG. 2. (Color online) Molecular beam profiles of Ba (a) and Ba$_2$ (b): The intensity of Ba and Ba$_2$ is measured with a TOFMS for 20 positions of the slit. The crosses (dots) are measured without (with) electric field. The deflection of the beam is determined either by fitting Gaussians to experimental data points (blue lines: without electric field; green lines: with electric field) or by shifting the data points detected with electric field against the point recorded without field until the mean square deviation becomes a minimum. The beam deflection for an applied electric potential $\Delta\phi=28$ kV amounts to 241 ± 18 μm for the Ba atom and 328 ± 22 μm for the Ba dimer.

apparatus function C have to be determined. Mean cluster velocities of 1410 m/s for Ba and 1380 m/s for Ba$_2$ are measured with the chopper unit with an accuracy of $\pm(2-3)\%$. Taking the velocities of Ba and Ba$_2$ into account, the ratio of the polarizabilities per atom could be obtained to $\frac{\alpha(\mathrm{Ba}_2)}{2\alpha(\mathrm{Ba})}=1.30\pm0.13$. The apparatus function has been obtained by calibration with the well known value of the polarizability of the Ba atom. With this procedure the absolute value of the polarizabilty of Ba$_2$ is determined to be 103.2 Å$^3\pm10\%$. Comparing this value with theory, due to the calibration, the additional uncertainty of the polarizability of the Ba atom of ±8% also has to be taken into account [5].

For the Ba atom we theoretically obtain $\alpha=40.82$ Å^3 at the CCSD(T) level of theory, which is in good agreement with the estimated experimental value by Bederson and coworkers of 39.7 ± 3.2 Å^3 (see Ref. [3] for a review on accepted atomic dipole polarizabilities). The Hartree-Fock (HF) value is too large (47.96 Å^3) whereas the MP2 value is far too low (32.81 Å^3). In a similar way density functional theory can give results which vary substantially between the functionals applied. For example, using various density functionals we get for the dipole polarizability 34.86 Å^3 local density approximation (LDA), 39.03 Å^3 (PW91), and 37.62 Å^3 (B3LYP). Our coupled cluster value is also smaller than the recently determined scalar relativistic CAS-PT2 value of Roos and co-workers (46.2 Å^3) [6], but in perfect agreement with the all-electron Douglas-Kroll CCSD(T) value of Sadlej and co-workers (40.58 Å^3) [8] or with a recent result by Porsev and Derevianko using configuration interaction and many-body perturbation theory (40.53 Å^3) [7]. We note that the perturbative triple contributions in the coupled cluster procedure cannot be neglected, i.e., at the CCSD level of theory we have $\alpha=42.02$ Å^3. We can also give an estimate of the first hyperpolarizability, which is $\gamma=7.69\times10^5$ a.u.$=2.47\times10^{-47}$ C^3 m^3/J^2.

TABLE I. Absolute values of the polarizability for Ba and Ba$_2$; polarizability ratio $\frac{\alpha(\mathrm{Ba}_2)}{2\alpha(\mathrm{Ba})}$.

	α(Ba) (Å^3)	α(Ba$_2$) (Å^3)	α(Ba$_2$)/[2α(Ba)]
HF	47.96	111.53	1.16
MP2	32.81	73.99	1.13
LDA	34.86	78.48	1.13
PW91	39.01	87.27	1.12
B3LYP	37.62	84.92	1.13
CCSD	42.02	100.41	1.19
CCSD(T)	40.82	97.88	1.20
Roos *et al.* [6]	46.02		
Sandley *et al.* [7]	40.58		
Porsev *et al.* [8]	40.53		
Expt.	39.7±8% [4]	103.2±10% ±8%	1.30±10%

For Ba$_2$ we obtain $\alpha_\parallel=160.11$ Å^3 and $\alpha_\perp=66.76$ Å^3 at the CCSD(T) level of theory. This gives an isotropic value of $\alpha=97.88$ Å^3 and an anisotropic value of $\beta=\alpha_\parallel-\alpha_\perp=93.35$ Å^3. Again the perturbative triple contributions in the coupled cluster procedure cannot be neglected, i.e., at the CCSD level of theory we have $\alpha=100.41$ Å^3 and $\beta=96.77$ Å^3. This compares to the HF level of theory $\alpha=111.53$ Å^3 and $\beta=103.71$ Å^3 and the MP2 level of theory $\alpha=73.99$ Å^3 and $\beta=53.04$ Å^3. Again, second-order perturbation theory is not sufficient to obtain even reasonable polarizabilities and electron correlation leads to significant changes. A similar picture is obtained at the density functional theory level, i.e., $\alpha=78.48$ Å^3 and $\beta=58.02$ Å^3 (LDA), $\alpha=87.27$ Å^3 and $\beta=64.44$ Å^3 (PW91), and $\alpha=84.92$ Å^3 and $\beta=65.64$ Å^3 (B3LYP). Comparing to the atomic value we get an increase in the polarizability (the so-called interaction polarizability) of $\Delta_{\mathrm{int}}=\alpha(\mathrm{Ba}_2)-2\alpha(\mathrm{Ba})=16.12$ Å^3. This can be easily explained as two closed-shell atoms interacting, giving an antibonding molecular orbital, which becomes more polarizable with decreasing interatomic distance.

The experimental and theoretical results are summarized in Table I. A comparison of the experimental value of the polarizability ratio of Ba$_2$ and Ba with the coupled cluster results demonstrates a quantitative agreement within the uncertainty of the experiment. From the measured molecular beam profiles of Ba_2 it is not possible to derive a value for the polarizability anisotropy β, since values of up to 300 Å^3 for β did not significantly influence the experimental data [25]. In order to obtain sound results for the anisotropy the resolution of the apparatus has be to significantly improved.

The analysis of the experimental beam deflection has been performed under the condition that an alignment of the Ba_2 molecules does not take place during the supersonic expansion. This seems to be a reasonable assumption, if one compares the expansion conditions in our experiments with those reported in the literature [26,27]. However, if the ensemble of Ba_2 molecules becomes slightly aligned the ratio of the isotropic polarizabilities $\frac{\alpha(Ba_2)}{2\alpha(Ba)}$ will be larger than 1.30.

We mention that Ortiz and Ballone give a much smaller bond distance of about 4.5 Å from density functional calculations [13], which, however, does not agree well with density functional results of Chen *et al.* (4.96 Å) [14]. However, density functional theory without the inclusion of a long-range dispersive type of interaction cannot describe the bonding in barium clusters well [15]. Nevertheless, at a distance of 4.5 Å we obtain α=73.88 Å^3 and β=54.86 Å^3 at the MP2 level and basically no change for the isotropic polarizability at this shorter distance, which points toward strong overlap effects. Furthermore, we tested the basis set incompleteness for Ba_2 at the MP2 level of theory by additional diffuse and hard functions, which gave only small changes. We also checked the basis set superposition error by using the Boys-Bernardi counterpoise correction for the total energy [28], which lowers the parallel component of the Ba_2 polarizability by only 0.009 Å^3. In order to improve on our current result, an accurate equilibrium bond distance of Ba_2 is required.

The physical origin of the experimental and theoretical results can be discussed by considering the dipole-induced dipole (DID) model of Silberstein [29,30]. This approach is based on a point-charge approximation and describes the polarizability for intermediate and long-range interatomic separation reasonably well. The interaction of the induced dipole moments of the two Ba atoms results in a polarization, which depends on the orientation of the Ba_2 molecule relative to the external electric field, giving rise to a parallel and a perpendicular component $\alpha_{\parallel}(Ba_2)$ and $\alpha_{\perp}(Ba_2)$ of the polarizability

$$\alpha_{\parallel}(\mathrm{Ba}_2) = \frac{2\alpha(\mathrm{Ba}) + 4\alpha(\mathrm{Ba})^2/R^3}{1 - 4\alpha(\mathrm{Ba})^2/R^6}, \tag{2}$$

$$\alpha_{\perp}(\mathrm{Ba}_2) = \frac{2\alpha(\mathrm{Ba}) - 2\alpha(\mathrm{Ba})^2/R^3}{1 - \alpha(\mathrm{Ba})^2/R^6}. \tag{3}$$

Taking a bond length of R=4.881 Å and the experimental value of α(Ba)=39.7 Å^3 into account, one calculates within the DID model $\alpha_{\parallel}(Ba_2)$=250.3 Å^3, $\alpha_{\perp}(Ba_2)$=59.2 Å^3, and $\alpha(Ba_2)$=122.9 Å^3. Hence the DID model predicts that the increase in the parallel component more than offsets the decrease in the perpendicular component for the isotropic polarizability, which is also found experimentally. However, the quantitative agreement between the DID model and the experimental and quantum chemical results is rather poor, because this model neglects overlap effects, which will reduce the anisotropy compared to the DID model at short interatomic separations.

V. CONCLUSION

We have measured molecular beam deflection profiles of Ba and Ba_2. The ratio of the polarizabilities per atom between Ba_2 and Ba has been obtained to 1.30 with an accuracy of ±10%. This result is compared with coupled cluster calculations taking energy-consistent scalar relativistic small-core pseudopotentials for Ba into account, demonstrating a quantitative agreement between theory and experiments. This indicates that the interaction of closed-shell heavy elements could be accurately described by an in-depth treatment of electron correlation and relativistic effects.

ACKNOWLEDGMENTS

We acknowledge support from the Deutsche Forschungsgemeinschaft by Grant No. SCHA885/7-1 and by the Marsden Fund administered by the Royal Society of New Zealand. S.S. acknowledges financial support from Fonds der Chemischen Industrie.

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