closed-shell structures). In the present case, the magic number (8,12) observed in Fig. 2 is consistent with the closing of a cage-like pentagonal dodecahedron structure (Fig. 1A) (*1*). As for the subsequent growth of larger cluster sizes, there are two possibilities whereby the structure can rearrange to accommodate more atoms: (i) the breaking of pentagon rings and the formation of hexagon rings, as in the case of pure carbon clusters and water clusters, for example, and (ii) the addition of extra metal-carbon atoms to the basic unit, with the subsequent formation of multicage structures. In the case of pure carbon clusters, it is well known that an exceptionally stable cage exists with a total of 60 carbons, with other stable clusters involving different combinations of pentagons and hexagons (*5*). Likewise, for the system of water clusters, a pentagonal dodecahedron structure forms with 20 water molecules, whereas larger ones (such as 24 water molecules form a cage that consists of 2 hexagons and 12 pentagons) account for the observed magic number patterns (*6*). These structures cannot explain any of the magic numbers observed in the large cluster sizes of Zr_mC_n. However, multicage structures (discussed below) can account for all of our observations.

A completed double-cage structure is shown in Fig. 1B. A minimum of 35 atoms is required to construct the double cage, in accordance with the magic number at (13,22). For this combination, one of the possible metal positions, in Fig. 1B, is occupied by a carbon atom. In order to explain the magic number at (13,22) and the truncation at (14,23), the formation mechanism must be considered. As discussed in our earlier reports (*1, 2*), the (8,12) species is very stable due to its lack of reactivity or growth, but the (8,13) and (8,14) species do exist and correspond to species with carbons on the periphery of the cage. These are identified as the origin of the multicage structures; growth by (1,2) and (2,3) additions (*3*) leads to formation of the (13,22) peak. Direct additions of (2,3) units lead to the (14,23) peak. The latter is a completed double-case structure having two additional carbons bridging between two metal sites, thereby closing another pentagon. Preliminary metastable studies reveal that these two carbons are relatively weakly bonded and are not members of the complete double cage (14,21) shown in Fig. 1B. Closed triple-cage (Fig. 1C) and quadruple-cage structures (Fig. 1D) require a minimum number of atoms corresponding to 47 and 57, respectively, in agreement with the experimental findings that magic numbers at (18,29) and (22,35) are observed in the mass spectrum.

It is instructive to compare and contrast these findings with another metal-carbon system that builds through the formation of cubic clusters. A typical TOF mass spectrum of Ta_mC_n clusters is shown in Fig. 3. A completely different magic number pattern exists for this system. All of the magic numbers at (14,13), (18,18), (24,24), (32,32), (40,40), and (50,50) are consistent with cubic structures (*7*) that have closed packings of 3 × 3 × 3, 3 × 3 × 4, 3 × 4 × 4, 4 × 4 × 4, 4 × 4 × 5, and 4 × 5 × 5. The failure to observe similar patterns in clusters Zr_mC_n implies that the cubic structures do not exist in this system, but rather, the cage-like structures are responsible for the magic numbers of metallo-carbohedrenes. Hence, while it might be suggested that a cubic structure with 8 metals at the corners and 12 carbons connecting in between could also explain the magic peaks we find at (8,12), such an explanation is not compatible with the growth mechanism of the metallo-carbohedrenes, nor could it account for the very definitive pattern seen for the development of multicage structures. This growth mechanism distinguishes the metallo-carbohedrenes as an unusual class of cluster materials.

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UV Spectrum and Proposed Role of Diethylberyllium in a ^{7}Li-^{7}Be Solar Neutrino Experiment

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Although measurement of the solar neutrino flux via the ^{7}Li(ν_e,e$^-$)^{7}Be reaction was proposed many years ago, no experiment has been implemented since it has been difficult to identify a sensitive ^{7}Be detection technique. Here it is proposed that the ^{7}Be atom be incorporated into a volatile molecule, placed in a buffer-gas–filled cell, and then extracted by photodissociation; after excitation by a tunable laser, bursts of photons would be detected. The absorption spectrum of the molecular candidate diethylberyllium has been measured between 186 and 270 nanometers in a spectrophotometer to determine the required photodissociation laser wavelength and intensity.

The solution to the long-standing discrepancy between the calculated flux of the standard solar model and the smaller measured fluxes of the chlorine detector in the Homestake mine (*1*) and of the Kamiokande II water Čerenkov detector (*2*) may lie in the solar model or may have its roots in new neutrino physics. With results from the Soviet-American gallium experiment becoming available (*3*), there is increasing speculation that new physics may be required. As the neutrino spectrum would be different depending on whether solar model corrections or new physics is required, it is necessary to perform a number of complementary measurements with detectors having a range of energy thresholds.

A proposed measurement of the solar neutrino flux with a ^{7}Li detector, via the ^{7}Li(ν_e,e$^-$)^{7}Be reaction, has been discussed for over 25 years (*4, 5*). Lithium is a first-rate detector choice: it is cheap, the rate of neutrino events per ton is high, the neutrino energy threshold (862 keV) is relatively low, and the neutrino absorption cross sections can be calculated accurately. Techniques for extracting the ^{7}Be atoms from the lithium target have been developed, and a 1/100 scale model, with 2000 liters of 12 M lithium chloride, has been tested at Brookhaven National Laboratory, showing that it is possible to extract 100 μg of natural beryllium efficiently (*6*). Sources of background from α particles, neutrons, and cosmic rays were also studied. An experiment using metallic lithium is under development (*7*).

What has been lacking thus far is a means for efficiently detecting the few ^{7}Be atoms that would be produced by solar neutrinos. This nucleus has a half-life of 53 days and would be extremely hard to detect in small quantities by nuclear decay. The ^{7}Be nucleus decays 90% of the time to the ground state of ^{7}Li, producing Auger electrons with energy of only 50 eV, and only 10% of the time to

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an excited state of ^{7}Li, which emits a 478-keV gamma ray. This gamma ray would be difficult to detect above background, although coincidence techniques are being considered (7). Laser techniques have been suggested as a solution (6). Here I discuss a specific scheme and report a key measurement required for its implementation.

The standard solar model predicts a rate of 52 SNU (units of 10^{-36} events per target atom per second) for a ^{7}Li detector (2). Such a detector is mostly sensitive to neutrinos from ^{8}B decay in the sun but also to ^{15}O neutrinos and $p+e^-+p$ neutrinos. There are several smaller contributing neutrino sources: ^{7}Be, ^{13}N, ^{17}F, and ^{3}He+p. A detector with 10 tons of lithium would yield 3.5 ^{7}Be atoms per day (standard solar model prediction). Single atoms of ^{7}Be may be counted with photon burst detection (8). When an atom remains in a laser beam (tuned to excite one of the atomic states) for a period that is long compared to the lifetime of the excited atomic state (as is the case when a buffer gas is present), the atom may emit a burst of many photons, as it is repeatedly excited and then spontaneously decays. The strength of this technique, compared to others such as resonance ionization, lies in the potential of detecting many radiations from a single atom. As beryllium is a two-level atom (transition $^1S_0$ to $^1P_1^o$ at 235 nm) with an upper-level atomic lifetime of only 1.85 ns, it is ideally suited for the photon burst detection technique with little extension of present technology. Excitation and detection would be at 235 nm.

In the chemical separation procedure for a ^{7}Li solar neutrino experiment developed at Brookhaven (6), the end product was elemental beryllium. It is difficult to begin the laser detection sequence with atomic beryllium, however, as the small number of atoms would rapidly deposit on walls unless the cell were maintained at very high temperature (giving light that would generate intolerable backgrounds). The wall problem can be solved by placing the ^{7}Be atom from the chemical separation in a volatile molecule. The photon burst technique requires that the molecule be converted back to the neutral atom (to get a two-level cycling transition).

I thus propose to photodissociate the molecules with a small-diameter laser beam that is coaxial with the larger diameter frequency-doubled dye laser beam tuned to the atomic transition. Upon breakup of the molecule, the ^{7}Be atoms would slowly diffuse from the axis and through the dye laser beam, emitting a burst of photons. Use of a pulsed dissociation laser would allow additional sensitivity because the time at which the ^{7}Be atom is formed would be known. Because the isotope shift between ^{7}Be and ^{9}Be is large, the normal mass shift being 22 GHz, only ^{7}Be would be detected. The primary unknowns here are (i) whether it is possible to dissociate the chosen molecule with a laser beam of readily obtainable wavelength and intensity and (ii) whether the dissociation products will include neutral atomic beryllium a large fraction of the time. The measurement may still be feasible if ionic beryllium were produced, but neutralization would have to occur within the diffusion time.

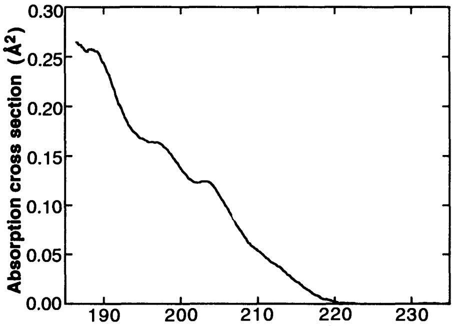

Fig. 1. Absorption spectrum for diethylberyllium.

The molecule diethylberyllium, $(C_2H_5)_2Be$, has been chosen as an initial molecular candidate. The measurement of its ultraviolet spectrum, a knowledge of which is required for choosing a laser for further photodissociation studies, is described here. Diethylberyllium has been used in the semiconductor industry as a source of metallic beryllium for doping and film deposition. It is known that when this molecule is heated, it dissociates, leaving elemental beryllium. The photodissociation dynamics for a Group IIA diethyl molecule such as diethylberyllium might be expected to be similar to that for a Group IIB diethyl molecule such as diethylzinc, for which there have been several experimental studies. Borsella and Larciprete (9) have studied the photodissociation dynamics of diethylzinc by time-of-flight mass spectroscopy. In one of their measurements, diethylzinc was bombarded by 248-nm laser radiation, and a dye laser was used to probe the neutral fragments after a 700-ns delay. They concluded that the main dissociative channel at 248 nm produced zinc atoms.

The diethylberyllium sample (10) was enclosed in a Teflon-lined stainless steel cylinder. After the cylinder was pumped out (at liquid nitrogen temperature), diethylberyllium was distilled (from the cylinder at −35°C) into a glass tube (dipped in liquid nitrogen). It was then transferred to a stainless steel cell (2.2 cm in diameter and 7.6 cm long) with synthetic fused silica (11) windows (attached with epoxy) for the absorption measurement. The glass and stainless steel vacuum system (constructed primarily with 5-mm-inside-diameter stainless steel tubing) in which the distillation and transfer were done was sealed by metal gaskets (no rubber O-rings or grease) and was pumped by a cryopump via a tube dipped in liquid nitrogen. The vacuum system was baked gently before use. The leak rate was 0.002 torr/day. The transfer of the diethylberyllium to the absorption cell was made a few hours before the absorption measurement. The pressure of the diethylberyllium in the cell was measured with a baratron (12) to be 0.163 torr. After transfer of diethylberyllium into the cell, the valve to the cell was closed and the cell was disconnected from the vacuum manifold.

The absorption measurement was made with a spectrophotometer (13) purged with argon to reduce absorption of light by atmospheric oxygen. The cell was placed in the sample chamber of the spectrophotometer; the reference chamber was empty. A stainless steel side tube was attached to the cell. Absorption measurements were made both at room temperature and with this tube dipped in liquid nitrogen. Three scans were made alternately at each of the two temperatures, the bandwidths ranging from 0.03 to 0.4 nm.

The intensity transmitted by the diethylberyllium ranged from 30 to 100%, depending on the absorption cross section at the particular wavelength. The signals (the logarithms of the reference-to-sample chamber ratios) acquired with a chart recorder were digitized to obtain computer-readable output, and the background (liquid nitrogen) signal was subtracted. Results of the three passes were averaged and converted to cross sections with the use of the pressure and the cell length. The cross sections are shown in Fig. 1 for the range 186 to 235 nm. Absolute errors are estimated to be 5%, dominated by pressure measurement errors. Relative values are estimated to be good to 0.002 Å^2, dominated by the consistency of the three scans. The spectrophotometer has a wavelength accuracy of ±0.04 nm. The cross section was also measured (for two of the passes) in the range 235 to 270 nm and found to be zero (less than 0.01 Å^2).

It can be seen that the cross section rises to large values below 220 nm, with a structure, presumably due to vibrational modes, similar to that observed in other metallic dialkyls such as diethylzinc (14). This spectrum is shifted to significantly shorter wavelengths as compared to diethylzinc (which peaks at 225 nm), but it has the same general structure. Unfortunately, the range of the spectrophotometer was inadequate to trace over the peak of the absorption spectrum. For the purposes of the present photodissociation question, it can be seen that the cross section is significant, for example, at 193 nm, so the molecule might be dissociated by an ArF excimer laser. The similarity of the absorption spectrum to that of diethylzinc and the expectation that a metallic atom (or at least a metallic ion) often results in the zinc case give us reason to expect a large quantum yield for beryllium, at least for some frequency range, in diethylberyllium photodissociation.

For a cross section of 0.18 Å^2 and a beam diameter of 0.1 mm, the 193-nm laser energy required for unit probability of absorbing a photon during one pulse is only 5 μJ (assuming the pulse length to be small compared to relevant diffusion times, which is easily the case for a typical pulse length of 20 ns). If the dye laser beam at 235 nm has a diameter of 0.5 mm, the diffusion time from the beam center for 250 torr of helium is 87 μs [assuming a diffusion constant of 1.8 cm^2/s, derived from magnesium and cadmium data (*15*)]. If the dye laser beam power is 5 mW, the Doppler broadening is 6.0 GHz (room temperature), and the collision broadening is 3.7 GHz [extracted from data for magnesium, calcium, and strontium in helium (*16*), with scaling as the 0.3 power of the temperature], then 870 photons will be emitted as the atom diffuses from the cell center. If the detection efficiency is 5% (light collection and quantum efficiency of the photomultiplier tube at 235 nm), 43 photons will be detected. With careful baffling and absorption of stray laser light, the primary source of background will be Rayleigh scattering from the helium gas in the focal volume. This Rayleigh yield will be 84 detected photons if the length of the imaged region along the beam is 2 mm. By looking at the number of counts during the 87-μs period after the 193-nm pulse, one can thus count bursts above background. A measurement could be completed in a few minutes.

The efficiency for detecting a beryllium atom formed at the center of the dye laser beam and within the imaging region of the phototube is approximately unity. However, the total efficiency is reduced by the ratio of the length of the imaged region to the length of the cell traversed by the photodissociation laser. A major experimental problem that will have to be resolved is balancing the efficiency of detecting a beryllium atom and the reduction of scattered light. If the entrance and exit windows were closed to the region that the phototube images, there would be scattered light produced as the dye laser beam passes through (in addition to Rayleigh-scattered light from the buffer gas). If these windows were far from the imaged region, there would be significant volumes inside the cell where the molecule would be dissociated but the beryllium atom would not be detected. If the windows were placed far away, thin plastic membranes (about 10 μg/cm^2) 4 mm apart enclosed the diethylberyllium molecules, and the imaged region were 2 mm long, as above, the total efficiency would be 50%. The number of atoms in the membranes (outside the focal volume) exposed to the laser beam would be less than the number of helium atoms in the focal volume, so Rayleigh scattering from the helium would remain the major source of background. Looking only at delayed photons when the dye laser is rapidly modulated on and off may help, but this would have to be done on a nanosecond time scale. An alternative would be to use two-photon rather than one-photon dissociation and to focus the dissociating laser into the imaged region.

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Synthesis and Single-Crystal X-ray Structure of a Highly Symmetrical C_{60} Derivative, $C_{60}Br_{24}$

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C_{60} and liquid bromine react to form $C_{60}Br_{24}$, a crystalline compound isolated as a bromine solvate, $C_{60}Br_{24}(Br_2)_x$. The x-ray crystal structure defines a new pattern of addition to the carbon skeleton that imparts a rare high symmetry. The parent C_{60} framework is recognizable in $C_{60}Br_{24}$, but sp^3 carbons at sites of bromination distort the surface, affecting conformations of all of the hexagonal and pentagonal rings. Twenty-four bromine atoms envelop the carbon core, shielding the 18 remaining double bonds from addition. At 150° to 200°C there is effectively quantitative reversion of $C_{60}Br_{24}$ to C_{60} and Br_2.

Early studies on fullerene carbon clusters point to an unusual chemical reactivity of this class of molecules. Of great interest are patterns that may develop on the surfaces of these polyhedra by repeated addition of atoms or more complex chemical groups. Although structures have been determined for compounds where C_{60} (*1*) is attached to as many as six metal complexes (*2*), structural information has not been available for derivatives with large numbers of addends.

We report the synthesis and structure of a new compound in which 24 bromine atoms bond to C_{60} (*3*). The product, $C_{60}Br_{24}$, displays T_h symmetry, only slightly reduced from the I_h symmetry of the parent molecule (Fig. 1). The pattern of the 24 bromines may be viewed as arising from 1,4-additions to fused pairs of six-membered rings with the closest Br,Br placement being 1,3 (*4*). Any further addition of Br is then unlikely because some Br atoms would necessarily be located on adjacent carbons.

When C_{60} and liquid bromine are combined at ambient temperatures, a solution is produced from which a yellowish-orange solid slowly precipitates (*6*). Although the solid is crystalline, the dimensions of the largest crystals are ~1 μm in size, much too small for a single-crystal x-ray structure determination. However, enough information could be obtained from infrared (IR) and Raman vibrational spectra to postulate a structure. When a crystal of sufficient size

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