

# Polarizability of fullerenes

V. A. Mal'tsev, O. A. Nerushev, S. A. Novopashin, and B. A. Selivanov\*  
*Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences,  
630090 Novosibirsk, Russia*

\**Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,  
630090 Novosibirsk, Russia*

(Submitted 15 February 1993; resubmitted 15 April 1993)

Pis'ma Zh. Eksp. Teor. Fiz. **57**, No. 10, 634–637 (25 May 1993)

An anomalously high polarizability of fullerene molecules in the gas phase has been observed experimentally at a wavelength of 540 nm.

The recent discovery of fullerenes<sup>1</sup> and the development of a method for synthesizing them in macroscopic quantities<sup>2</sup> have triggered a widespread, multifaceted study of these molecules. Many experimental methods have been used to obtain information on the electrical and optical properties of these molecules. The experimental results on absorption<sup>2,3</sup> in the UV, IR, and visible regions; on NMR;<sup>4</sup> on the ionization potential;<sup>5</sup> on the electron affinity;<sup>6</sup> and on the magnetic susceptibility<sup>7</sup> agree well with theoretical predictions<sup>8,9</sup> and numerical calculations.<sup>10–12</sup> The polarizability of a fullerene was calculated in Ref. 10 by the self-consistent-field method for an incomplete electron basis. The value  $7 \times 10^{-23}$  cm<sup>3</sup> was found; this is close to the polarizability predicted by the theory of an additive polarizability of bonds for complex molecules<sup>13</sup> (for thirty C=C bonds and sixty C–C bonds, the polarizability is  $8 \times 10^{-23}$  cm<sup>3</sup>). In this letter we are reporting measurements of the fullerene polarizability at the wavelength 540 nm. In these measurements we made use of the known expression relating the Rayleigh-scattering intensity in a low-density gas to the polarizability of the molecules:

$$I_s = AI_0 N a^2, \quad (1)$$

where  $I_s$  is the intensity of the scattered light,  $A$  is a geometric factor,  $I_0$  is the intensity of the incident light,  $N$  is the density of molecules, and  $a$  is the polarizability of the molecule at the frequency of the laser light.

In the experiments we used a 4:1 C<sub>60</sub>:C<sub>70</sub> mixture produced by the plasma-arc method<sup>2</sup> followed by extraction by the Soxhlet method. The solvents were driven off at 280–300 °C in a vacuum of  $10^{-2}$  Pa for 2 h. The resulting powder was analyzed by studying the IR, UV, and visible-range absorption and by small-angle x-ray diffraction. The results agreed well with data found elsewhere. Figure 1 shows the IR absorption spectrum of a sample prepared by compressing the fullerene mixture with powdered KBr.

Figure 2 shows the experimental layout. A microscopic-crystal fullerene powder was placed in cylindrical Knudsen cell 1 (the inside diameter was 40 mm, and the height was 30 mm) with an aperture of 3 mm in diameter for the outflow of the fullerene mixture in the gaseous phase. The cell was placed in vacuum chamber 2 with



FIG. 1. IR absorption spectrum of the fullerene.

a background pressure of  $10^{-2}$  Pa. The cell temperature could be varied over the range 300–1000 K.

The beam from pulsed laser 3 (wavelength of 540 nm, pulse length of 20 ns, and energy of 20 mJ in the pulse) intersected the flow at a distance of 6.5 mm from the outlet aperture of the cell. This beam was focused by lens 4 (with a focal length of 400 mm) onto the flow axis, in a spot about 0.1 mm in diameter. The scattered light was observed at an angle of  $90^\circ$  from the propagation direction of the reference beam and from the polarization vector. The scattered light was collected by objective 5 and fed through optical fiber 7 to photomultiplier 6. The intensity of the scattered light was normalized to the energy of reference light, which was measured by photodiode 8. The output signals from the photomultiplier and the photodiode were recorded by CAMAC charge-to-digital converter 9. Each experimental point was averaged over 20 laser pulses, so the error was about 5%. The geometric factor in Eq. (1) was calculated from a calibration based on scattering in nitrogen at a pressure of 200 Pa.

Storage oscilloscope 10 was used to measure the temporal profile of the scattered signal.

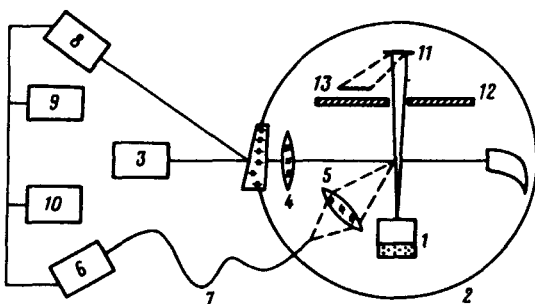


FIG. 2. Experimental layout. 1—Knudsen cell; 2—vacuum chamber; 3—Nd:YAl laser; 4—lens; 5—objective; 6—photomultiplier; 7—optical fiber; 8—photodiode; 9—charge-to-digital converter; 10—oscilloscope; 11, 13—quartz microbalances; 12—skimmer.

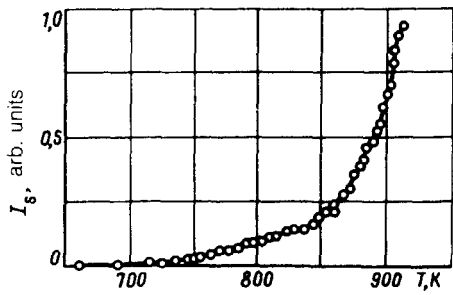


FIG. 3. Scattering intensity in the flow versus the temperature in the Knudsen cell.

A quartz balance 11 was placed 130 mm along the flow axis in order to measure the fullerene flux. The density of fullerene molecules was calculated from these measurements, from the known thermal velocity of fullerene molecules at the cell temperature, and from the sticking factor of the substrate surface for the molecules. An absolute calibration of the balance was carried out through interference measurements of the thickness of the deposited film. A skimmer (12) was installed in the chamber in order to measure the sticking factor of the substrate for fullerene molecules. A molecular beam was tapped from the flow with the help of this skimmer. The flux density of molecules scattered by the surface of balance 11 was measured by quartz balance 13. The ratio of fluxes measured by balances 11 and 13, corrected for the relative positions of the balances, gave us the reflection coefficient of the substrate for the molecules. In all experiments, the surface of the quartz sensor of the balance was already coated with a thin fullerene film from previous experiments, so the conditions for the interaction of the flow with substrate were reproducible.

Experiments showed that the sticking factor of the substrate for the fullerene molecules was no less than 0.85. This value was calculated under the assumption of a diffuse scattering of molecules by the surface.

Figure 3 shows the temperature dependence of the scattered light. The corresponding plot for the flux measured by the quartz microbalance, corrected for the temperature dependence of the flow velocity, and expressed in relative units, agrees with the plot shown here, within the experimental errors. The highest density of fullerene molecules in the cell according to calculations from the flux measurements was  $5 \times 10^{-13} \text{ cm}^{-3}$  (at a temperature of about 900 K). The minimum Knudsen number over the outlet aperture in these experiments was thus on the order of unity, and the flow was collisionless over the entire range of parameter values. It was thus possible to establish a one-to-one correspondence between the density of molecules at the points at which the scattered light and the molecular flux were measured.

The polarizability calculated from the experimental data is  $(0.8-1.2) \times 10^{-21} \text{ cm}^3$ . This result refers to the mixture of  $C_{60}$  and  $C_{70}$ . However, the ratio of the polarizabilities of  $C_{60}$  and  $C_{70}$  can be estimated to be 60/70, on the basis of the numbers of valence electrons and the approximately equal ionization potentials.<sup>5</sup> Taking into account the mixture composition (4:1) and the quadratic dependence of the measured signal on the polarizability [see expression (1)], we conclude that the measured value may be 5% higher than the polarizability of pure  $C_{60}$ .

The value found for the polarizability at the given wavelength is an order of magnitude greater than the value calculated<sup>10</sup> for a static field. Since C<sub>60</sub> and C<sub>70</sub> are nonpolar molecules, the frequency dependence of the polarizability can be estimated from

$$a(\omega) = a(0)\omega_0^2 / (\omega_0^2 - \omega^2), \quad (2)$$

where  $a(\omega)$  is the polarizability of the frequency  $\omega$ , and  $\omega_0$  is a frequency characterizing the electron bond in the molecule. If we assume that  $\omega_0$  is determined by the ionization potential<sup>5</sup> (7.6 eV) and that  $\omega$  corresponds to 2.3 eV, we conclude that the maximum increase in the polarizability for the given frequency may be 20%. Note that there are no dipole-allowed transitions for fullerene molecules near the frequency of the reference light used.<sup>9,14</sup>

Let us examine the factors which might cause the measured polarizability to be too high: first, a contribution of photoluminescence to the scattering observed;<sup>15</sup> second, a scattering by electrons resulting from photoionization<sup>15</sup> (which would be a multiphoton process in this case); third, simply a multiphoton absorption and a subsequent reradiation; fourth, the possible presence of clusters of fullerene molecules in the flow. The effects of these processes were checked experimentally.

The temporal profile of the scattered light intensity has the shape of the reference signal. Consequently, photoionization and photoluminescence do not contribute to the detected signal.

The intensity of the scattered light was observed to be a linear function of the intensity of the reference light in the range 5–20 mJ. We can thus also conclude that multiphoton processes do not contribute to the observed process.

Since the conditions in the flow beyond the Knudsen cell were collisionless, we can rule out the formation of clusters of several fullerene molecules in the flow beyond the outlet aperture. The presence of microscopic fullerene particles in the flow could thus result only from the presence of such particle inside the cell, due to thermodynamic fluctuations. We detected no effect of the temperature on the measured polarizability over the range 600–900 K. As Fig. 3 shows, the particle density in the flow and thus the Knudsen number in terms of the cell size vary by more than an order of magnitude. This result means that we can ignore an effect of clusters of fullerene molecules on the measurements.

We thus see that the observed emission is a Rayleigh scattering by fullerene molecules, and that this emission characterizes the anomalously high polarizability of this substance.

The polarizability of a free electron at the frequency used is about  $2 \times 10^{-23}$  cm<sup>3</sup>. For a system of 240 electrons (corresponding to the total number of valence electrons in a fullerene molecule), we thus find a total polarizability of  $5 \times 10^{-21}$  cm<sup>3</sup>.

This study was carried out with the financial support of the Soros Fund.

<sup>1</sup>H. W. Kroto, J. R. Heath, S. C. O'Brien *et al.*, *Nature* **318**, 162 (1985).

<sup>2</sup>W. Kratchmer, L.D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature* **347**, 354 (1990).

- <sup>3</sup>C. I. Frum, R. Engelman, H. G. Hedderich *et al.*, Chem. Phys. Lett. **176**, 504 (1991).
- <sup>4</sup>A. Zahab, J. L. Sauvajol, L. Firley *et al.*, J. Phys. (Paris) **12**, 1 (1992).
- <sup>5</sup>J. A. Zimmerman, J. R. Eyler, S. B. H. Bach, and S. W. McElvany, J. Chem. Phys. **94**, 3556 (1991).
- <sup>6</sup>S. H. Yang, C. L. Pettiette, J. Conceicao *et al.*, Chem. Phys. Lett. **139**, 233 (1987).
- <sup>7</sup>R. C. Haddon *et al.*, Nature **350**, 46 (1991).
- <sup>8</sup>D. A. Bochvar and E. G. Gal'pern, Dokl. Akad. Nauk SSSR **209**, 609 (1973).
- <sup>9</sup>S. Larsson, A. Volosov, and A. Rosen, Chem. Phys. Lett. **137**, 501 (1987).
- <sup>10</sup>P. W. Fowler, P. Lazaretti, and R. Zanasi, Chem. Phys. Lett. **165**, 79 (1991).
- <sup>11</sup>P. W. Fowler, P. Lazaretti, M. Malagoli, and R. Zanasi, Chem. Phys. Lett. **179**, 174 (1991).
- <sup>12</sup>M. Kataoka and T. Nakajima, Tetrahedron **42**, 6437 (1986).
- <sup>13</sup>M. F. Vuks, *Electrical and Optical Properties of Molecules and Condensed Media* (Nauka, Moscow, 1984).
- <sup>14</sup>S. Leach *et al.*, Chem. Phys. **160**, 451 (1992).
- <sup>15</sup>P. Wurtz and K. R. Lykke, J. Chem. Phys. **95**, 7008 (1991).

Translated by D. Parsons