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Raman and Fluorescence Spectra of Size-Selected, Matrix-Isolated C\textsubscript{14} and C\textsubscript{18} Neutral Carbon Clusters

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The surface plasmon polariton-enhanced Raman spectra of size-selected, matrix-isolated C\textsubscript{14} neutral clusters are presented along with the calculated vibrational frequencies for the ring and linear chain isomers. The Raman spectra show resonance enhancement over a range of excitation wavelengths from 457.9 to 514.5 nm. The measured vibrational spectra are most consistent with the linear chain isomer. In addition, fluorescence spectra of neutral, mass-selected C\textsubscript{14} (n = 14 and 18) clusters are presented. The isolated C\textsubscript{14} clusters display strong fluorescence with vibrational structure between 520 and 700 nm. The origins of the observed fluorescence for both C\textsubscript{14} and C\textsubscript{18} are investigated using the ZINDO/S, CIS, and TD-B3LYP methods.

Introduction

An enormous effort has been devoted to understanding the structures and properties of pure carbon clusters.\textsuperscript{1,2} Despite this considerable effort, experimental measurements on neutral carbon clusters with more than a few atoms are still limited. Results from infrared spectroscopy\textsuperscript{3-5} and surface-enhanced Raman spectroscopy\textsuperscript{6,7} are available for neutral carbon clusters, but few experiments have been performed for molecules larger than C\textsubscript{13}. The linear isomers of neutral C\textsubscript{4} to C\textsubscript{10} have been verified by ESR measurements in neon matrices.\textsuperscript{8} In addition, electronic absorption spectra of matrix-isolated neutral C\textsubscript{n} clusters\textsuperscript{9,10} have produced evidence of linear chain structures for C\textsubscript{4}-C\textsubscript{10} and of cyclic structures for C\textsubscript{10}-C\textsubscript{14} neutral species. Recently, Krätschmer and co-workers have reported the fluorescence spectrum of neutral C\textsubscript{3} molecules isolated in an argon matrix; however, no mass selection was used during the cluster deposition.\textsuperscript{11}

Previously, we presented the first vibrational spectra of mass-selected, matrix-isolated C\textsubscript{16}, C\textsubscript{18}, and C\textsubscript{20} neutral clusters. These spectra were recorded using surface plasmon polariton (SPP) enhanced Raman spectroscopy.\textsuperscript{7} The observed spectra were found to be most consistent with linear chain structures. In addition, strong fluorescence (between 620 and 760 nm) was observed from C\textsubscript{18} when excited with several argon ion laser lines. No fluorescence was detected from C\textsubscript{16} or C\textsubscript{20}.

In this paper, we present the SPP Raman spectra of mass-selected, matrix-isolated C\textsubscript{14} neutral atomic clusters as well as the calculated vibrational frequencies for the ring and linear chain isomers. Similar to our previous studies of C\textsubscript{16}, C\textsubscript{18}, and C\textsubscript{20}, the Raman spectrum for C\textsubscript{14} appears to be most consistent with a linear chain structure. In addition, the first fluorescence spectra of neutral, mass-selected C\textsubscript{n} clusters are reported: C\textsubscript{14} clusters, like C\textsubscript{18}, display strong fluorescence between 520 and 700 nm when excited with an argon ion laser. The origins of the observed fluorescence from C\textsubscript{14} and C\textsubscript{18} have been investigated using the ZINDO/S, configuration interaction-singles (CIS) and time-dependent Becke 3-parameter—Lee—Yang—Parr (TD-B3LYP) density functional methods.

Experimental Methods

The experimental apparatus has been described previously.\textsuperscript{12,13} Briefly, carbon cluster cations are created by laser ablation (308 nm, 100 Hz) of a graphite rod in a continuous flow of He buffer gas (99.9999%) at ~15 Torr. A 1 kV electron beam is injected into the buffer gas flow to enhance the production of cations. The cluster ions are focused into a low energy beam, injected into a quadrupole mass spectrometer for size selection, and passed through a double-bend quadrupole deflector into the ultrahigh vacuum (UHV) chamber. Following the deposition of a 50 Å N\textsubscript{2} buffer layer, carbon cluster ions are codeposited with N\textsubscript{2} onto a silver-coated (550 Å thickness) hemicylindrical sapphire prism cooled to 10 K. The cluster ions are deposited at ~25 eV. The measured spectra are independent of the deposition energy, indicating that fragmentation did not occur during deposition. The ions in the matrix are neutralized by low-energy electrons from a hot filament during deposition. The sample contains approximately 5 x 10\textsuperscript{13} clusters in an 1100 Å thick matrix. After cluster deposition, a 2 μm thick capping layer of N\textsubscript{2} is added to provide the correct conditions for the surface plasmon enhancement and to protect the cluster sample from contamination.

The 457.9, 488.0, and 514.5 nm lines of an argon ion laser (Spectra-Physics model 164) and 635 and 647 nm from an argon ion laser (Spectra-Physics model 2060) pumped dye laser (Coherent model 590) using DCM are used for excitation. Raman scattered light is focused into a triple grating spectrometer (SPEX Triplet 1) with either 600 or 1800 gr/mm gratings and is imaged onto a charge-coupled device (CCD) detector (Princeton Instruments model LN/ccd-512). Data acquisition times range from 60 to 300 s at laser powers between 10 and 200 mW.
Experimental Results

Figure 1 shows the Raman signal for C\textsubscript{14} in analog-to-digital converter units (ADU s\textsuperscript{−1} mW\textsuperscript{−1}) at excitation wavelengths of 457.9 (A), 488.0 (B), and 514.5 (C) nm as a function of wavenumber shift (in cm\textsuperscript{−1}). The spectra exhibit resonance enhancement as shown by the change in intensity of the features at 1627 and 1655 cm\textsuperscript{−1} as the incident wavelength changes. Fluorescence from C\textsubscript{14} was observed between 520 and 700 nm at excitation wavelengths of 457.9, 488.0, and 514.5 nm. At excitation wavelengths of 635 and 647 nm, very weak Raman signals with shifts between 200 and 600 cm\textsuperscript{−1}, and weak fluorescence peaks between the excitation wavelength and 700 nm were observed.

The experimental frequencies reported in Table 1 were determined by matching peaks present at nearly all of the excitation wavelengths. Previously, we reported\textsuperscript{7} systematic shifts in the frequencies for the series of peaks at 250, 223, and 198 cm\textsuperscript{−1} for C\textsubscript{16}, C\textsubscript{18}, and C\textsubscript{20} clusters, respectively. This progression suggests that the spectra do not result from a isomers analogous to a C\textsubscript{20} bowl or cage isomer since such structures are not feasible for C\textsubscript{16} and C\textsubscript{18}. The observed spectra were found to most closely agree with those calculated for linear chains. This progression is continued by the C\textsubscript{14} peak at 282 cm\textsuperscript{−1}. The first overtone of this feature is also present at 564 cm\textsuperscript{−1}. The addition of the C\textsubscript{14} data to this frequency set indicates that the four clusters share similar structures and suggests that the Raman spectra of C\textsubscript{14} are probably due mainly to a linear chain isomer. As noted previously, the chain isomers do not seem to account for all of the observed features. This may indicate the presence of another isomer, for example, a monocyclic ring.

Figures 2 and 3 show the fluorescence spectra acquired for C\textsubscript{14} and C\textsubscript{18}, respectively. The measured fluorescence peak origins reported in Table 2 were determined by matching peaks at excitation wavelengths of 457.9, 488.0, and 514.5 nm. The frequencies of the progressions were determined using the same method. The C\textsubscript{14} spectrum shows an electronic transition at 526 nm which serves as an origin for progressions that occur with spacings of 108 and 437 cm\textsuperscript{−1}. Similarly, the C\textsubscript{18} spectrum shows an electronic transitions at 624 and 666 nm (1006 cm\textsuperscript{−1} separation), which are origins for progressions that occur with spacings of 408 and 877 cm\textsuperscript{−1} and 440 and 877 cm\textsuperscript{−1}, respectively. The assignment of the peaks at 624 and 666 nm to transitions from two different excited electronic states is supported by calculations for C\textsubscript{6} that show close-lying electronic states (1200–2300 cm\textsuperscript{−1}).\textsuperscript{14}

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**TABLE 1: Vibrational Parameters for C\textsubscript{14}**

<table>
<thead>
<tr>
<th>C\textsubscript{14}\textsuperscript{c}</th>
<th>C\textsubscript{14}(D\textsubscript{7}h)\textsuperscript{b}</th>
<th>C\textsubscript{14}(D\textsubscript{4}h)\textsuperscript{b,c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>96 (E\textsubscript{2}′)</td>
<td>58 (Π\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>282</td>
<td>171 (Π\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>342 (A\textsubscript{1}′)</td>
<td>295 (Σ\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>489 (A\textsubscript{1}′)</td>
<td>297 (Π\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>536 (E\textsubscript{2}′)</td>
<td>455 (Π\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>602 (E\textsubscript{1}′)</td>
<td>515 (Π\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>829</td>
<td>637 (Π\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>851</td>
<td>1199 (E\textsubscript{2}′)</td>
<td></td>
</tr>
<tr>
<td>1211</td>
<td>1351 (Σ\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>1394</td>
<td>1791 (Σ\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>1627</td>
<td>1884 (Σ\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>1655</td>
<td>1926</td>
<td></td>
</tr>
<tr>
<td>1807</td>
<td>2089</td>
<td></td>
</tr>
<tr>
<td>1926</td>
<td>2101 (E\textsubscript{2}′)</td>
<td></td>
</tr>
<tr>
<td>2089</td>
<td>2180 (Σ\textsubscript{g})</td>
<td></td>
</tr>
<tr>
<td>2218</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental SPP-enhanced Raman frequencies in cm\textsuperscript{−1}. \textsuperscript{b}Calculated Raman-active frequencies in cm\textsuperscript{−1}. \textsuperscript{c}Cumulene chain isomer.

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**Figure 2.** Fluorescence spectra of matrix-isolated, neutral C\textsubscript{14} clusters over the 515–655 nm range at an excitation wavelength of 457.9 nm. The origin is at 526 nm, and sticks indicate the vibrational progression at spacings of 108 and 437 cm\textsuperscript{−1}.
using the B3LYP functional and the 6-31G* basis set.18

**Table 2: Electronic Transition Parameters for C14 and C18**

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Exper.</th>
<th>ZINDO/S</th>
<th>CIS</th>
<th>TD-B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulene Chains</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14 D_πh</td>
<td>526</td>
<td>446 (0.0425)</td>
<td>410 (5.7300)</td>
<td>784 (0.0011)</td>
</tr>
<tr>
<td>C16 D_πh</td>
<td>480</td>
<td>435 (0.0115)</td>
<td>440 (0.0115)</td>
<td>891 (0.0004)</td>
</tr>
<tr>
<td>C18 D_πh</td>
<td>624</td>
<td>513 (0.0118)</td>
<td>430 (0.0118)</td>
<td>779 (0.0001)</td>
</tr>
<tr>
<td>C20 D_πh</td>
<td>666</td>
<td>542 (0.1008)</td>
<td>547 (7.1074)</td>
<td>769 (0.0001)</td>
</tr>
<tr>
<td>Cumulene Rings</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14 D_σh</td>
<td>526</td>
<td>542 (0.0096)</td>
<td>417 (0.0048)</td>
<td>416 (0.0004)</td>
</tr>
<tr>
<td>C16 D_σh</td>
<td>562</td>
<td>521 (0.0013)</td>
<td>429 (0.0071)</td>
<td>427 (0.0001)</td>
</tr>
<tr>
<td>C18 D_σh</td>
<td>624</td>
<td>749 (0.0019)</td>
<td>555 (0.0054)</td>
<td>509 (0.0001)</td>
</tr>
<tr>
<td>C20 D_σh</td>
<td>666</td>
<td>470 (0.0003)</td>
<td>539 (0.0007)</td>
<td>457 (0.0001)</td>
</tr>
<tr>
<td>C14 C_πh</td>
<td>516</td>
<td>516 (0.0006)</td>
<td>574 (0.0012)</td>
<td>769 (0.0001)</td>
</tr>
<tr>
<td>C16 C_πh</td>
<td>507</td>
<td>507 (0.0006)</td>
<td>574 (0.0012)</td>
<td>769 (0.0001)</td>
</tr>
<tr>
<td>C18 C_πh</td>
<td>539</td>
<td>539 (0.0007)</td>
<td>457 (0.0001)</td>
<td>457 (0.0001)</td>
</tr>
</tbody>
</table>

Experimental fluorescence peak positions in nanometers.  
Calculated orbitally allowed electronic transition values in nanometers.  
Calculated oscillator strength.

**Theoretical Methods**

The geometry optimization and frequency calculations were performed using GAUSSIAN 98W (Revision A.7),15 using the B3LYP (Becke 3-parameter—Lee—Yang—Parr) functional16 and the cc-pVDZ (correlation consistent polarized valence double-
ξ, a [3s2p1d] contraction of the (9s6p1d) primitive set) basis set.17 The B3LYP/cc-pVDZ harmonic frequencies were uniformly scaled down by 2% to account for the systematic overestimation that results from the neglect of anharmonic effects.

Excited electronic state calculations were performed with stationary state structures obtained from geometry optimizations using the B3LYP functional and the 6-31G* basis set.18–20 The ZINDO/S calculations were performed using ZINDO, a comprehenive semiempirical SCF/CI package developed by Zerner and co-workers.21–23 The CIS24 and TD-B3LYP calculations were performed using GAUSSIAN 98W (revision A.7), using the 6-31G* basis set.

**Theoretical Results**

The lowest energy ring or chain isomer found for the C14 cluster is a D_πh cumulene ring, with a D_σh cumulene chain lying 3.0 eV higher in energy. Optimizations performed with polyacetylene ring or chain structures as the initial geometries converged to cumulene species identical to those above. Table 1 shows the measured vibrational frequencies and the predicted Raman-active frequencies predicted for the ring and linear chain isomers of C14 by density functional theory.

Table 2 shows the predicted, orbitally allowed vertical electronic transitions (excitation) for the ring and linear chain isomers of C14 and C18 from the ZINDO/S, CIS, and TD-B3LYP calculations. The electronic configurations of neutral D_πh C14 and C18 cumulene chains are ... (ζ\textsuperscript{6})\textsuperscript{4}, resulting in 3\Sigma\textsuperscript{g} ground states. The expected electronic transitions for neutral carbon chains with even numbers correspond to 2\Sigma\textsuperscript{u}−X 3\Sigma\textsuperscript{g} and 3\Pi\textsubscript{u}−X 3\Sigma\textsuperscript{g}−symmetry. The electronic configurations of neutral cumulene D_πh C14 and D_πh C18 rings are (ζ\textsuperscript{4})\textsuperscript{2}, resulting in 'A1' ground states. The expected electronic transitions for the neutral carbon 14 and 18 rings correspond to 1E\textsuperscript{g}−X\textsuperscript{1}A1\textsuperscript{g}−symmetry.

**Discussion**

From comparison of the measured frequencies and the calculated frequencies for the C14 ring and linear chain isomers (see Table 1) it appears that the chain structure gives the closest matches to the experimental. The frequencies at 282 cm\textsuperscript{-1} and 851 cm\textsuperscript{-1} match the first two totally symmetric fundamentals calculated for the chain isomers of C14. As in the previous studies of C16, C18, and C20, definitive determination of the fundamental frequencies of C14 from the spectra is complicated by the resonance enhancement and in some cases the strong fluorescence of the cluster. Excitation with longer wavelengths reduced the resonance contribution; however, a corresponding decrease in signal-to-noise ratio and the absence of weak fluorescence features only allow for identification of the 282 cm\textsuperscript{-1} fundamental vibration.

The measured fluorescence origins are compared in Table 2 to the calculated, orbitally allowed vertical electronic transitions for the ring and linear chain isomers. For the linear chain isomers, the results from the ZINDO/S and CIS calculations are in qualitative agreement and strongly differ from the results of the TD-B3LYP calculations. The TD-B3LYP calculations are strongly shifted toward the infrared region of the spectrum and have two different sets of transitions: one that increases in wavelength with increasing cluster size and one that decreases. The transitions predicted for the linear chain isomers by ZINDO/S, CIS, and one set of transitions from the TD-B3LYP calculations show a shift toward longer wavelengths as the carbon chain gets longer. This trend is in qualitative agreement with the experimental observations for C14 and C18. Such a shift is also apparent in the electronic spectra of carbon chains C4, C6, C8, and C10 reported by Maier and co-workers.9 The ZINDO/S and CIS results are in qualitative agreement with a second state of 3\Sigma\textsuperscript{u}− symmetry with large oscillator strengths that has been reported by Maier.9 However, the ZINDO/S and CIS calculations suggest that fluorescence spectra should be observed from C16 and C20 clusters, but as reported previously, no fluorescence is observed from C16 and C20.

The results of the calculations on the ring isomers using the three methods are in qualitative agreement with each other (with the exception of the ZINDO/S predictions for D_πh C18), but they are not in agreement with the experimental observations. The transitions predicted by the ZINDO/S calculations suggest that fluorescence should be observed from all four cluster species. The CIS calculations predict transitions that suggest fluorescence should not be seen from C14 but should be seen from C16, C18,
and C_{20}. The transitions predicted by the TD-B3LYP calculations suggest that fluorescence should only have been seen from C_{14} and perhaps C_{20}. However, even in these cases, the experimental results are red shifted from the predicted transitions.

The poor agreement between theory and experiment suggests that the observed fluorescence spectra may be due to transitions to orbitally forbidden electronic states that become accessible through vibrational coupling. For a vibronic transition, the transition moment integral has the form

\[ M = \int \psi_e^* \psi_v^* \hat{\mu}_e \psi_e \psi_v \, dr_{en} \tag{1} \]

and the combined electronic–vibration integral must be nonzero for a vibronic transition to be allowed. Any vibration of the molecule with symmetry that makes the integral nonzero can make a transition allowed. Therefore, by the coupling of an orbitally forbidden electronic transition with a vibrational transition of the right symmetry, it is possible that the selection rules can be satisfied and some intensity may be observed. Since the fluorescence results from a downward, vertical electronic transition (in accordance with the Franck-Condon principle), the vibrational structure in the fluorescence spectra are characteristic of vibrations in the ground electronic state.

Potential vibrationally allowed electronic transitions for the chain species are considered first since the observed Raman spectra of C_{14} and C_{18} are found to most closely agree with those calculated for linear chains. The CIS and TD-B3LYP electronic excited-state calculations find several orbitally forbidden transitions to \( \Sigma_g, \Delta_g, \) and \( \Delta_u \) excited states in the 500–700 nm range for C_{14} and C_{18} chains. These orbitally forbidden transitions can become allowed by coupling with vibrational transitions having \( \Sigma_u \) or \( \Pi_u \) or \( \Pi_g \) symmetry, respectively. (The two components of the dipole moment operator, \( \mu_e \), for the \( D_{nh} \) point group are \( \mu_{eu} \) and \( \mu_{eh} \).)

For a C_{14} linear chain, the CIS and TD-B3LYP calculations find a \( \Delta_u \) state at 539 nm and a \( \Sigma_u \) state at 545 nm, respectively. For the chain isomer, the B3LYP calculations find a \( \Pi_u \) mode at 109 \text{ cm}^{-1} \) and a \( \Pi_g \) mode at 455 \text{ cm}^{-1}. These are the closest matching vibrations to the vibrational progressions of 108 and 437 \text{ cm}^{-1} \) that are present in the fluorescence spectrum for C_{14}. For a C_{18} linear chain, the CIS calculations find \( \Delta_u \) states at 572 and 740 nm. The TD-B3LYP calculations find a \( \Delta_u \) state at 609 nm, a \( \Sigma_u \) state at 683 nm, and a \( \Delta_g \) state at 701 nm. The only feature in the C_{18} Raman spectra that is close to the frequencies observed in the fluorescence spectra (407 and 877 \text{ cm}^{-1}, \) origin at 624 nm, and 440 and 877 \text{ cm}^{-1}, \) origin at 666 nm) is an unassigned peak at 430 \text{ cm}^{-1}. For the chain isomer, the closest matching vibrations from the calculations are a \( \Pi_u \) mode at 452 \text{ cm}^{-1}, \) a \( \Sigma_u \) mode at 455 \text{ cm}^{-1}, \) a \( \Sigma_g \) mode at 884 \text{ cm}^{-1}, \) and a \( \Pi_g \) mode at 895 \text{ cm}^{-1}. The consideration of vibrational coupling results in better agreement between the experimental fluorescence spectra and the electronic excited-state calculations.

The CIS and TD-B3LYP electronic excited-state calculations also find several orbitally forbidden transitions to \( \Sigma_g, \Delta_g, \) and \( \Delta_u \) excited states in the 500–800 nm range for C_{16} and C_{20} chains. As shown above, these orbitally forbidden transitions can become vibrationally allowed. Therefore, the excited-state calculations are not in agreement with the experimental observations which have detected fluorescence from C_{14} and C_{18} clusters but not from C_{16} and C_{20} clusters.

The alternating fluorescence properties may be due to vibrationally allowed electronic transitions of monocyclic ring species present in the matrix. Due to limitations in the Gaussian 98W program, the ring excited-state symmetries cannot be readily determined. However, it should be noted that, for the C_{14} ring isomer, the nearest matching calculated vibrations to the vibrational progressions of 108 and 437 \text{ cm}^{-1} \) that are present in the fluorescence spectra are an \( \Sigma_g^{\prime} \) mode at 126 \text{ cm}^{-1} \) and an \( \Sigma_g \) mode at 427 \text{ cm}^{-1}. For the C_{18} ring isomer, the nearest matching calculated vibrations to the vibrational progressions of 407 and 877 \text{ cm}^{-1} \) and 440 and 877 \text{ cm}^{-1} \) are an \( \Sigma_g^{\prime} \) mode at 397 \text{ cm}^{-1}, \) an \( \Sigma_g \) mode at 415 \text{ cm}^{-1}, \) an \( \Sigma_g \) mode at 456 \text{ cm}^{-1}, \) an \( \Delta_g \) mode at 464 \text{ cm}^{-1}, \) an \( \Sigma_g \) mode at 788 \text{ cm}^{-1}, \) and an \( \Sigma_g \) mode at 976 \text{ cm}^{-1}. It is plausible that the fluorescence results from ring isomers because theoretical calculations have found that \( C_{14} \) (C_{14} and C_{18}) rings have \( D_{2h} \) cumulene ring geometries and C_{14} (C_{16} and C_{20}) rings have \( D_{2h} \) polyacetylene ring geometries.\(^{7,20,29}\) The alternating ring structures could explain why fluorescence spectra are seen for C_{14} and C_{18} and not for C_{16} and C_{20}. Conversely, C_{18} linear chains with even number of carbon atoms all have the same type of cumulene structure.\(^{7,30,28}\)

In conclusion, the SPP-Raman spectra for size-selected C_{14}, C_{16}, C_{18}, and C_{20} clusters appear to most closely agree with those calculated for linear chains. The most reasonable interpretation of the C_{14} and C_{18} fluorescence is that it results from cumulene rings. However, further theoretical studies of the excited states of C_{14}, C_{16}, C_{18}, and C_{20} isomers are required in order to resolve the discrepancies between experiment and theory.

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References and Notes