Strong long-range forces between C_{60} and Na atoms and microclusters

Vitaly V. Kresin, V. Kasperovich, G. Tikhonov, and K. Wong
Department of Physics and Astronomy, University of Southern California, Los Angeles, California 90089-0484
(Received 18 August 1997)

We describe a measurement of the long-range van der Waals interaction $V=-C_6/r^6$ between free neutral sodium atoms and clusters (Na_n, $1\leqslant n\leqslant 20$) and C_{60} fullerenes. The C_6 coefficients were derived from absolute integral cross sections for low-energy scattering of a supersonic beam of metal particles by C_{60} vapor. Their values are extremely high, ranging from $\sim 10^4$ a.u. up to more than 10^5 a.u., corresponding to center-of-mass scattering cross sections of up to ~ 6000 Å^2 (which exceeds the hard-sphere dimensions of the particles by a factor of 20). These experimental values of C_6 are in excellent quantitative agreement with the predictions of the London theory of dispersion forces based on atom and cluster spectral properties. The strength of the long-range potential is due to high cluster polarizabilities. [S1050-2947(98)05901-0]

PACS number(s): 34.20.Gj, 36.40.−c, 61.48.+c

Long-range forces between neutral species (atoms, molecules, surfaces, etc.) are due to quantum fluctuations of their electronic moments, that is, to virtual polarization effects [1–4]. At sufficiently large separations a pair of neutral particles A and B attract each other with the van der Waals (vdW), or dispersion, potential:

$$V^{AB}=-\frac{C_6^{AB}}{R^6}. \tag{1}$$

The interaction coefficient C_6 is given by

$$C_6^{AB}=-\frac{3}{\pi}\hbar\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega, \tag{2}$$

where $\alpha(\omega)$ are the dipole dynamic polarizability functions [3]. The long-range attraction is thus fully determined by the dipole spectra of isolated particles. Beam-scattering experiments can measure the vdW force, and thereby establish a bridge between collision phenomena and spectroscopy. In this paper we describe a measurement of C_6 dispersion coefficients between C_{60} fullerenes and sodium atoms and clusters (Na_n, $1\leqslant n\leqslant 20$). These coefficients are determined from elastic-scattering cross sections of a supersonic sodium cluster beam by fullerene vapor.

There has been significant experimental and theoretical interest in the dipole photoabsorption spectra and electric polarizabilities of both species [4–7], as well as in collision phenomena involving these clusters (see, e.g., recent papers and reviews [7–12]). Since both metal and fullerene clusters are highly polarizable, their vdW attraction must be extraordinarily strong. As will be shown below, the experimental cross sections are indeed remarkably large, and the vdW coefficients extracted from them are in excellent agreement with dispersion theory and spectroscopic data [13].

Let us note in passing that, by following the development of C_{60}-metal cluster potentials with cluster size, one is essentially observing the gradual evolution of the interaction between fullerenes and metallic structures (e.g., nanoparticles, scanning microscope tips [15], etc. and surfaces all subjects of considerable practical importance.

Cluster scattering cross sections were determined by measuring the depletion of a highly collimated sodium cluster beam by fullerene vapor in a heated cell. An outline of the experimental setup is shown in Fig. 1. The supersonic beam of neutral Na atoms and clusters is produced by seeded expansion of sodium vapor through a small nozzle. The beam is collimated by a small aperture ($d=0.5$ mm) located in front of a heated copper scattering cell. The cell was loaded with 0.5 g of C_{60} powder (99.5% pure, MER Corp., Tucson, AZ) and heated to a series of temperatures between 380 and 460 °C (stable and uniform to ± 1 °C), generating C_{60} vapor pressures of up to 10^{-4} bar. The effective scattering path through the cell is calculated to be $L=3.25\pm 0.10$ cm (corresponding to the inner diameter of the cell plus one-half the thickness of both walls [14]). After a long free-flight region, the beam enters the detector through a second collimation aperture ($d=1.4$ mm). Since the reconstruction of vdW coefficients from measured cross sections is very sensitive to the scattering geometry (see below), accurate beam collimation and alignment are important.

In the detector the atoms and clusters are ionized by a filtered UV lamp, mass selected by a quadrupole mass spectrometer, and detected by an ion counter. Soft near-threshold ionization with filtered light ionizes the clusters without significant fragmentation [16,17]. Beam velocities were measured with the help of two identical fast (100–200 Hz) chopper wheels located 128 cm apart: the mass spectrometer was set to a particular cluster size, and the beam was alternately chopped by wheels 1 and 2. The time difference between the detection of pulses from the two locations directly yields the beam velocity without a need for calibration of detector delays. The measured velocities increased from 1080 m/s for the Na atom to 1170 m/s for Na_4, and then gradually decreased to 1120 m/s for Na_{20}. The variation of cluster velocities in a seeded supersonic beam depends somewhat on the expansion parameters; however, a velocity increase from the atom to the dimer has been indeed observed in alkali beams [18], and the ''velocity slip'' for larger clusters is a well-known feature of cluster beams [19]. The fact that there are clear differences between the velocities of individual peaks in the mass spectrum confirms the statement that they correspond to original beam constituents and not to fragmentation products.

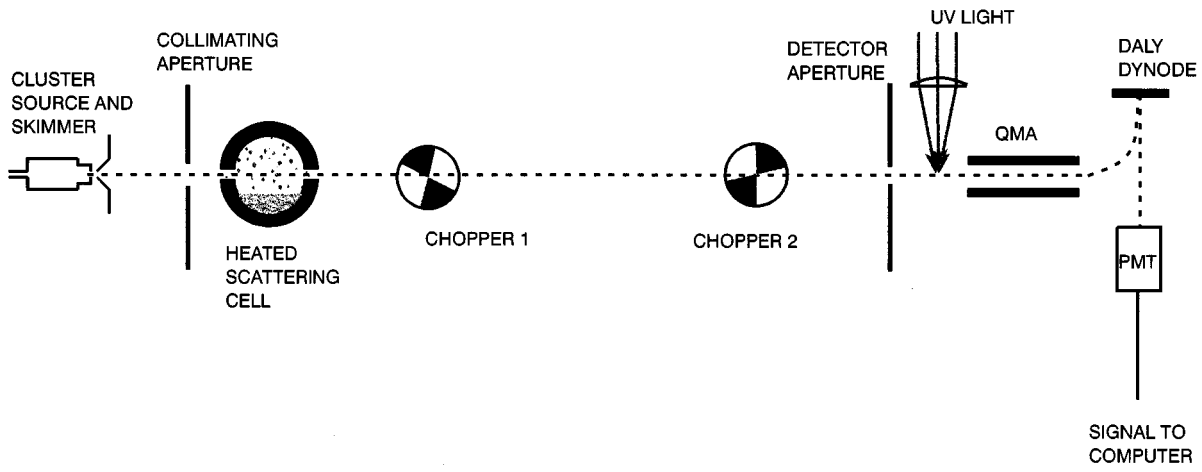

FIG. 1. Outline of the experimental arrangement. The supersonic cluster source is operated at $T=890$ K (Na vapor pressure 0.04 bar), with an argon carrier gas pressure of 8 bar. The nozzle and skimmer diameters are 0.075 and 0.4 mm, respectively; the nozzle temperature is maintained at $T=1030$ K. The heated atomic vapor cell is 40 cm downstream from the skimmer. The collimating and detector entrance apertures are located 5 cm before and 164 cm after the scattering cell, respectively. The detector ionizing lamp is filtered to transmit light in the range of 240–410 nm (Kopp CS 7-54 glass). The cluster beam velocity is measured with the aid of two chopper wheels as described in the text.

Thanks to the small velocity spread of the supersonic beam, the center-of-mass (CM) collision energies were well defined for each pair, and ranged from 0.13 eV for $Na+C_{60}$ to 1.8 eV for $Na_{20}+C_{60}$. It is to be expected that at such low energies cluster-fullerene scattering is governed primarily by the long-range vdW tail of the interaction potential. We shall see below that this is indeed the case.

The absolute scattering cross sections σ_0 were measured by varying the temperature of the scattering cell (and thereby the fullerene vapor density, $N_{C_{60}}$) and plotting the integrated intensities I of individual cluster peaks from the mass spectra versus $N_{C_{60}}$ [20]: $I=I_0\exp(-\sigma_0 N_{C_{60}}L)$. Here I_0 is the reference cluster intensity measured with the scattering cell moved out of the beam path. The plots of $\ln(I/I_0)$ displayed a linear decrease with $N_{C_{60}}$, demonstrating that beam depletion was caused by single collisions. Several calibrations of C_{60} vapor pressure have been published; we used the average of cross sections obtained with the results of Abrefah *et al.* [21] and Mathews *et al.* [22] (see below). The values of σ_0 obtained from linear fits to these plots are shown as open circles in Fig. 2.

Before fitting vdW potential parameters to these experimentally measured ''apparent'' cross sections σ_0, it is important to realize that they are smaller than the true CM integral cross sections σ because of finite angular resolution of the apparatus: only those metal clusters which are scattered by more than a certain limiting angle are deflected out of the detector entrance. The small-angle corrections are increasingly more significant for the heavier clusters. In fact, one can easily show [20,23] that they are responsible for the fact that the apparent cross sections σ_0 remain practically constant even as the true CM cross sections increase strongly with size (see Fig. 2).

Specifically, the apparent values are related to the CM differential cross sections $Q(\theta)\equiv 2\pi(d\sigma/d\theta)\sin\theta$ by

$$\sigma_0=\int [1-\eta(\theta)]Q(\theta)d\theta. \tag{3}$$

Here $\eta(\theta)$ is the experimental resolution function [24] which gives the probability that a cluster deflected by an angle θ in the scattering region will still be able to enter the detector aperture. This function is determined by the experimental geometry; a thorough discussion and explicit formulas for the case of circular collimators were given in Ref. [25]. The largest geometric uncertainty in our experiment concerns the

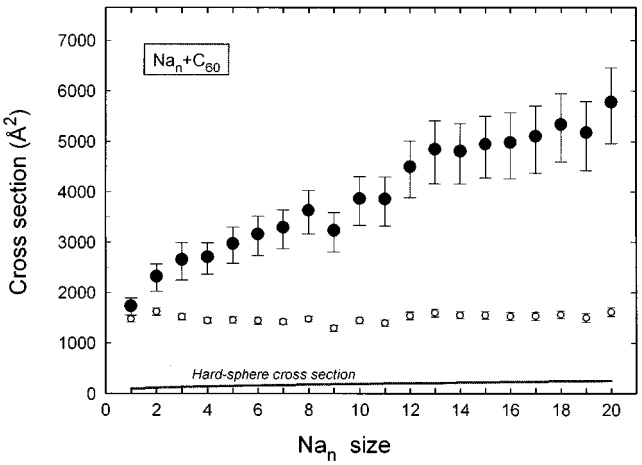

FIG. 2. Integral scattering cross sections for collisions between Na atoms and clusters and C_{60}. Empty circles: experimentally measured ''apparent'' cross sections. Solid circles: center-of-mass cross sections [Eq. (4)] calculated from the extracted van der Waals interaction parameters. The resolving power of the beam apparatus detects most of the Na-atom cross section, but for larger clusters the small-angle scattering correction becomes important (see text for details). A comparison with the hard-sphere geometrical cross sections demonstrates that we are dealing with a strong long-range interaction.

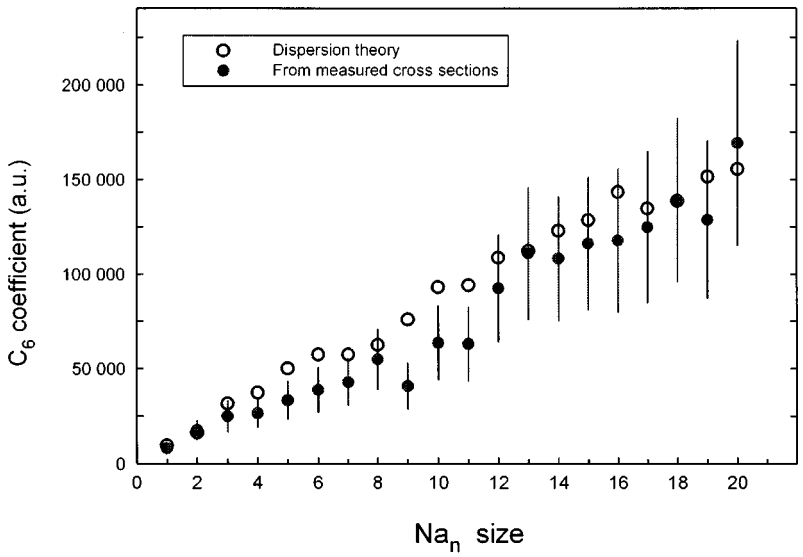

FIG. 3. van der Waals C_6 interaction coefficients, in atomic units, for collisions between Na_n and C_{60}. Closed circles: determined from the experimental data. Open circles: prediction of the dispersion formula [Eq. (5)] based on the cluster response properties.

transverse density profile of the cluster beam. Even though the supersonic beam emerges from a very small nozzle and is highly directional, it possesses a certain transverse velocity distribution which tends to spread out the beam profile. This effect can be replicated by introducing a so-called ''virtual source'' of the beam [26] which is located in the nozzle plane but is larger than the true nozzle opening. The precise dimensions of this virtual source are difficult to estimate because they are quite sensitive to parameters of the expansion. We have therefore calculated $\eta(\theta)$ for the limiting cases of (1) a small virtual source ($D_{\text{source}} \ll D_{\text{skimmer}}$), and (2) a large virtual source ($D_{\text{source}} > D_{\text{skimmer}}$). Both limits lead to similar results (see below). The angular resolution of the apparatus, defined as $\eta(\theta_{1/2})$ is found to be $\theta_{1/2} \approx 2.4$ min of arc.

Having calculated $\eta(\theta)$, the procedure for extracting vdW parameters from the experimental data is now straightforward. For the $V = -C_6/r^6$ scattering potential, the analytical form of the CM differential cross section $Q(\theta)$ is known [27]; corrections for the thermal motion of the scattering vapor can also be incorporated [25]. We substitute this function into Eq. (3) and determine the C_6 coefficient which reproduces the measured apparent cross section. This procedure is repeated for each Na_n particle. Note that it does not involve any adjustable parameters.

The vdW coefficients determined in this way are shown in Fig. 3. The corresponding full integral CM scattering cross sections can be calculated from these C_6 values by means of the formula [27]

$$\sigma = 8.083 \left(\frac{C_6}{\hbar v} \right)^{2/5}, \tag{4}$$

where v is the collision velocity. These cross sections are shown as filled circles in Fig. 2 for velocities corresponding to our cluster beam. For comparison, the figure also shows the geometrical hard-sphere cross sections. Note that the huge CM cross sections exceed the latter by a factor of ≈ 20, reflecting the long range of the interaction. As will be discussed below, the magnitude of the cross sections reflects the very high polarizability of the collision partners.

Let us comment briefly on the sources of the error bars in Fig. 3. The overall uncertainty in the determination of C_6 parameters is approximately $\pm 30\%$. The primary contributions to this number arise from (a) uncertainty in the literature value of the vapor pressure of C_{60}, (b) uncertainty in the size of the virtual source, (c) temperature stability in the scattering cell (≈ 1 K); and (d) statistical scatter in the linear fit of $\ln(I/I_0)$ vs $N_{C_{60}}$. As mentioned above, the values shown here were obtained by averaging the results found using vapor pressures from Refs. [21,22], and those for a small and large virtual beam source. Item (a) contributed errors estimated at $\approx 20\%$ [28–30], items (b) and (c) errors of $\approx 10\%$ each, and item (d) errors of ≈ 10–15%. The final uncertainty value quoted above was derived by adding these contributions in quadrature [29,30].

At last, we are in a position to compare the experimental results with the dispersion theory prediction (2). This general equation simplifies considerably if the dipole transition strengths of the colliding particles are concentrated in relatively narrow spectral ranges. In this case, the expression for the vdW interaction reduces to the ''London dispersion formula'' [1,31]

$$C_6^{AB} = \tfrac{3}{2} \hbar \alpha^A \alpha^B \frac{\omega^A \omega^B}{\omega^A + \omega^B}, \tag{5}$$

where α and ω are the static dipole polarizabilities and the characteristic dipole transition frequencies, respectively (we neglect the higher-order effects of cluster shape anisotropy). This equation is perfectly appropriate in the present case because alkali atoms and clusters as well as fullerenes display strong resonant photoabsorption (see e.g., Refs. [5,6,32,33]).

Both the static polarizabilities and the dipole resonance frequencies are independently known quantities, and so we can use Eq. (5) to compute $C_6^{\text{Na}_n - \text{C}_{60}}$ values from the spectral data and compare them with the experimental results. The

static polarizabilities of alkali atoms and clusters have been measured directly [4,34,35]; they range from 23.6 Å^3 for Na to 307 Å^3 for Na_{20}. The experimental and theoretical values for C_{60} aggregate around $\alpha^{C_{60}} \approx 85$ Å^3 [4]. The frequencies ω correspond to the D line (for the sodium atom) or to collective electronic resonances (for larger Na clusters and for C_{60}). In free fullerenes this resonance is centered at $\omega^{C_{60}} = 20$ eV, while in Na_n atoms and clusters it is located at 2–3 eV. For $\omega^{Na_{n>2}}$, we make use of the values given by the theoretical expression derived in Refs. [6,36]: it gives an excellent description of the position of the centroid of dipole resonances in metal clusters.

Figure 3 shows that C_6 parameters calculated from the dispersion formula (5) is in excellent agreement with the experimentally determined values. This confirms that neutral atom-cluster and cluster-cluster collisions at present beam energies are governed by the long-range van der Waals force. Dispersion theory, making use of independent spectral data on fullerenes and on alkali atoms and clusters, fully accounts for the very high strength of vdW interaction, with C_6 coefficients exceeding 10^5 a.u.

The close agreement between experimental and calculated values implies that competing fragmentation or reactive channels do not make a significant contribution to the scattering process. In particular, the data confirm the earlier conclusion [14] that electron-transfer associative reactions of the type $Na_n + C_{60} \rightarrow Na_n{}^+ C_{60}^-$, if present [37–40], proceed with cross sections much lower than what one could expect from an electron-jump harpooning model. This observation was recently explained [41] by pointing out that nuclear dynamics strongly restricts the phase space available for the above reaction, and therefore significantly reduces its probability.

At higher collision eneries, $E > \mathrm{IP}_{Na_n} - \mathrm{EA}_{C_{60}} \approx 1 - 2.5$ eV for the cluster range studied here (IP is the ionization potential and EA is the electron affinity), one expects to observe an electron-exchange reaction $Na_n + C_{60} \rightarrow Na_n{}^+ + C_{60}{}^-$ [42]. Collision energies in our experiment are generally below or barely above the required magnitudes (see above), so direct charge exchange does not make a significant contribution to the measured cross sections. It would be interesting to study the interplay between elastic and charge-exchange scattering in the higher-energy range. Another interesting question concerns the role of higher-order vdW interaction terms $(-C_8/r^8 - C_{10}/r^{10} - \cdots)$. The experimental results are quite satisfactorily explained without a need to invoke these dipole-quadrupole, etc., potentials. On the other hand, there are indications in preliminary data on Na_n-Na cluster-atom scattering [43] that in this case such terms may make a noticeable contribution. It would be interesting to address the question of the relative magnitudes of the dipole and quadrupole polarizabilities of C_{60}, and the corresponding relative importance of the multipolar terms in elastic scattering processes.

In summary, we have described a new, accurate measurement of the long-range van der Waals attraction $V = -C_6/r^6$ between neutral sodium atoms and clusters (Na_n, $1 \leq n \leq 20$) and C_{60} fullerenes. Interaction constants C_6 were determined from a fit to integral cross sections measured for collisions between a metal cluster beam and fullerene vapor. These interaction coefficients turn out to be extraordinarily high, ranging from $C_6 \approx 8 \times 10^3$ a.u. for $Na + C_{60}$ up to $C_6 \approx 1.6 \times 10^5$ a.u. for $Na_{20} + C_{60}$. The corresponding center-of-mass cross sections range from ≈ 1700 Å up to ≈ 5800 Å^2, which exceeds the geometrical hard-sphere area of the particles by well over an order of magnitude. The experimentally determined values of C_6 are in excellent agreement with the prediction of the London dispersion equation (5) based on the electric polarizabilities and dipole resonance frequencies of the colliding particles. The origin of the high interaction strength is in the large electric-dipole polarizabilities of both Na_n and C_{60}.

This work was supported by the U.S. National Science Foundation under Grant No. PHY-9600039.

[1] H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, 2nd ed. (Pergamon, Oxford, 1971).
[2] J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, London, 1991).
[3] A. Dalgarno, Adv. At. Mol. Phys. **2**, 1 (1966).
[4] K. D. Bonin and V. V. Kresin, *Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters* (World Scientific, Singapore, 1997).
[5] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
[6] V. V. Kresin, Phys. Rep. **220**, 1 (1992).
[7] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[8] F. Rohmund, A. V. Glotov, K. Hansen, and E. E. B. Campbell, J. Phys. B **29**, 5143 (1996).
[9] S. Nonose, H. Tanaka, T. Mizuno, N. J. Kim, K. Someda, and T. Kondow, J. Chem. Phys. **105**, 9167 (1996).
[10] A. S. Hira and A. K. Ray, Phys. Rev. A **54**, 2205 (1996).
[11] A. Ruiz, J. Breton, and J. M. Gomez Llorente, Chem. Phys. Lett. **270**, 121 (1997).
[12] D. C. Lorents, Comments At. Mol. Phys. **33**, 125 (1997).
[13] This correspondence was first demonstrated in Ref. [14], but with a significantly lower accuracy because of beam geometry uncertainties. In addition, the present work also includes previously unavailable atomic cross-section data.
[14] A. A. Scheidemann, V. V. Kresin, and W. D. Knight, Phys. Rev. A **49**, R4293 (1994).
[15] X. Bouju, Ch. Girard, H. Tang, C. Joachim, and L. Pizzagalli, Phys. Rev. B **55**, 16 498 (1997).
[16] K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer, and W. D. Knight, Phys. Rev. B **40**, 5417 (1989).
[17] L. Bewig, U. Buck, Ch. Mehlmann, and M. Winter, Z. Phys. D **26**, S104 (1993).
[18] K. Bergmann, U. Hefter, and P. Hering, Chem. Phys. **32**, 329 (1978).
[19] Bu. Wrenger and K. H. Meiwes-Broer, Rev. Sci. Instrum. **68**, 2027 (1997).
[20] V. V. Kresin and A. Scheidemann, J. Chem. Phys. **98**, 6982 (1993).

[21] J. Abrefah, D. R. Olander, M. Balooch, and W. J. Siekhaus, Appl. Phys. Lett. **60**, 1313 (1992).
[22] C. K. Mathews, M. S. Baba, T. S. L. Narasimhan, R. Balasubramanian, N. Sivaraman, T. G. Srinivasan, and P. R. V. Rao, J. Phys. Chem. **96**, 3566 (1992).
[23] V. V. Kresin, A. Scheidemann, and W. D. Knight, Phys. Rev. A **49**, 2696 (1994).
[24] P. Kusch, J. Chem. Phys. **40**, 1 (1964).
[25] F. von Busch,Z. Phys. **193**, 412 (1966).
[26] H. C. W. Beijerinck and N. F. Verster, Physica (Amsterdam) **111C**, 327 (1981).
[27] H. Pauly and J. P. Toennies, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1965), Vol. 1.
[28] It should be noted that Refs. [29] and [30] report C_{60} vapor pressures which are higher by factors of 4 and 16, respectively, than those found in Refs. [21] and [22]. These calibrations would result in interaction cross sections reduced by approximately the same factor, and in a correspondingly larger uncertainty in the coefficient C_6. Here we made use of the two latter references, as they are in close agreement with each other, and permit a consistent interpretation of our results.
[29] V. Piacente, G. Gigli, P. Scardala, A. Giustini, and D. Ferro, J. Phys. Chem. **99**, 14 052 (1995).
[30] A. Popovic, G. Drazic, and J. Marsel, Rapid Commun. Mass Spectrom. **8**, 985 (1994).
[31] F. London, Z. Phys. Chem. Abt. B **11**, 222 (1930).
[32] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).
[33] I. V. Hertel, H. Steger, J. de Vries, B. Weiser, C. Menzel, B. Kamke, and W. Kamke, Phys. Rev. Lett. **68**, 784 (1992).
[34] W. D. Knight, K. Clemenger, W. A. de Heer, and W. A. Saunders, Phys. Rev. B **31**, 2539 (1985).
[35] K. Clemenger, Ph.D. thesis, University of California, Berkeley, 1985 (unpublished).
[36] V. V. Kresin, Phys. Rev. B **39**, 3042 (1989).
[37] Agglomeration of alkali atoms on C_{60}^{+} ions has been observed in the gas phase; see, e.g., Refs. [38–40].
[38] S. Frank, N. Malinowski, F. Tast, M. Heinebrodt, I. M. L. Billas, and T. P. Martin, Z. Phys. D **40**, 250 (1997).
[39] P. Weis, R. D. Beck, G. Bräuchle, and M. M. Kappes, J. Chem. Phys. **100**, 5684 (1994).
[40] S. Pollack, D. Cameron, M. Rokni, W. Hill, and J. H. Parks, Chem. Phys. Lett. **256**, 101 (1996).
[41] V. V. Kresin and V. Z. Kresin, Z. Phys. D **40**, 381 (1997).
[42] O. Hampe, T. Bergen, G. M. Koretsky, M. Gegenheimer, and M. M. Kappes, Chem. Phys. Lett. **275**, 7 (1997).
[43] V. Kresin, V. Kasperovich, G. Tikhonov, and K. Wong (unpublished).