Giant Plasmon Excitation in Free C_{60} and C_{70} Molecules Studied by Photoionization

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Single-photon ionization of C_{60} and C_{70} has been studied using synchrotron radiation in an energy range from the ionization potential (7.54 ± 0.04 eV for C_{60}; 7.3 ± 0.2 eV for C_{70}) up to 35 eV. The photoion yield is dominated by a strong resonance at about 20 eV with a FWHM of ~ 10 eV. We interpret this as being due to autoionization via the giant plasmon resonance recently predicted in the RPA approximation. C_{60} and C_{70} offer the unique possibility for a quantitative comparison of this collective excitation in the free molecule with that observed in the solid phase by electron-energy-loss spectroscopy at about 28 eV.

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Presently much theoretical [1–4] and experimental [4–13] effort is devoted to studying the electronic properties of the fullerenes, in particular, C_{60} and C_{70}. Most of the recent studies focused on thin films of C_{60}, using ultraviolet photoemission spectroscopy (UPS) [5], x-ray photoemission spectroscopy (XPS) [6], electron-energy-loss spectroscopy (EELS) [7,8], and high-resolution electron-energy-loss spectroscopy (HREELS) [9], while up to now only one UPS study [10] has been reported for free C_{60} clusters, showing features very similar to those observed for solid films [5]. A very broad plasmon resonance with a maximum around 28 eV is reported in the electron-energy-loss studies. On the other hand, collective excitations by optical absorption are the subject of great current interest in the physics of small metal clusters with the general goal "to bridge the gap" between atom and solid. However, to our knowledge, up to now no direct quantitative comparison of energies and line shapes of optical plasmon excitation in free clusters and the respective electron-energy-loss (EELS and HREELS) studies in the solid has been possible, mainly due to the difficulties in preparing a beam of mass-selected neutral clusters and establishing their structure.

In contrast, the well characterized fullerenes offer the unique possibility for such a study, especially since in a very recent Letter Bertsch *et al.* [1] predict such a resonance. They use linear-response theory for the determination of the optical-absorption spectrum, starting with single-particle wave functions from a tight-binding model and including the Coulomb interactions of the charge and the dipole on the carbon atoms for the 240 electrons. As a key result the absorption spectrum shows very little resemblance with the single-particle energy levels. Several bands below the C_{60} ionization threshold are predicted and are in good agreement with the optical-absorption spectrum in the liquid. But the most remarkable theoretical result is the giant plasmon resonance peaking at around 22 eV which arises from collecting the strength of the individual one-electron transitions into a single collective excitation. Several narrower features are present and yield an overall width of about 8 eV. The total integrated oscillator strength is ~ 90 as compared to a maximum of 240 if all valence electrons were active, illustrating the incompleteness of the basis for these calculations. So far, it has been unclear whether such a resonance can actually be excited by photons in the free C_{60} or C_{70} molecule and, if so, how it relates to the bulk plasmon observed at 28 eV in the EELS and HREELS investigations.

In the present Letter we report the first observation of this giant plasmon excitation by vacuum ultraviolet (VUV) light in the isolated C_{60} and C_{70} molecules. We find it at approximately the position predicted theoretically and we are able to compare it in a quantitative manner with the EELS data [8]. Since the excitation energy of this resonance lies above the ionization threshold of C_{60} and C_{70} we expect the cluster to autoionize in a manner similar to that observed, e.g., for clusters of antimony [14]. We thus study the photoionization efficiency (PIE) spectra, i.e., we measure the C_{60}^+ and C_{70}^+ photoion signal as a function of the wavelength of VUV light ionizing a beam of neutral fullerenes. This also allows us to determine the photoionization potential (IP) of the isolated clusters very directly and accurately without the ambiguities often encountered in multiphoton laser experiments. We use synchrotron radiation from BESSY in Berlin in an apparatus which we have developed over the years to investigate the photoionization dynamics of various clusters (see, e.g., [15]). In a very preliminary study [13] in an energy range between 7 and 8.5 eV we have been able to determine the ionization potential for C_{60} to be 7.58 ± 0.04 eV, which we consider to be the adiabatic value.

The experimental setup is, in principle, very simple and has been described in detail on several occasions (e.g., [13,15]). Its essential ingredients are (a) a molecular beam of C_{60} (with about 10% of C_{70}) effusing from an oven ($\sim 500\,^\circ$C) which contains the purified fullerene sample (MER Corp., Tuscon, AZ); (b) monochromatized synchrotron radiation (SR), the wavelength of which can be scanned from 35 nm (35 eV) to 200 nm (6 eV) with a resolution set to 0.4 nm (corresponding to an energy resolution between 20 meV at 7.5 eV and 400 meV at 35 eV); and (c) a time-of-flight mass spectrometer for mass analyzing and detecting the different ions

which are created in the photoionization process so that the components of the fullerene sample may be distinguished as well as potential fragments. The total ion yield for each mass is recorded as a function of the ionizing photon energy $E=\hbar\omega$. The intensity of the SR is monitored continuously in order to normalize the ion signal to the incoming photon flux. The SR intersects the molecular beam at right angles in the center of a homogeneous extraction field. The ions are extracted perpendicular to both the molecular beam and the SR beam by pulsing the extraction field to 400 V/cm with a pulse rate of a few kHz. The time-of-flight (TOF) arrangement uses a linear geometry with spatial focusing conditions and ions are detected by a secondary electron multiplier. The time of flight of the ions is measured with a time-to-digital converter. The mass resolution thus achieved is $m/\Delta m \sim 100$.

For each wavelength step in the scanning range a histograming memory converts and stores the flight times of the detected ions into a TOF mass spectrum which is then fed into the memory of a microcomputer. A set of mass spectra is recorded by repeatedly scanning the monochromator over the wavelength region of interest and averaging the data from successive scans. Several partially overlapping wavelength ranges, each 17 nm wide, were scanned and joined to each other after careful normalization. For each individual wavelength and mass the TOF peaks were integrated and corrected for background. Thus the total photoionization efficiency spectrum for each mass was obtained. The procedure has been described in detail elsewhere [13,15]. In the present work photoelectrons are not detected so that all ions created at a given photon energy are counted, irrespective of their internal energy.

Figure 1 shows a typical TOF mass spectrum integrated over a wavelength range from 50 to 67 nm (24.8 to 18.5 eV), giving a ratio of C_{60}/C_{70} signal quite typical of the purified fullerene sample (note, however, that the abundance of the different species is multiplied by the respective, unknown vapor pressures and the ionization probabilities). The inset in Fig. 1 shows that a small fraction of C_{76}, C_{78}, C_{82}, and C_{84} was also present in the beam. In contrast, a careful analysis of the spectra shows no evidence for C_{58} or smaller fullness, i.e., we do not observe any significant C_2 evaporation from C_{60} for the whole range of photon energies. For our experimental setup this implies fragmentation rates of less than some $10^6\ s^{-1}$ at an excess energy of $\sim$20 eV above a typical dissociation threshold ($\sim$4 eV). Even though this may seem surprising at first, it is readily understood from a simplified Rice-Ramsperger-Kassel consideration and reflects the very low probability of channeling sufficient energy from the 174 vibrational degrees of freedom into a fragmenting mode.

Figures 2 and 3 show the PIE spectra for C_{60} and C_{70} (C_{76}, C_{78}, and C_{84} behave very similarly but are not shown here). The insets in Figs. 2 and 3 display details of the threshold region for C_{60} and C_{70}, respectively. For C_{60} this region is dominated by a fairly steep rise of the ion yield above threshold. The ionization potential of C_{60} is estimated by a linear extrapolation to be $IP(C_{60}) = 7.54 \pm 0.04$ eV. For C_{70} the IP cannot be determined with the same accuracy, but we tentatively place it at around $IP(C_{70}) = 7.3 \pm 0.2$ eV, somewhat lower than the charge-transfer [11] value (7.61 ± 0.11 eV). Beyond the threshold region the PIE spectra are dominated by an extremely strong rise towards the resonance maximum centered at around 20 eV for both C_{60} and C_{70}, with a total width (FWHM) of about 11.5 eV. The peak position is in very satisfactory agreement with the prediction of the

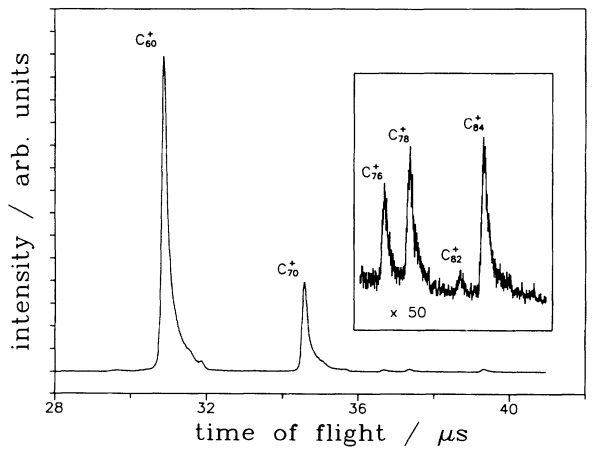

FIG. 1. Time-of-flight mass spectrum of an effusive beam of purified fullerene ionized with SR in the wavelength range 50 to 67 nm.

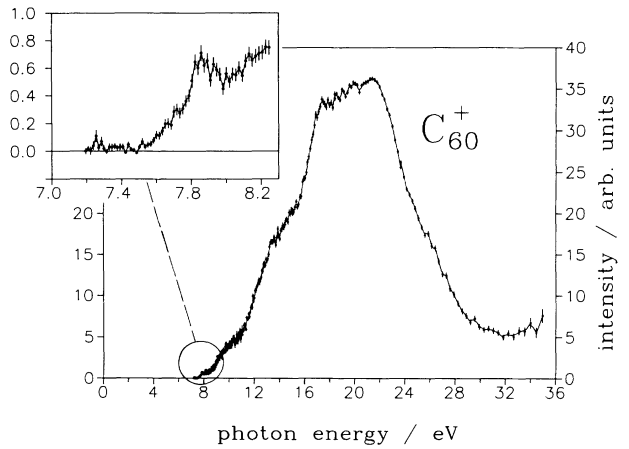

FIG. 2. C_{60}^+ photoion yield as a function of photon energy displaying excitation of the giant plasmon resonance. Inset: The threshold region on a magnified scale. Note the fine structure above threshold as well as on the shoulders of the giant resonance between 15 and 25 eV.

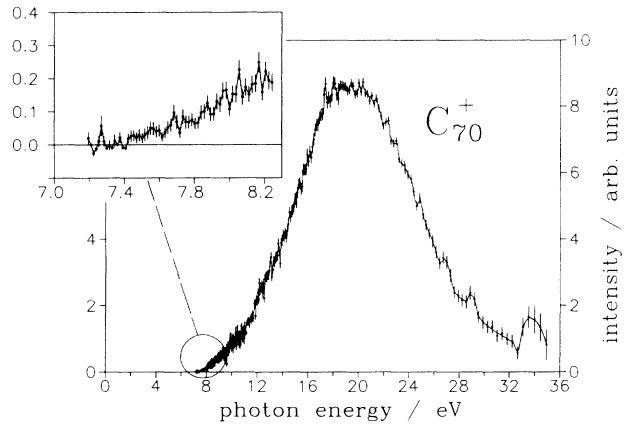

FIG. 3. C_{70}^+ photoion yield. No fine structure is observed close to the ionization threshold or on the shoulders of the giant resonance.

RPA linear-response theory [1] described above, but the predicted width is somewhat smaller. However, as the authors point out, the hitherto neglected electron exchange and continuum states are expected to further broaden the resonance. For C_{70} the overall position and width of the resonance are very similar to C_{60} (as well as for C_{84}) in accordance with the classical interpretation as a Mie-type resonance which depends on the charge density only. We expect the latter to be more or less independent of the cluster size. We note, however, that the molecules differ in that there is distinctively more structure on the C_{60}^+ signal: In the threshold region (inset in Fig. 2) a first small resonance is seen at about 7.85 eV while the signal rises smoothly for C_{70}^+. More importantly, we see several pronounced shoulders on the low-energy side of the giant resonance in C_{60}^+ but not in C_{70}^+.

Can we understand the large 7–8-eV difference in the energetic position of the giant plasmon maxima between our present PIE measurements and the electron-energy-loss data [8,9], and how does the observed additional structure in the C_{60} signal compare for both methods? We note that the photoion yield is determined by several factors, all of which may depend on the photon energy $E=\hbar\omega$: (a) the direct photoionization probability into the continuum, (b) the excitation probability of the plasmon resonance $p_{\rm res}(E)$, and (c) the probability for autoionization $p_{\rm ion}(E)$, i.e., the coupling of the resonance to the continuum. For the sake of simplicity and since the ion signal close to threshold is very low we will assume that (a) can be neglected. We may then factor the ion signal $I(E)=p_{\rm res}(E)p_{\rm ion}(E)$, where the resonance excitation probability is given by the energy-dependent polarizability $\alpha(E)$ of the C_{60} molecule $p_{\rm res}\propto{\rm Im}[-\alpha(E)]$. In contrast, the EELS experiment records ${\rm Im}[-1/\epsilon(E)]$, where $\epsilon(E)$ is the complex dielectric constant of the solid. Approximating our data by a Lorentzian and assuming reasonable numbers for the static polarizability and bulk

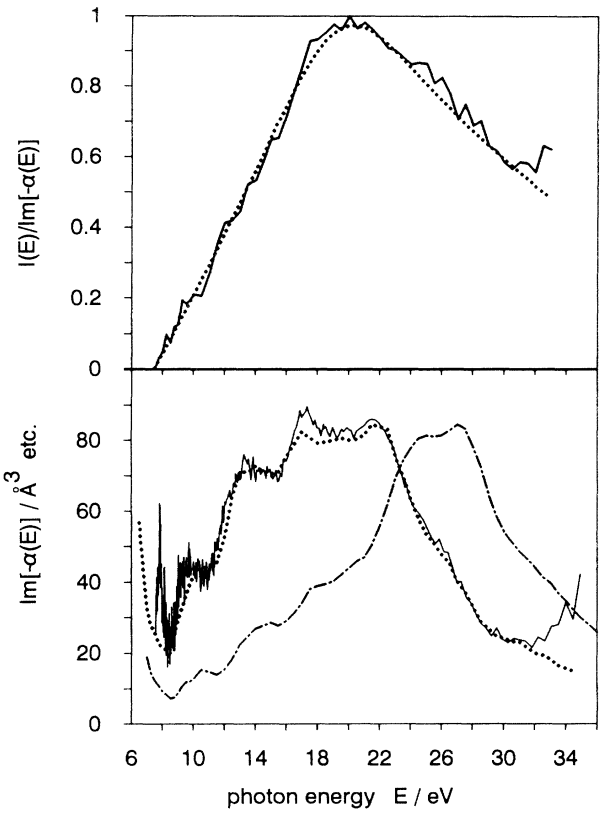

FIG. 4. Comparison of the present PIE signal $I(E)$ for C_{60} with the electron-energy-loss data (EELS) [8]. Upper panel: ratio of the measured $I(E)$ to ${\rm Im}(-\alpha)$ calculated from the EELS data, giving the autoionization probability $p_{\rm ion}(E)$; the solid line is derived from data; the dotted line is a smooth analytic fit. Lower panel: the dotted line is ${\rm Im}(-\alpha)$; the solid line is the rescaled PIE signal $I(E)/p_{\rm ion}$; and the dash-dotted line is the original EELS signal ${\rm Im}(-1/\epsilon)$.

density of C_{60} and C_{70} we can indeed explain the shift of 6–8 eV without difficulty. Note that the EELS data are taken in a cubic crystalline solid so that ϵ and α are related by the Clausius-Mosotti formula, $3(\epsilon-1)/[(\epsilon+2)4\pi n]=\alpha(\omega)$, where n is the density of the molecules in the solid ($=1.83\times10^{-2}$ Å^{-3} for C_{60}) [9]. However, for a most stringent quantitative comparison with the EELS data we evaluate $\alpha(E)$ by inserting into the above equation the very recently reported $\epsilon_1={\rm Re}(\epsilon)$ and $\epsilon_2={\rm Im}(\epsilon)$ values, obtained by a Kramers-Kronig analysis [8]. A word of caution may be appropriate since our evaluation neglects any interactions between the C_{60} molecules in the bulk. We assume nevertheless that, considering the weak cohesive forces in solid C_{60}, we can leave this aspect to future refinements.

The thus derived ${\rm Im}[-\alpha(E)]$ (dotted line in the lower panel of Fig. 4) can be compared directly to the photon yield $I(E)$ for C_{60} reported in Fig. 2. The photoionization probability is then given by the ratio $I(E)/{\rm Im}[-\alpha(E)]$ which is displayed in the upper panel of Fig.

4 (solid line). It can be approximated remarkably well by a smooth, simple analytic function $p_{ion}(E)$, given by two straight lines joined together (dotted line in the upper panel of Fig. 4). The shape of this autoionization probability p_{ion} appears to indicate that the coupling between bound and free states in the continuum is in itself closely related to the collective motion. We have performed a similar analysis for C_{70} which leads to a $p_{ion}(E)$ almost identical to that for C_{60} shown in Fig. 4. These findings clearly support our assumption that the ion yield can be factored into $p_{res}p_{ion}$ and constitute a key result of the present work. The autoionization probability determined in that way warrants a quantitative theory of the underlying photoionization dynamics and the high symmetry of the system should allow a sophisticated treatment.

In addition, a quantitative comparison of the observed additional structures is of interest. To visualize these particularly clearly, we compare in Fig. 4 (lower panel) $\mathrm{Im}[-\alpha(E)]$ calculated from the EELS data with our experimental PIE signal after rescaling the latter with the smooth analytical function $p_{ion}(E)$, i.e., we plot $I(E)/p_{ion}(E)$. In this way, Fig. 4 displays again the striking similarity between the results of these two completely independent and methodologically complementary studies, even in the details. Only the narrow resonance seen in the PIE just above the ionization threshold at about 7.8 eV is not found from the EELS data. For completeness, the original EELS signal [8] $\mathrm{Im}[-1/\epsilon(E)]$ is also reproduced (dash-dotted curve) documenting the 8-eV shift in this type of measurement. To our knowledge, the present extremely satisfactory direct comparison between bulk and gas phase is the first of its kind. It illustrates that the Clausius-Mosotti formula is indeed applicable in this case and that the intermolecular interaction in solid C_{60} obviously does not affect the electron-energy-loss studies significantly. It also shows that the observed secondary structures at 10, 13, 17, and 21 eV are real and may serve as a very crucial test for a rigorous improvement of the RPA [1] calculations. We recall at this point that the RPA calculations collect within the model configuration space less than 50% of the maximum possible oscillator strength, and inclusion of the continuum is absolutely mandatory. Our photoionization data will allow a crucial test for theoretical improvements, particularly so since we probe the coupling to the continuum directly. Additional information will come from photoion-photoelectron coincidence experiments which will allow us to also determine the energy content of the cluster after each ionization process.

In summary, we have observed for the first time a giant collective plasmon resonance in the photoionization yield of fullerenes in close agreement with the theoretical prediction from linear-response theory with RPA. Also for the first time a direct comparison of such a collective excitation of an isolated cluster and the solid material has become possible, showing an extremely remarkable agreement in the details of its structure which originates from the individual C_{60} molecule and which will be a challenge to future theoretical work.

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