TABLE I. Spectroscopic constants for C₂.

<table>
<thead>
<tr>
<th>Band</th>
<th>$v_0$ (cm$^{-1}$)</th>
<th>$B^+$ (cm$^{-1}$)</th>
<th>$B^-$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>22 334.2 ± 0.2</td>
<td>1.85 ± 0.02</td>
<td>1.95 ± 0.02</td>
</tr>
<tr>
<td>(b)</td>
<td>22 449.2 ± 0.2</td>
<td>1.81 ± 0.02</td>
<td>1.90 ± 0.02</td>
</tr>
</tbody>
</table>

this is not surprising given the small values of $\lambda$ and $\gamma$ which are typical for the $^3\Sigma$ states of C₂. The $B$ constants for the upper state are larger than those of any of the known states, and indicative of a very tight binding. Most probably the exceptional stability of this state results from the promotion of both antibonding electrons to bonding orbitals. The lowest energy $^3\Sigma_u^+$ state with this electronic configuration is obtained by exciting the $(\sigma_g 2s)$ electron to the $(\sigma_g 3s)$ orbital.

Experiments conducted at high source pressures revealed that multiple collisions with Ar will induce transfer from $c^3\Sigma_u^+$ to $a^3\Pi_u$. Figure 1 (b) shows a spectrum taken at a source pressure of 540 psi. Here the $c^3\Sigma_u^+$ band has been completely replaced by the 10–8 band of the $d$–$a$ system (absorption from both $c$ and $a$ is seen at intermediate pressures). This process is analogous to the $c$–$d'$ transfer which was proposed by Nieuwpoort and Bleekrode to account for the intensity anomalies observed in the $d$–$a$ spectrum emitted by a low-pressure oxacycylene flame.

A tentative vibrational assignment of the lower state of band (a) to $v = 2$ can be made on the basis of the energetics governing the transfer process. The $c, v = 2$ level lies 14 289.5 cm$^{-1}$ above the ground state minimum. The nearest level of $a^3\Pi_u$ is $v = 8$, which lies at 13 824.6 cm$^{-1}$. Thus direct transfer into $v = 8$ is energetically favored. Electronic transfer which is preceeded or followed by vibrational energy transfer is unlikely as relaxation between the widely spaced vibrational levels is very inefficient. In support of this argument we note that the intensity of the 10–8 band was undiminished at source pressures as high as 1000 psi. Further studies of the new band system are currently in progress.

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The UV absorption spectrum of C₆₀ (buckminsterfullerene): A narrow band at 3860 Å

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For some time we have been searching for a spectral probe of the special cluster, C₆₀, which has been proposed to have the structure of a truncated icosahedron. The high symmetry of this structure, extensive theoretical calculations have been possible, and increasingly detailed predictions have begun to appear in the literature.2–17 There is general agreement that the ground state of such a molecule would be a closed-shell $^1A_g$ state with a HOMO of $h_{1u}$ symmetry. The LUMO is predicted to be of $t_{1u}$ symmetry, followed a bit higher in energy by one of $t_{1u}$ (LUMO + 1). Promotion of an electron from the HOMO to the LUMO gives no excited electronic states with electric dipole allowed transitions from the ground state. The lowest electric dipole allowed transition involves excitation from the HOMO to LUMO + 1 to produce a state of $^3T_{1u}$ symmetry. The most detailed prediction thus far of these excited electronic states is that of Larsson, Volosov, and Rosen, whose calculations show numerous forbidden excited low-lying electronic states in the 2–3 eV region, with the longest wavelength allowed $^1T_{1u} \rightarrow ^1A_g$ (LUMO + 1 – HOMO) transition predicted at 3.6 eV with an oscillator strength of 0.08. The next allowed transition is predicted to occur at 4.8 eV. As pointed out by Haddon et al., a small Jahn–Teller effect and little vibrational activity would be expected in the spectrum of such a rigid molecule. In the region of the lowest $^3T_{1u} \rightarrow ^1A_g$ transition, one therefore expects a single strong 0–0 band, perhaps somewhat broadened by coupling to the underlying vibrational quasicontinuum.

With such low-lying forbidden excited electronic states, all previous experience with large polyatomic molecules suggests that the lifetime of the excited $^3T_{1u}$ state should be exceedingly short and that multiphoton or fluorescence techniques would probably not succeed. Nonetheless, we performed extensive R2PI spectral searches on this C₆₀ mol-
ecule in a supersonic beam throughout broad regions of the visible and ultraviolet with both one- and two-color ionization techniques.\textsuperscript{19} Unfortunately no R2PI spectrum was found.

However, we can report success with a different spectral technique: laser depletion spectroscopy\textsuperscript{20} of cold van der Waals complexes of C\textsubscript{60} with two distinctly different adducts: C\textsubscript{6}H\textsubscript{6} and CH\textsubscript{2}Cl\textsubscript{2}. Using an apparatus similar to that described earlier,\textsuperscript{1} intense supersonic expansions were produced with carbon clusters. Formation of van der Waals complexes was aided by a 20 cm long, 30° expansion cone on the exit of the supersonic nozzle. Direct one-photon ionization with an F\textsubscript{2} excimer laser (7.9 eV) followed by time-of-flight mass spectrometry was used to probe the neutral cluster beam. The concentration of the desired adduct in the helium carrier was adjusted such that the only substantial van der Waals cluster peaks in the mass spectrum corresponded to the C\textsubscript{60} adduct, with only a small amount of the C\textsubscript{60}(adduct)\textsubscript{2} detectable. Confirmation that C\textsubscript{60}--adduct\textsuperscript{+} ion signal was due to ionization of the corresponding weakly bound neutral van der Waals complex was obtained by photofragmenting the mass-selected ion in a tandem time-of-flight apparatus\textsuperscript{11,15,21} at 3530 Å. The C\textsubscript{60}--adduct\textsuperscript{+} species readily one-photon dissociated to form C\textsubscript{60}\. In contrast, the large carbon cluster ions in this mass region are known to fragment only after high order multiphoton excitation.\textsuperscript{11}

By monitoring the depletion of the C\textsubscript{60}--adduct\textsuperscript{+} signal as a dye laser was scanned, careful spectral searches were performed in the following regions: 335–345, 365–400, 435–445, and 575–590 nm. Throughout this region only one spectral feature was observed, as shown in Fig. 1. This absorption band occurs at 3860 Å for the C\textsubscript{60}--CH\textsubscript{2}Cl\textsubscript{2} complex and at 3863 Å for the C\textsubscript{60}--C\textsubscript{6}H\textsubscript{6} complex. In both complexes the absorption feature is roughly 50 cm\textsuperscript{-1} wide and rides on an otherwise structureless absorption continuum. Spot checks with fixed wavelength lasers revealed that this absorption continuum rises from less than 2×10\textsuperscript{-19} cm\textsuperscript{2} at 532 nm (YAG second harmonic) to roughly 5×10\textsuperscript{-18} in the near ultraviolet (354, 308, 266 nm) and then rises to 2×10\textsuperscript{-16} cm\textsuperscript{2} at 248 nm (KrF), 7×10\textsuperscript{-17} cm\textsuperscript{2} at 222 nm (KrCl), and 7×10\textsuperscript{-18} cm\textsuperscript{2} at 193 (ArF). The cross section at the peak of the 3860 Å absorption band was estimated to be 1–2×10\textsuperscript{-17} cm\textsuperscript{2}, which is 2–4 times higher than the underlying continuum.

Although this depletion spectroscopy method is rather insensitive, from the comparison of many scans taken over several weeks we are certain this absorption band is a real and reproducible spectral signature of the neutral van der Waals complex of C\textsubscript{60}. No other such feature was found, although in such a low signal/noise experiment it is possible that substantially weaker absorptions might have been missed. The observed small spectral shift toward longer wavelengths when benzene is substituted for CH\textsubscript{2}Cl\textsubscript{2} suggests the corresponding transition in the bare C\textsubscript{60} molecule is only slightly perturbed.

The energy of this transition (3.22 eV) is in fair agreement with the calculations of Rosen\textsuperscript{2} (3.6 eV) for the energy of the lowest electric dipole allowed transition of icosahedral C\textsubscript{60}. We, therefore, tentatively assign this feature as the 0–0 band of the first allowed \textsuperscript{1}T\textsubscript{1u} → \textsuperscript{1}A\textsubscript{g} electronic transition. The observed oscillator strength (0.004) is less than that calculated (0.08), but this discrepancy may have similar roots to that found for the S\textsubscript{1} → S\textsubscript{0} transition in napthalene.\textsuperscript{22} The underlying absorption continuum is thought to arise from vibronically induced transitions to the lower-lying excited electronic states with the transition strength coming from vibronic coupling to the very strongly allowed states in the 4–6 eV range. This vibronic induction mechanism would be expected to give intensity to many vibrational levels of the upper states. The vibrational structure would then be smoothly distributed by coupling to the underlying ground state vibrational quasicontinuum.

Observation of a single narrow feature, the 3860 Å band, in a molecule with this many atoms argues strongly for a rigid, highly symmetrical structure.

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NOTES

ASSOCIATIVE IONIZATION IN COLLISIONS OF K(nd) RYDBERG ATOMS WITH MOLECULES

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Properties of atoms in high-Rydberg states are frequently discussed in terms of the "essentially free" electron model, in which the Rydberg electron and core ion are viewed as independent particles. This model suggests that studies of Rydberg atom collision processes in which the interaction between the core ion and target is important can provide information on thermal-energy ion–molecule reactions. However, for values of principal quantum number n ≤ 20, the classical orbital period of the Rydberg electron (~ 1.5 × 10^{-16} n^3 s) is less than the characteristic times typically associated with thermal-energy ion–molecule reactions. Thus, especially for states of low orbital angular momentum, the possibility exists that during the core–target interaction, the Rydberg electron might pass sufficiently close to modify this interaction by, e.g., carrying off excess energy. Evidence of such behavior is provided by observations of the formation of stable product ions through associative ionization reactions of the type

\[ \text{X}^* + \text{AB} \rightarrow \text{XAB}^+ + e^- \tag{1} \]

Although this reaction clearly involves the core ion, the Rydberg electron must also play an important role because XAB^+ ions formed in binary X^+–AB collisions are unstable and, typically, have short lifetimes. In the present work we have extended, using K(nd) Rydberg atoms, measurements of associative ionization to include a wide variety of molecular targets in an attempt to identify the factors that govern the rate constants for such reactions.

The present measurements were undertaken using an apparatus and technique described in detail elsewhere. Briefly, K(nd) Rydberg atoms are created by pulsed two-photon excitation in the presence of a mixed target gas comprising the species of interest and SF_6. After a selected collision time (typically ~ 1–10 μs), the associative ionization signal (XAB^+) and the SF_6^− ion signal resulting from K(nd)–SF_6 collisions are measured and their ratio normalized to equal target gas densities (typically ~ 3 × 10^{10} cm\(^{-3}\) for SF_6 and ~ 1 × 10^{11}–1 × 10^{12} cm\(^{-3}\) for the target gas). Rate constants for associative ionization are then derived from these normalized ratios R by use of the known rate constants for SF_6^- formation. As expected, the time evolutions of both the associative and SF_6^- ion signals were identical and consistent with the known effective lifetimes of the parent nd states. This indicates that the observed associative ionization signals do not result from collisions involving K^+ (or K_n^+) ions produced by laser and blackbody-radiation-induced photoionization and that associative ions produced via reaction (1) are stable, or at least long lived, on the time scale (~ 10 μs) of the present experiments.

The normalized ratios R are presented in Table I, to-