

Experimental and theoretical electric dipole polarizabilities of Al and Al₂

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The static electric dipole polarizabilities of the aluminum atom and dimer have been measured by deflecting a molecular beam in an inhomogeneous electric field. Collimated aluminum-cluster beams are produced by a pulsed laser vaporization source. Deflections are determined by means of a novel position-sensitive time-of-flight mass spectrometer. The measured polarizabilities are 6.8 ± 0.3 and $19 \pm 2 \text{ \AA}^3$ for the atom and dimer, respectively, in good agreement with the *ab initio* calculations presented here. The experimental techniques described here allow precise determination of the mean deflections and velocities of the particles in the beam and are generally applicable for beams produced by laser vaporization sources.

I. INTRODUCTION

Molecular-beam measurements of static dipole polarizabilities date back more than 50 years and up to now the polarizabilities have been measured for only a dozen or so elements.^{1,2} The static dipole polarizability of an atom can be measured by deflecting a highly collimated beam of particles in an inhomogeneous electric field. In the standard method the deflections are measured by scanning a slit across the molecular beam and recording the transmitted intensity as a function of the slit position, so that a profile of the deflected beam is obtained. This profile is compared with that obtained for the undeflected beam and the polarizability is found using the relationship

$$\alpha = Kv^2md / \left[E \frac{dE}{dz} \right], \quad (1)$$

where d is the deflection, α the polarizability, v the beam velocity, dE/dz the component of the field gradient perpendicular to the beam, and K a geometrical constant. Due to the small deflections attainable, it is necessary to have long beams (on the order of 2 m) for the particles to be deflected several tenths of a millimeter at the detector. The beam must be highly collimated and a narrow detector slit must be used in order to have adequate resolution. It is clear that intense and stable molecular beams are required and this is the reason why polarizabilities of so few elements have been measured.

In this paper we introduce a new method of measuring deflections based on a position-sensitive time-of-flight mass spectrometer (PSTOF),³ to accurately measure deflections without scanning a slit. The source used is a modified laser vaporization source (LVS),⁴ which produces intense and stable beams of refractory materials. Since the LVS has a lower duty cycle compared to continuous hot sources, the use of PSTOF makes it possible to measure the polarizabilities of the aluminum atom, dimer, and clusters for the first time. Here we will focus on the atom and dimer; the cluster results have been dis-

cussed in a previous publication.⁵ The paper is organized as follows: in the next section we will describe the experimental method, followed by the experimental results for the atom and dimer. In Sec. IV we will present the results of local-density approximation calculations performed by one of us (I.M.), followed by a concluding section.

II. APPARATUS AND EXPERIMENTAL METHODS

A schematic overview of the apparatus is shown in Fig. 1. The cluster beam is produced by an improved pulsed-laser vaporization source⁴ that we briefly describe here. An aluminum rod is irradiated with the focused light from the second harmonic of a neodymium-doped yttrium aluminum garnet (Nd: YAG) laser (60 mJ/pulse, 10 Hz). A plasma of the metal is formed and then cooled in a flow of He gas from a pulsed nozzle, which is timed to coincide with the laser pulse. The inert-gas metal-vapor mixture is expanded out of a nozzle into a vacuum thereby producing a supersonic beam of atoms and clusters.

A thin-walled aluminum tube filled with lithium was

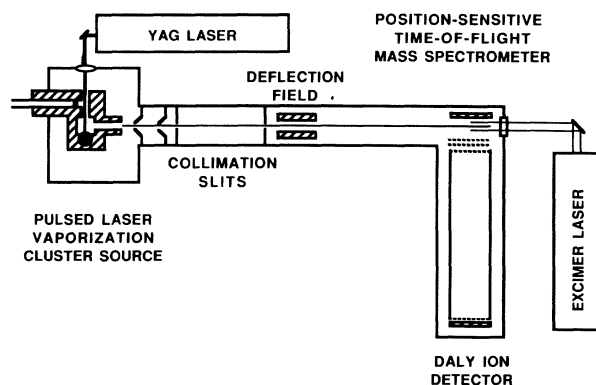


FIG. 1. Schematic diagram of the apparatus (not to scale). The distance from the source to the deflecting field is 1.4 m and from the source to the mass spectrometer is 2.4 m.

also utilized in order to produce a beam consisting of lithium and aluminum atoms. This mixed beam is used to measure the Al atom polarizability relative to that of the lithium atom, as will be explained below. The beam is skimmed (3-mm-diam orifice) and then collimated by two 0.8-mm slits separated by 100 cm. The collimated beam then passes through an inhomogeneous electric field, 12.5 cm in length, with field gradients up to 300 kV/cm². After a drift path of 100 cm the deflected beam enters the position-sensitive mass spectrometer.

Once in the spectrometer the particles are photo-ionized by an ArF excimer laser [193 nm, 0.1 (mJ/cm²)/pulse, 15-ns width]. The ions are then accelerated perpendicular to the molecular beam trajectory by means of three successive uniform electric fields.

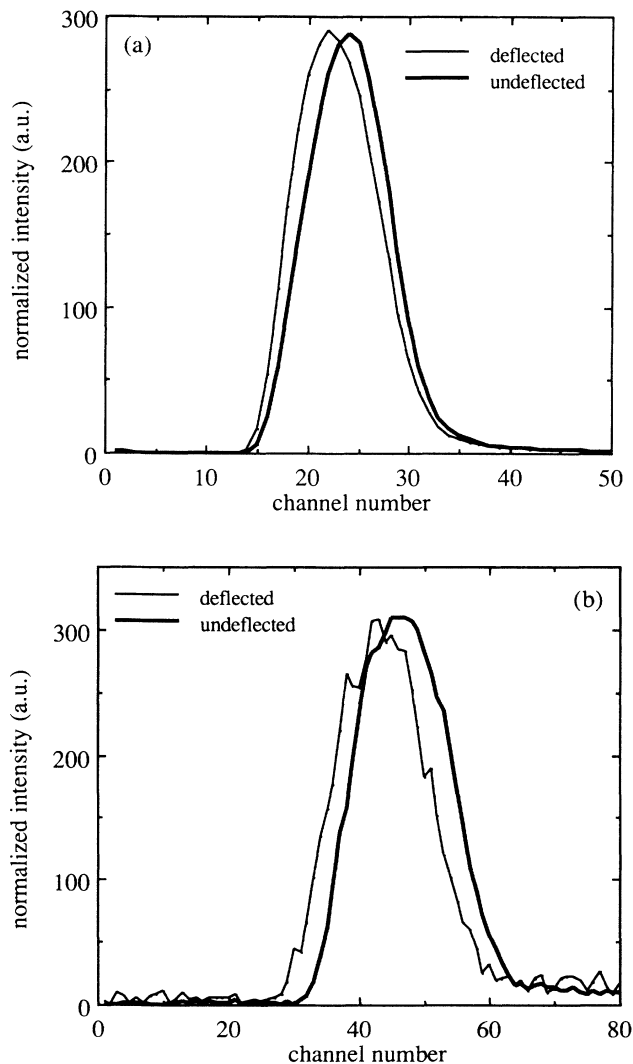


FIG. 2. Time-of-flight mass spectra of collimated beam of aluminum atoms and dimers taken in the position sensitive mode. (a) Shift of the aluminum atom peak due to an applied deflection potential of 28 kV. Each channel corresponds to 10 ns. (b) Shift of the aluminum dimer peak due to an applied deflection potential of 20 kV. Each channel corresponds to 10 ns.

After a 100-cm drift path they are detected by an ion Daly detector.⁶ A fast digital oscilloscope records the analog signal from the detector. In the position-insensitive mode the accelerating electric fields are adjusted so that the time-of-flight (TOF) of the ions of a specific mass is independent of their initial position at the time of the ionization. However, the fields may also be chosen so that the TOF depends on the mass as well as on the initial position where the ionization took place. In this way the displacements of the deflected particles are reflected in the shifts of the TOF mass peaks. In Fig. 2 we show the TOF spectra of a collimated beam of aluminum atoms and dimers with and without the deflecting field activated. The shift in the peaks position is caused by the deflections, demonstrating the position-sensitive detection method.

The great advantage of this method compared with the conventional one outlined in the Introduction is that the deflections of all particles in the beam are measured simultaneously, and that the entire beam is detected. Moreover, the entire deflected beam profile is recorded rather than a small fraction of it, as in the case where a detector slit is used. Therefore beam intensity fluctuations do not affect the shape of the detected beam profile, as they do with the standard method. The relative polarizabilities are determined by comparing the deflected and undeflected beam profiles, using the information on the particle velocities.

III. RESULTS AND DATA ANALYSIS

The velocities of the particles in the molecular beam must be accurately measured [see Eq. (1)]. The velocities are selected and determined by the time interval between the vaporization laser pulse and the ionization laser pulse and by the distance from the source to the detector. However, due to the finite dwell time of the particles in the source,⁴ the velocities are measured in an auxiliary experiment for increased accuracy. For these measurements the TOF spectrometer is mounted coaxially with the molecular beam, rather than perpendicularly, and mass spectra are taken in the position-insensitive mode. In this configuration the TOF depends both on the mass of the ion as well on its initial velocity along the axis of the spectrometer. In the perpendicular configuration, the ions have negligible velocities along that axis. The shift of the positions of the corresponding mass peaks in the two configurations gives the velocities of the particles. The measured atom and dimer velocity distributions are found to be very narrow [0.02×10^5 cm/sec (FWHM)], and the mean velocities are practically identical: $(1.876 \pm 0.005) \times 10^5$ and $(1.868 \pm 0.005) \times 10^5$ cm/sec respectively, under the experimental conditions of the deflection measurements. Note that the narrowness of the velocity distributions is due to the experimental method which, in fact, selects the cluster velocities.

The geometrical constant K [Eq. (1)] is determined from measurements of lithium atoms for which the polarizability is well known.¹ For this purpose we produced a beam with aluminum and lithium atoms, using the latter as a reference. Since Eq. (1), the polarizability ratio is found to be

$$\frac{\alpha_2}{\alpha_1} = \frac{d_2}{d_1} \frac{m_1}{m_2} \left(\frac{v_2}{v_1} \right)^2, \quad (2)$$

where d is the deflection and v is the velocity. We used the fact that the electric field and the electric-field gradient in (1) are proportional to the potential V , therefore the deflections are proportional to the square of V . Measurements have been performed for electric-field gradients ranging from 120 to 300 kV/cm². The deflections are found to be proportional to the square of the applied voltages, as expected (Fig. 3). Deflections of the beam are reflected by the variation of the TOF in the position-sensitive detection mode. The average shift in the TOF of a mass peak is determined by numerical integration:

$$\Delta t = \int I^*(t')t' - I(t')t' dt, \quad (3)$$

where t is the time which corresponds with the channel number in the digital oscilloscope, and I^* and I are normalized intensities of the deflected and undeflected peaks.

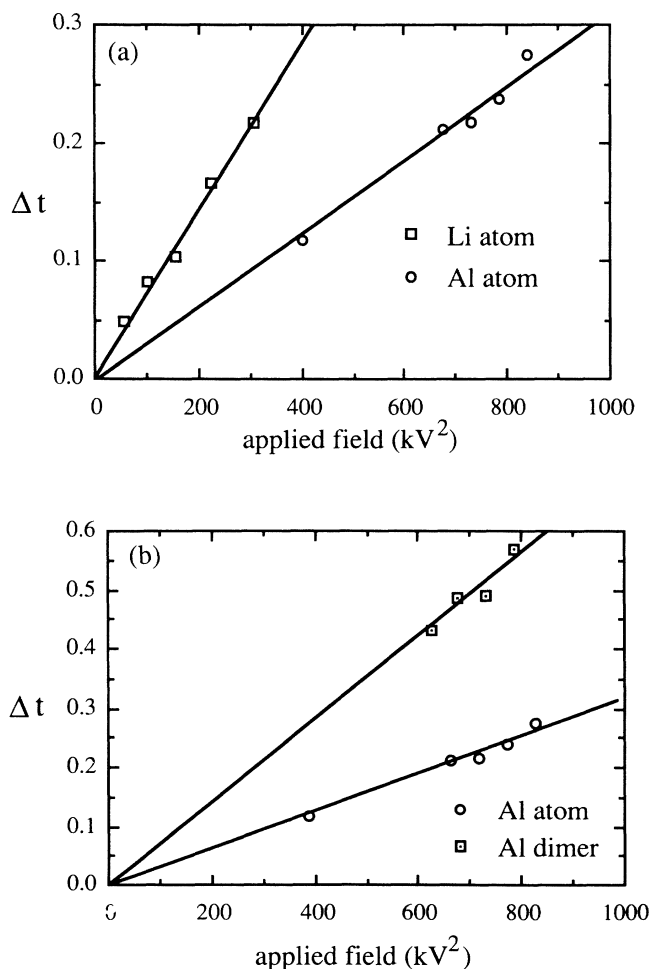


FIG. 3. Electric deflection for atomic Al and Li atom beams and for Al dimer as a function of the square of the applied deflection voltage. (a) Al and Li atoms normalized deflections. (b) Al atom and dimer normalized deflections.

As shown in Fig. 3, we find linear dependence between Δt and V^2 . The ratio of the slope of the linear fits for lithium and aluminum gives the ratio of the deflections and hence the ratio of the polarizabilities. The final results of these measurements, using as calibration the lithium atom polarizability, are as follows:

$$\alpha(\text{Al}) = 6.8 \pm 0.3 \text{ \AA}^3, \quad (4)$$

$$\alpha(\text{Al}_2) = 19 \pm 2 \text{ \AA}^3. \quad (5)$$

IV. COMPUTATIONAL METHOD AND THEORETICAL RESULTS

The total energy of the molecules is calculated using density-functional theory⁷ with a local approximation for the exchange-correlation energy,⁸ and takes into account the spin polarization (LSDA). The molecular orbitals are expanded on a localized Gaussian basis set including some d -polarization functions ($4s4p2d$). We checked carefully that the calculated molecular properties are well converged with respect to the basis-set size. To treat the electron-ion interaction, a norm-conserving *ab initio* pseudopotential⁹ has been used. Performing all-electron calculations for the atom, we find that the ionization potential is reproduced within a precision of 0.3% as we use this pseudopotential.

The method used to calculate the polarizability of the aluminum atom and dimer has already been applied to sodium clusters and has been described in detail elsewhere.¹⁰ The symmetric polarizability tensor is obtained from the derivative of the induced dipole moment with respect to the static electric field \mathbf{E}

$$\mathbf{P}_{\text{ind}} = \alpha \mathbf{E} + O(\mathbf{E}^2). \quad (6)$$

The derivative is calculated numerically from the solutions of the Kohn-Sham equations⁷ including the static electric potential $\mathbf{E} \cdot \mathbf{r}$. Since the experimental values of the applied electric field mentioned above are too small to align the molecule along a preferred direction, the rotationally averaged polarizability has to be compared with experiment. In the case of the dimer, it is obtained from

$$\bar{\alpha} = \frac{2\alpha_{\perp} + \alpha_{\parallel}}{3}. \quad (7)$$

The values used for the electric field are in the range of 5×10^7 and 5×10^9 V m⁻¹. They are sufficiently small so that all linear effects are dominant, and large enough to avoid the numerical noise.

These are essentially three candidates for the ground state of Al₂ distinguished by the symmetry of the highest occupied molecular orbitals: one singlet state $^1\Sigma_g^+$ and two triplet states $^3\Pi_u$ and $^3\Sigma_g^-$. Experimentally, the ground state of the dimer has not yet been established unambiguously. Ginter *et al.*¹¹ find the $^3\Sigma_g^-$ state as the electronic ground state, Douglas *et al.*¹² predicted from the absorption spectra of Al₂ that $^1\Sigma_g^+$ is the ground state. While several theoretical configuration interaction calculations predict that the singlet state is higher in energy,¹³⁻¹⁵ the energy difference between the two triplet

TABLE I. Experimental and theoretical results for the dimer polarizability. The values of the polarizabilities are given in \AA^3 .

	Theor.		Expt.
	${}^3\Sigma_g^-$	${}^3\Pi_u$	
α_1	19.1	16.6	
α_{\parallel}	23.1	26.3	
$\bar{\alpha}$	20.4	19.8	19.0 ± 2.0
$\bar{\alpha}/2\alpha_1$	1.54	1.49	1.40 ± 0.21

states is small compared to the numerical precision of *ab initio* calculations.^{14,16} Therefore, we will present the polarizability results for the two triplet states of the dimer.

As found in previous calculations,¹⁴ we obtain that the two triplet states of the dimer are almost degenerate, the ${}^3\Sigma_g^-$ state being lower in energy by only 50 meV. We obtain, respectively, 4.66 a.u. and 354 cm^{-1} for the bond length and vibrational frequency of the ${}^3\Sigma_g^-$ state, compared to the experimental values of 4.66 a.u. and 350 cm^{-1} .¹⁷ The good agreement with experiment for the equilibrium distance strongly indicates that this state is the experimental ground state.

Our theoretical result for the atomic polarizability is 6.6 \AA^3 compared to the measured value of $6.8 \pm 0.3 \text{ \AA}^3$. The polarizability tensor elements of the two states of the dimer are presented in Table I and the rotationally averaged polarizability $\bar{\alpha}$ is compared to the measured values.

V. DISCUSSION AND CONCLUSIONS

The measured and calculated polarizabilities for the aluminum atom and dimer are in good agreement despite the approximation made in the calculations. Perhaps the most striking feature is that the polarizability per atom of the aluminum dimer is larger than that for the atom. This should be contrasted with the alkali-metal clusters, which are well described in the jellium approximation as alkali-metal clusters,¹⁸ where the reverse is the case. We note that aluminum cluster polarizabilities are at odds with jellium predictions also for clusters up to 40 atoms.⁵ Moreover, the ionization potential of aluminum clusters Al_n rises steeply for small n ,⁵ we would then expect that a rise of the ionization potential connected to a more tightly bound molecule corresponds to a decrease of the polarizability per atom, as it does for the alkalis.

Investigating the charge displacement occurring in the dimer as we apply the electric field, an interesting property is observed. Figure 4 shows the polarization charge of the theoretical ground state of Al_2 defined by

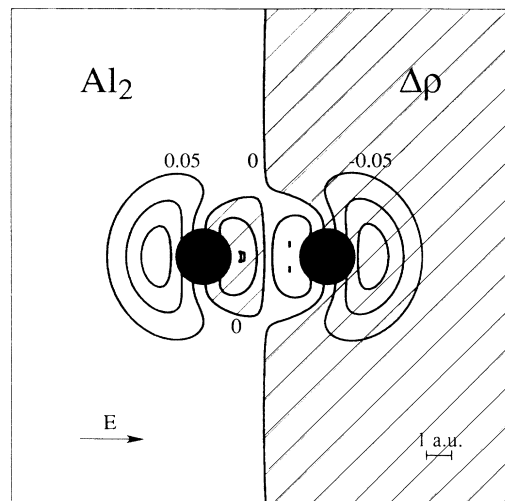


FIG. 4. Difference charge density $\Delta\rho$ as defined in the text for the theoretical ground state (${}^3\Sigma_g^-$) of Al_2 . The electric field is applied along the molecular axis. Shaded areas correspond to an electron depletion. Solid circles indicate the extension of the atomic cores. The spacing between contour lines is $0.05e$ (a.u.)⁻³ per unit of electric field.

$$\Delta\rho = \frac{\rho(\mathbf{r}) - \rho^{E=0}(\mathbf{r})}{|\mathbf{E}|}, \quad (8)$$

where $\rho(\mathbf{r})$ is the total charge density of the molecule. We note an inversion of the polarization between the bonding region and the periphery of the molecule. This inversion does not take place in systems with lower electronic valency, such as alkali-metal dimers.¹⁹

In conclusion, we have presented a method to accurately measure polarizabilities of refractory metals using a novel position-sensitive TOF spectrometer. The method is generally applicable for beams produced by a laser vaporization source. This will facilitate molecular beam polarizability measurements over a wide range of materials, notably those which previously were not experimentally accessible. Experimental results and calculations emphasize that assumptions more realistic than a spherical droplet have to be used to model the response to a static electric field of the aluminum atom and dimer.

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