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## Infrared Resonance Enhanced Multiphoton Ionization of Fullerenes

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Gas-phase fullerenes are resonantly heated by a train of high power subpicosecond pulses from a free electron laser (FEL) to internal energies at which they efficiently undergo delayed ionization. When the laser is tuned from 6–20  $\mu\text{m}$  while the amount of laser produced parent ions is recorded, resonant absorption of 200–600 IR photons, resulting in almost fragmentation-free ion spectra, is observed. Infrared resonance enhanced multiphoton ionization with a FEL is shown to enable extremely sensitive IR spectroscopy with mass selective detection of gas-phase fullerenes. [S0031-9007(97)04923-5]

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A large amount of information on molecular structure results from the analysis of vibronic structure obtained by Infrared (IR) spectroscopy. A difficulty in conventional IR spectroscopy is its limited sensitivity and its lack of selectivity, i.e., it is not known *a priori* which molecular species is responsible for absorption or emission of IR light. Resonance enhanced multiphoton ionization (REMPI) using a tunable, intense IR laser could offer both high sensitivity as well as molecular selectivity in obtaining vibronic information. For this, however, many IR photons are needed to be absorbed by a single molecule and most molecules will dissociate rather than ionize when being brought to sufficiently high energies. Fullerenes are a known exception where (auto)ionization competes favorably with fragmentation, and they thereby offer a unique opportunity for the study of IR-REMPI processes.

The interaction of intense laser light in the visible and UV wavelength range with gas-phase fullerenes is known to lead to high internal excitation of the parent molecule [1]. Internal energies up to tens of eV, corresponding to temperatures of thousands of K, can be achieved by absorption of many photons and rapid conversion from electronic to vibrational excitation. These superheated neutral molecules are observed to undergo delayed ionization [2,3], fragmentation [4], and optical emission [5], the microscopic analogs of well-known macroscopic cooling processes like thermionic emission, evaporation, and blackbody emission, respectively [1]. Detection of superheated neutral  $\text{C}_{60}$  via delayed ionization becomes very efficient once the internal energy reaches 35–40 eV [1]. Recently, it has been reported that IR multiphoton excitation of  $\text{C}_{60}$  with an intense pulsed  $\text{CO}_2$  laser, leading to ionization and fragmentation, can indeed be observed [6]. Weak off-resonant absorption of IR photons is presumably responsible for the efficient transfer of energy into the molecule in this case [6]. At higher fluences, multiphoton ionization with intense pulsed IR lasers is universally possible for atoms and molecules once the electric field of the laser is sufficiently high to pull an electron away from the ionic core.

This is, however, a different regime requiring intensities higher than  $10^{13} \text{ W/cm}^2$ , and, as electronic processes then dominate over vibrational excitation, the presence of IR resonances will play no role for the overall ionization efficiency [7].

In this Letter we report on the possibility of using an infrared free electron laser (FEL) to resonantly heat fullerenes, and to obtain, for the first time, IR-REMPI spectra of gas-phase molecules. The mass spectra recorded on top of a resonance are almost fragmentation-free, and species selective IR spectroscopy on gas-phase fullerenes in mixed samples is shown to be possible.

Multiphoton excitation with a FEL has recently been studied for gas-phase NO [8], where ladder climbing up to five quanta appeared to be feasible, and for dissociation of selected Freons, requiring absorption of 30–40 IR photons per molecule [9]. At least several hundred IR photons need to be absorbed by a  $\text{C}_{60}$  molecule before it will ionize in the experimental time window and this might therefore appear to be a rather unlikely process. One should realize, however, that with 174 internal degrees of freedom and with an averaged vibrational frequency of  $950 \text{ cm}^{-1}$  [10], on average less than two quanta need to be put in each vibrational mode of  $\text{C}_{60}$  to reach the required energy of 35–40 eV. By sequential pumping of IR photons into the molecule, accompanied by thermalization via fast internal vibrational redistribution, the  $\text{C}_{60}$  molecule can then be resonantly heated up to energies at which ionization becomes efficient.

The experiments have been performed at the “free electron laser for infrared experiments” (FELIX) user facility in Nieuwegein, The Netherlands [11,12]. This laser produces pulsed IR radiation that is continuously tunable over the 100–2000  $\text{cm}^{-1}$  range with a bandwidth that can be varied from 0.5% to 5% of the central frequency. The light output consists of macropulses of about 5  $\mu\text{s}$  duration containing 30 mJ of energy. Each macropulse consists of a train of micropulses which are 1 ns apart. In the present experiment, the micropulses have a full width at half maximum of approximately ten optical cycles, i.e., a

pulse duration of 0.3 ps at 10  $\mu\text{m}$ , and FELIX runs at a 10 Hz repetition rate.

The experimental apparatus consists of a turbo-pumped vacuum system containing a compact effusive molecular beam source and a time-of-flight (TOF) mass spectrometer, as schematically shown in Fig. 1. This apparatus is directly connected to the beam delivery system of FELIX, with only a KRS5 window separating the vacuum systems. The FELIX beam has a near-Gaussian spatial intensity profile with a full width at half maximum of 1 cm and is focused with a KRS5 lens with a focal length of 7.5 cm in the region between the extraction plates of the TOF mass spectrometer. The beam waist varies from approximately 60 to 200  $\mu\text{m}$  in scanning FELIX from 6 to 20  $\mu\text{m}$ , yielding maximum power densities of  $1 \times 10^{12}$  to  $3 \times 10^{10}$  W/cm<sup>2</sup> per micropulse, respectively.

An effusive molecular beam of C<sub>60</sub> is generated by evaporating pure C<sub>60</sub> (Hoechst, "Super Gold Grade" C<sub>60</sub>, purity  $\geq 99.9\%$ ) from a quartz oven. A 2 mm hole in a stainless steel plate placed 1 cm away from the oven between the extraction electrodes serves to better

define the molecular beam geometry. The density of C<sub>60</sub> in the interaction region is determined in a separate experiment by measuring the time-integrated flux of C<sub>60</sub> deposited on a KBr substrate (placed in between the extraction electrodes) via Fourier-transform infrared absorption spectroscopy. With an oven temperature of 875 K the density of C<sub>60</sub> in the interaction region is thus determined to be  $(8 \pm 2) \times 10^9$  molecules/cm<sup>3</sup>, in accordance with a crude estimate based on the vapor pressure of C<sub>60</sub> at 875 K [13] and the experimental geometry. The effusive molecular beam crosses the laser beam perpendicularly. C<sub>60</sub> molecules with a most probable velocity of 190 m/s will interact with a train of 300 to 1000 micropulses, again depending on the size of the laser focus, i.e., depending on wavelength.

The TOF mass spectrometer used [14] is designed to fulfill second-order space focusing conditions [15]. The voltage on the extraction plates is switched on with a time delay of 20  $\mu\text{s}$  relative to the end of the FELIX macropulse. This time delay is a compromise between waiting long enough to accumulate a sufficient number of ions, yet short enough to avoid the escape of molecules and ions from the collection region. The mass resolution ( $m/\Delta m$ ) is about 200. Ions are detected on a double microchannel plate (MCP) detector. The ion signal is amplified and recorded on a digital oscilloscope (LeCroy 9430). For absolute frequency calibration as well as to monitor the bandwidth of FELIX, the absorption spectrum of a thin film of C<sub>60</sub> is recorded simultaneously. For this, part of the FELIX beam is passed through a 5  $\mu\text{m}$  thick C<sub>60</sub> film on a KBr substrate directly upon exiting the experimental apparatus, and the transmitted intensity is recorded on the oscilloscope as well. The data are transferred to a PC, which also controls the wavelength scanning of FELIX.

In the lower part of Fig. 1, a mass spectrum, recorded with FELIX on the C<sub>60</sub> resonance at 19.2  $\mu\text{m}$  (see Fig. 2),

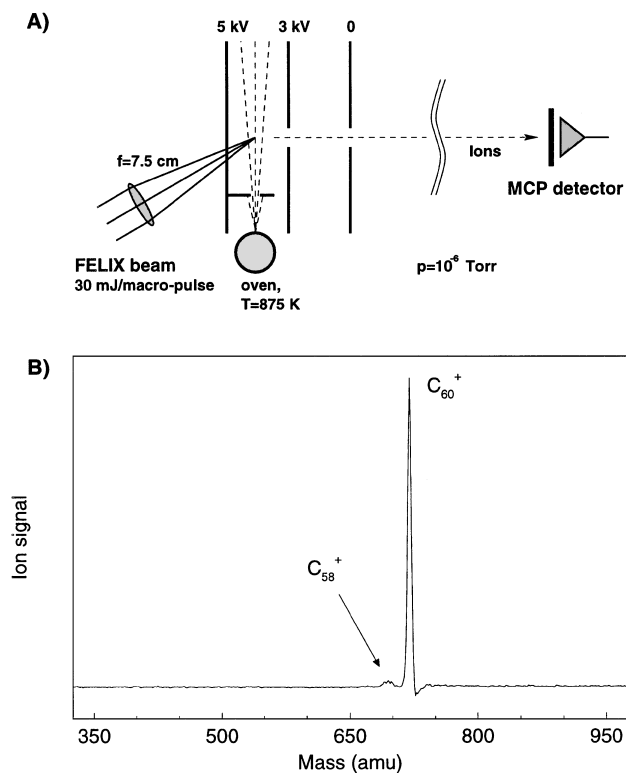


FIG. 1. (a) Scheme of the experimental setup. The FELIX beam is focused between the extraction plates of a TOF mass spectrometer. An oven containing fullerenes is placed 5 cm below the TOF axis. The voltages on the extraction plates are switched on 20  $\mu\text{s}$  after the end of the FELIX macropulse and the ions are detected with a MCP detector. (b) TOF mass spectrum, recorded with FELIX on the C<sub>60</sub> resonance at 19.2  $\mu\text{m}$  (see Fig. 2), i.e., following resonant absorption of about 600 IR photons. The only fragment observed is due to C<sub>2</sub> loss.

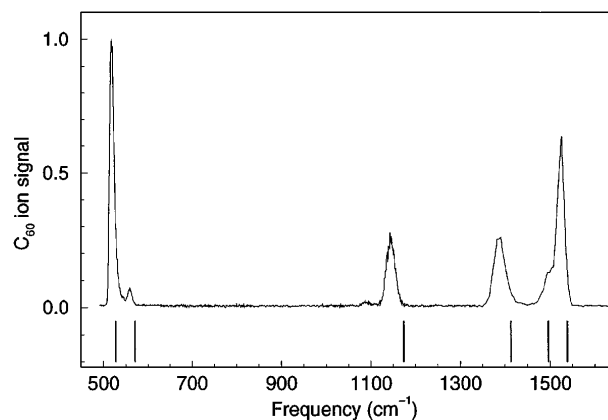


FIG. 2. IR-REMPI spectrum of gas-phase C<sub>60</sub> effusing from an oven at 875 K. The positions of the IR emission lines of gas-phase C<sub>60</sub> [17] at 875 K are indicated by solid lines underneath the IR-REMPI spectrum.

i.e., following resonant absorption of about 600 IR photons [16], is shown. Only a very small amount of fragment ions is observed, significantly less than commonly observed when visible or UV photons are used to heat  $C_{60}$  [1]. The use of many IR quanta to create superheated  $C_{60}$  leads to a much narrower internal energy distribution in the ensemble of molecules than obtained when visible or UV photons are used to create the same averaged internal energy. As fragmentation becomes relatively more important for higher internal energies [1], the better defined internal energy after IR excitation will indeed suppress the fragment channel. In addition, further excitation followed by ionization and/or fragmentation of neutral fragments, while certainly important when visible and UV lasers are used, is unlikely to occur in our setup as the IR radiation will most likely not be in resonance with those neutral fragments. As we are only resonantly heating  $C_{60}$ , the fragment ions have to be formed via the highly excited neutral  $C_{60}$  directly, either after fragmentation of the neutral followed by delayed ionization of the fragment or after fragmentation of  $C_{60}$  ions.

In Fig. 2 the IR-REMPI spectrum of  $C_{60}$  as recorded over the  $6.25\text{--}20\ \mu\text{m}$  range is shown. The spectrum is recorded by stepping FELIX in  $0.02\ \mu\text{m}$  steps and summing the  $C_{60}$  ion intensity over 40 macropulses at each wavelength setting. Strong resonances are observed in the yield of  $C_{60}$  ions for specific IR frequencies. The mass spectrum on each of the resonances is similar to the one shown in the lower part of Fig. 1. The maximum number of ions produced per macropulse on top of a resonance is on the order of  $10\text{--}100$ , implying an overall ionization efficiency of  $10^{-4}\text{--}10^{-5}$ . The REMPI spectrum could only be recorded in the present setup by using the maximum available FELIX power; reducing the overall intensity by a factor of 2 decreased the ion signal by more than an order of magnitude. As the REMPI experiments are performed on gas-phase  $C_{60}$  coming out of an oven at  $875\ \text{K}$ , the most relevant reference spectra for our IR-REMPI spectra are the IR emission spectra of hot gas-phase  $C_{60}$  [17]. The latter spectra show strong IR emission features at frequencies corresponding to those of the four IR allowed  $F_{1u}$  fundamental modes of icosahedral  $C_{60}$ . At least two additional relatively strong emission features corresponding to IR allowed combination modes are observed at the high frequency end of the spectrum, around  $1500\ \text{cm}^{-1}$  [17]. The full width at half maximum of all emission lines is in the  $10\text{--}15\ \text{cm}^{-1}$  range. The position of these six most prominent IR emission lines is indicated by solid lines underneath the IR-REMPI spectrum. The resonances in the IR-REMPI spectrum are systematically found at slightly lower frequencies than the gas-phase emission lines and show slightly asymmetric line shapes, tailing towards the position of the gas-phase IR emission lines. Both the frequency shift and the asymmetric line shape can be explained by anharmonic cross coupling of the IR active modes to all other excited

modes, as a result of which lines will gradually shift to lower frequency with increasing internal excitation [18]. Apart from sequential single photon absorption per micropulse, it cannot be excluded that multiphoton transitions occur during a micropulse. The most intense multiphoton transitions will be those that are in near resonance with IR allowed single photon transitions, which will therefore also lead to resonance lines that are shifted to lower frequencies due to the anharmonicity of the ladder to be climbed [18].

As can be seen in Fig. 2, those IR-REMPI resonances that show the least frequency shift relative to the IR emission lines yield the strongest ion signal. This is to be expected, as the laser radiation has to stay in resonance with the IR absorptions of the molecule while it is heated up from  $875\ \text{K}$  to approximately  $5000\ \text{K}$ , when thermionic electron emission occurs. By increasing the bandwidth of the laser, this is more readily accomplished and larger frequency shifts can be compensated for. This is explicitly shown in Fig. 3, where in the upper part the IR-REMPI spectrum of  $C_{60}$  in the  $500\text{--}600\ \text{cm}^{-1}$  region is shown for two different bandwidths of FELIX. In the lower part of the figure the simultaneously measured absorption spectra of a room-temperature  $C_{60}$  film are shown. The width of the lines in the absorption spectrum is almost exclusively

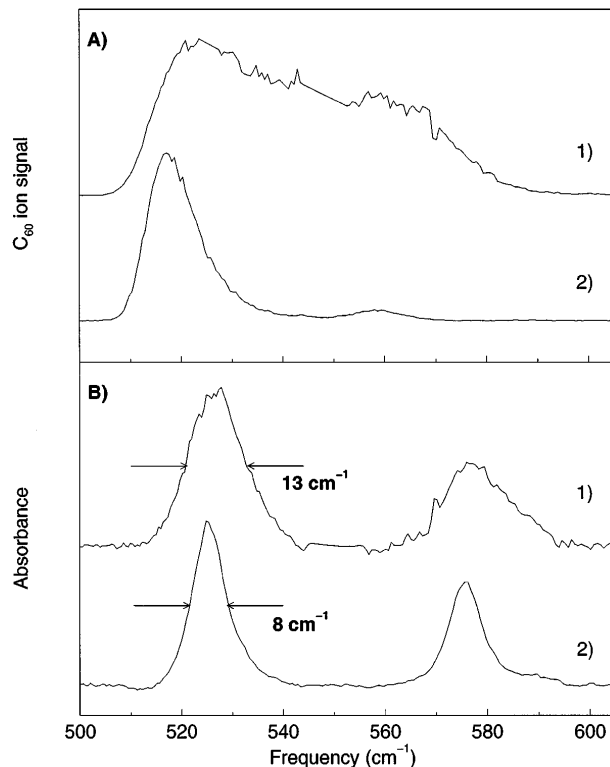


FIG. 3. (a) IR-REMPI spectra of  $C_{60}$  in the long wavelength region for two different bandwidths of FELIX. (b) Corresponding absorption spectra of a room-temperature  $C_{60}$  film as measured with FELIX. The bandwidth (indicated by arrows) decreases in going from  $1 \rightarrow 2$ .

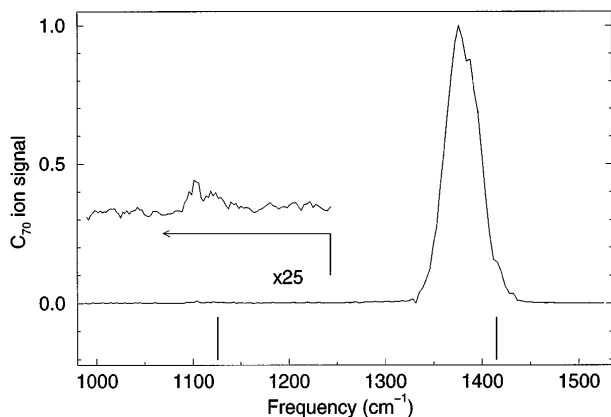


FIG. 4. IR-REMPI spectrum of gas-phase  $C_{70}$  effusing from an oven at 875 K. The positions of the IR emission lines of gas-phase  $C_{70}$  [17] at 875 K are indicated by solid lines underneath the REMPI spectrum.

determined by the laser bandwidth. The IR-REMPI resonance on the widely shifted, second  $F_{1u}$  mode around  $560\text{ cm}^{-1}$  gains dramatically in intensity relative to the intensity of the first, almost unshifted,  $F_{1u}$  mode around  $520\text{ cm}^{-1}$ , when the bandwidth of the laser is only moderately increased.

To exploit the mass-selective detection of the here presented method for IR spectroscopy of gas-phase fullerenes, we filled the oven with a  $C_{60}:C_{70}$  5:1 mixture (MER Corporation). In Fig. 4 the IR-REMPI spectrum of  $C_{70}$  as recorded in the  $6.5\text{--}10\text{ }\mu\text{m}$  region is shown. IR-REMPI spectra of  $C_{60}$  of comparable quality to the one shown in Fig. 2 were obtained simultaneously with the IR-REMPI spectra of  $C_{70}$ . The two solid lines underneath the spectrum in Fig. 4 indicate the position of the gas-phase IR emission lines of  $C_{70}$  at 875 K [17]. The IR-REMPI  $C_{70}$  resonance around  $1400\text{ cm}^{-1}$  is actually substantially stronger than the strongest  $C_{60}$  resonance that we observed. With a density of  $C_{70}$  in the interaction region that is about an order of magnitude less than the density of  $C_{60}$ , the more efficient ionization of  $C_{70}$  is presumably due to the presence of many IR active modes in  $C_{70}$  around this frequency [17,19], by which the resonance condition is much easier to be fulfilled.

In conclusion, we have demonstrated that extremely sensitive IR spectroscopy with mass-selective detection can be performed on gas-phase fullerenes by using a FEL. IR-REMPI spectroscopy as presented here holds great promise and offers unique possibilities for the study of exotic fullerenes and their (endohedral) complexes in the gas phase, without prior sample purification.

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