Collective electron motion in a C\textsubscript{60} molecule: bridging the gap between atoms and bulk matter

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Cross sections have been reported for photoionization of C\textsubscript{60} ions. The cross section shows two resonances as a function of photon energy: these resonances are attributed to a surface and a volume plasmon. A plasmon resonance is indicative of collective motion of the approximately 240 valence electrons. This manifestation of bulk matter is significant for a molecule containing only sixty carbon atoms.

Keywords: Photoionization; plasmon; fullerene.

Se reportan las secciones transversales para la fotoionización de iones C\textsubscript{60}. La sección transversal muestra dos resonancias como una función de energía fotónica: estas resonancias son atribuidas a una superficie y un volumen plasmon. Una resonancia plasmon es indicativa de movimiento colectivo de los aproximadamente 240 electrones de valencia. Esta manifestación de tanta materia es significativa para una molécula que contiene sólo sesenta átomos de carbón.

Descriptores: Fotoionización; plasmón; fulereno.

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1. Introduction

An important topic in physics is understanding the transition from atomic and molecular energy levels, which characterize an atom or small molecule, to band structure, which is characteristic of solids. Clusters have often been studied, as a cluster is intermediate in size between an atom or small molecule and bulk matter. Another approach is to study a molecule containing a large number of the same atoms. The carbon-60 (C\textsubscript{60}) molecule (also known as a buckyball or a Fullerene) is an interesting subject of study, as it consists of sixty carbon atoms in the form of a hollow conducting sphere. Observation of phenomena—plasmons—normally found in bulk matter in an object of this size is a significant step in bridging the gap between atoms and bulk matter; the observation of collective electron motion, a large-scale effect, is observed at the nano-level of matter.

Carbon is normally found in one of three forms: graphite, diamond, and Fullerenes (also known as buckyballs, of which C\textsubscript{60} is the most common). These three forms have very different properties. Graphite has two-dimensional bonding in the form of covalent bonds between carbon atoms in each layer; it is a soft and slippery material. Diamond has tetrahedral bonds to its neighbors, resulting in a rigid three-dimensional structure; it is well known as the hardest material. Fullerenes are three-dimensional hollow structures made entirely of carbon atoms. Carbon-60 consists of sixty carbon atoms bonded to their neighbors to form an alternating pentagonal and hexagonal structure; it is a hollow conducting sphere. The C\textsubscript{60} molecule is small: its diameter is approximately 0.7 nm, which is less than five times the diameter of a hydrogen molecule. There are many varieties of Fullerenes, including C\textsubscript{70} and C\textsubscript{84}, nanotubes, and other forms. Additionally, interesting structures are diamondoids, the most common of which is adamantane, whose chemical structure is C\textsubscript{10}H\textsubscript{16}. There is also graphene, a single plane of carbon atoms, whose electronic structure has been the topic of many recent studies.

Another interesting structure is Fullerenes with one or more atoms inside the cage structure; these are called endohedral Fullerenes. There is a great diversity of complexes of the form X@C\textsubscript{n}, meaning X is endohedral in the Fullerene C\textsubscript{n} cage. The endohedral atom X can be a metal (e.g., La, Ca), a nonmetal (e.g., Ne, P), or a molecule (e.g., N\textsubscript{2}, CO). Encapsulating an atom or molecule in a Fullerene structure provides a possibility to alter the atomic or molecular properties of the atom or molecule, creating matter with new features. There are many studies of endohedral Fullerenes, which can, for example, be superconducting.

Collective resonances are a characteristic of systems with a large number of particles. A plasmon, for example, is a collective effect of large numbers of electrons in matter—typically a metal—when the electrons are disturbed from equilibrium. A giant nuclear resonance is an elementary mode of oscillation of an entire nucleus. A plasmon observed in the cited experiment [1] described below is an indication of collective motion of the valence electrons in a C\textsubscript{60} molecule.
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2. Experiment

The experiment to measure photoionization of C$_{60}$ [1] was performed with a merged photon-ion beam apparatus at the Advanced Light Source located at Lawrence Berkeley National Laboratory. The apparatus, shown in Fig. 1, and method have been described in numerous publications [see references in Ref. 1 for example]. An ion beam from an ECR ion source is merged over a path length of approximately one meter with a counter-propagating photon beam produced by an undulator. A 30-cm portion of the interaction region is placed at voltage to energy label ions which are ionized in that region. Photon and incident ion-beam intensities are measured, photoions are counted, and the beam overlap is measured by means of three scanning slits (not shown in Fig. 1). Measurements are made with the photon beam time modulated (“chopped”) to subtract ionization of incident ions in background gas. The result is absolute photoionization cross sections.

An ultrabright light source was used in reported experiments [1]. The Advanced Light Source at Lawrence Berkeley National Laboratory is a third-generation light source, producing ultrabright beams of radiation from the infrared into the x-ray region of the spectrum. The merged-beams experiment requires a photon beam which has high intensity and is approximately parallel over a long path length to merge with the ion beam. High spectral resolution is another feature of an ultrabright light source, which is essential in many experiments, but which was not needed in the measurement of photoionization of C$_{60}$ ions.

The experiment to study excitation of a volume plasmon in C$_{60}$ was performed with C$_{60}$ ions rather than with neutral atoms. Although the experiment could have been performed [2] with neutral C$_{60}$, the cited experiment used an ion beam because of the excellent sensitivity of the experiment and the low-noise background. Essentially the same physics should be shown for photoionization of C$_{60}$ neutrals and ions in low charge states, because the collective oscillation which is a plasmon does not depend on the exact number of electrons, be it 238 or 239 or 240.

3. Results

Results for measurement of the cross section for photoionization of C$_{60}^+$ ions are shown in Fig. 2 [1]. Two resonances are seen by fitting the cross section as a function of energy.

4. Conclusion

The carbon-60 molecule, C$_{60}$, better known as a buckyball, is a large molecule, notable in part because it is entirely composed of carbon atoms, and additionally because it has the form of a hollow conducting sphere. It thus lies on the path from single carbon atom or small carbon molecule to a large carbon cluster or a small piece of solid carbon. Were it to behave like an atom or small molecules, the electronic properties of the valence electrons would be attributable to individual atoms. In a solid — bulk material — the electronic behavior of the valence electrons is a property of the ensemble. Buckyballs are between small molecules and bulk matter, with 240 valence electrons, and thus of intrinsic interest. It has long been known that the valence electrons of C$_{60}$ could act collectively, resulting in a “surface plasmon” — which can be described as a sloshing (back-and-forth oscillation) of the electrons relative to the cage of the carbon-atom core. A second resonance — “volume plasmon” — was reported in the cited experiment [1], which is best described as another normal mode of oscillation — a squeezing in and out perhaps — of the cloud of valence electrons on the surface of the C$_{60}$. These two collective resonances — plasmons — observed in the photoionization of the C$_{60}^{+}$ ion demonstrate behavior — normally seen in bulk matter — at the scale of a molecule. Additional information can be found in Ref. 6.

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