1.34 Å, C=C—C ca. 120°) may be largely responsible for the facile 6-endo cyclizations of **3**. Double bond shortening and angle tightening in **3** probably improve the interorbital alignment between the semioccupied orbital of the radical site and the π^*-orbital of the double bond in the transition structure[1p,11] for 6-endo closure, compared to that alignment in **13**. The fact that $(k_5/k_6)^{3a} > (k_5/k_6)^{3b}$ suggests that the *gem*-dimethyl effect (see above) may be operating to increase k_5^{3a}. Finally, the resonance stabilization of the cyclic hydrazyls $(R_2\ddot{N}\dot{N}R \leftrightarrow R_2\overset{+\cdot}{N}\text{-}\bar{N}R)$ probably means that the cyclizations that form them have transition states that are more reactantlike than those for corresponding cyclizations to C=C bonds and are therefore less selective and less sensitive to steric factors.

In summary, both aryl and alkyl radicals cyclize rapidly to the N=N functional group and the k_5/k_6 ratios in three cases lie between 0.45 and 5. High yields of heterocycles were obtained by working with concentrations of **2** much lower than those in Table I.

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Raman Spectroscopy of the High T_c Superconductor $YBa_2Cu_3O_7$ and the Semiconductor $YBa_2Cu_3O_6$

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The recent discoveries of superconducting materials with extraordinarily high-transition temperatures immediately raise the question of whether an electron–phonon mechanism as in the Bardeen–Cooper–Schrieffer (BCS) theory is operative or if some entirely new mechanism must be invoked.[1] The common structural features of these materials are extended Cu–O chains and sheets.[2-6] Since the standard BCS theory predicts that T_c is proportional to the Debye temperature, it has been suggested that the comparatively high frequencies of Cu–O breathing modes could be responsible for these very high-transition temperatures.[7-9]

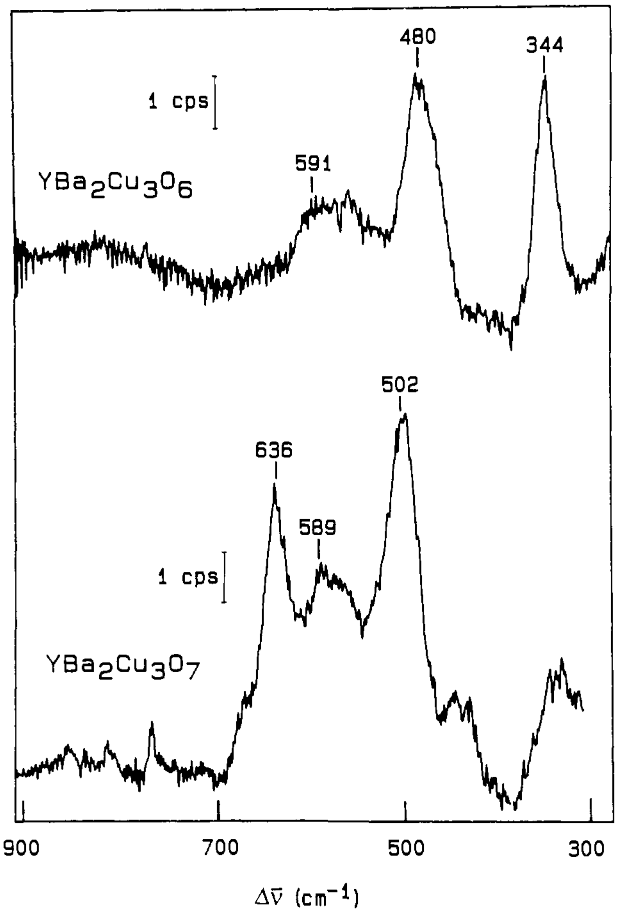

Figure 1. Raman spectra of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$: laser line 514.5 nm and laser power 20 mW for O_7 and 10 mW for O_6 measured at sample surfaces.

While this mechanism may be adequate to account for the T_c below 50 K in the lanthanum–copper oxide systems, it is difficult to see how it could apply to the 90 K materials, the yttrium–barium–copper oxides. There is also very recent evidence that there is no isotope effect in the latter system, in disagreement with the requirements of the standard theory.[10] Motivated by the generally accepted empirical correlation between the existence of phonon anomalies, lattice instabilities, and high T_c's in other materials,[11] we have begun to investigate the role of lattice phonons in high T_c superconductors. We report here the Raman spectra of the superconducting $YBa_2Cu_3O_7$ phase and the semiconducting $YBa_2Cu_3O_6$ phase.

The samples were prepared from starting materials Y_2O_3, CuO, and $BaCO_3$ of nominal purities 99.99%, 99.9%, and 99.8%, respectively. These compounds were mixed in a stoichiometric ratio of 0.165:0.335:0.50 (Y/Ba/Cu mole fractions as the oxides) and heated for 20 h at 950 °C in a platinum or zirconium crucible in air.[4] A single-phase material $YBa_2Cu_3O_{7-x}$ (based on powder X-ray diffraction analysis) was then obtained and was pressed into a disk and sintered at 950 °C. Two fragments of the sintered disk were further treated: one, by annealing at 350 °C in O_2 for 20 h to make $YBa_2Cu_3O_7$; and another, by heating in flowing Ar at 620 °C for 20 h to make $YBa_2Cu_3O_6$. The oxygen content analysis gave 6.96 and 6.11, respectively, for the two materials. Both the orthorhombic, superconducting and the tetragonal,

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semiconducting phases display ranges of oxygen solubility.[5,6]

Figure 1 shows the Raman spectra of both the $YBa_2Cu_3O_7$ and the $YBa_2Cu_3O_6$ phases in the Cu-O stretching region. These materials are very weak Raman scatterers, due primarily to the small volume sampled in such highly absorbing solids. Consequently, we found it necessary to use a very sensitive multichannel Raman spectrometer (described in detail elsewhere[12]) to acquire these data at the very low laser power (10~20 mW) necessary to avoid sample damage. The laser beam impinged on the sample disk at an angle of incidence of 75° to the surface normal with the scattered radiation collected along the normal. No significant polarization effects were found, which is consistent with the polycrystalline nature of the samples.

The striking feature of the spectra is the near invariance of two of the mode frequencies to composition, while there is a dramatic shift of the third to lower frequency in the oxygen deficient compound. The unit cell of the O_6 compound has D_{4h} symmetry, while the O_7 unit cell symmetry is D_{2h}. Of the ten Raman active modes in each compound, there are only four that involve Cu-O stretching motions; normal coordinate analysis identifies three associated with the CuO_2 sheets and one with the CuO_3 chains. We therefore assign the modes at 502 and 589 cm^{-1} to the symmetric and asymmetric stretches of the square pyramidal CuO_2 layers parallel to the *ab* plane (refer to Figure 1 in ref 5), since they are common to both structures. The asymmetric stretch is a degenerate pair in the O_6 compound but should be split in the O_7 compound; that we don't resolve the splitting reflects the small departure from D_{4h} symmetry and the relatively large line widths involved. We note, but do not assign, the appearance of a broad shoulder near 591 cm^{-1} in the O_6 material. The intense Raman band occurring at 636 cm^{-1} in the O_7 material is due to the corner sharing coplanar CuO_3 chains parallel to the *b*-axis in the *bc* plane. In contrast to the CuO_2 layer structural unit, there are two inequivalent types of Cu-O bonds in the CuO_3 chain structural unit, i.e., the terminal Cu-O bonds along the *c*-axis and the bridging Cu-O bonds along the *b*-axis. Only the symmetric mode involving the terminal Cu-O stretching motions is Raman active. The intensity of this mode is preserved in the O_6 material, but its frequency is shifted to 344 cm^{-1}. This large frequency shift is easily explained by considering the bonding in the two compounds. As the bridging oxygens are lost in the O_6 material the formal oxidation state on the copper is reduced from Cu^{III} to Cu^{I}, taking on a d^{10} configuration. In considering a filled d-shell, the bonding is expected to involve sp σ bonds which should be much weaker than the bonding in the O_7 material (which involves the $d_{x^2-y^2}$ orbital). The reduced bond strength manifests itself in the lower vibrational frequency. The only difficulty with this interpretation is that the crystal structure data show very similar terminal Cu-O bond lengths (~1.85 Å) in both compounds.[5,13]

In conclusion, we have identified a high-frequency mode in the Raman spectrum of the high temperature superconductor $YBa_2Cu_3O_7$ which is shifted to much lower frequencies in the oxygen deficient nonsuperconducting compound $YBa_2Cu_3O_6$. This mode is assigned to the symmetric stretch of the terminal Cu-O bonds in the linear chain of corner-shared CuO_3 units; this assignment is consistent with the structural models derived from diffraction experiments. While these experiments do not definitively establish a causal link between the frequency shift of this mode and superconductivity, the correlation is nevertheless intriguing. Polarization experiments using single crystals of these materials as well as determination of the behavior of the spectrum as the temperature is lowered through T_c are clearly required to firm up the spectral assignments and determine the relevance of the phonons to the superconducting behavior. Such experiments are underway in our laboratory.

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Silathione ($Me_2Si{=}S$) Extrusion in the Thermolysis of Silylthioketenes

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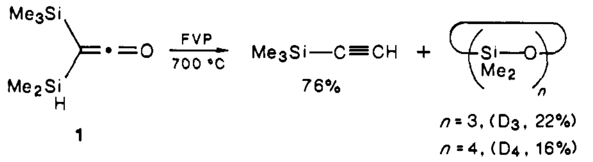
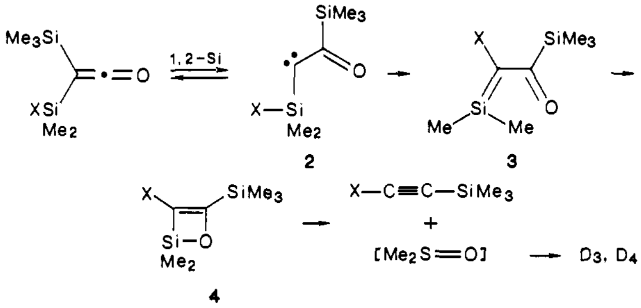
Recently we reported that certain silylketenes underwent a remarkable thermal extrusion of dimethylsilanone, $Me_2Si{=}O$.[1] Thus, for example, ketene **1** undergoes flash vacuum pyrolysis (FVP) at 700 °C to cleanly afford trimethylsilylacetylene and a mixture of permethylcyclosiloxanes, presumably derived from oligomerization of dimethylsilanone.

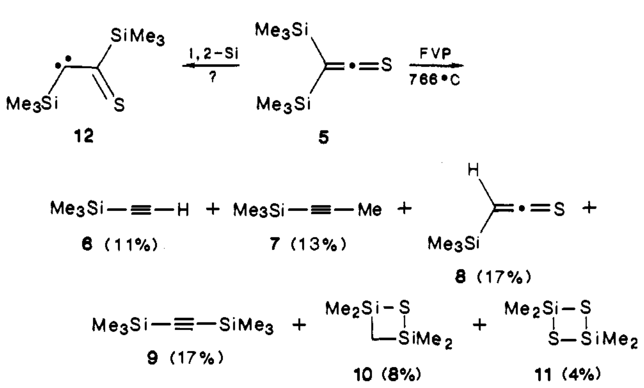


Of considerable interest is the possibility that the decompositions of silylketenes proceed through a "retro-Wolff" rearrangement. Such a process would be initiated by a 1,2-silyl shift to produce an α-ketocarbene **2** which could proceed to products by isomerization to silene **3**,[2] closure to silaoxetene **4**, and a formal retro "2 + 2" to silanone and acetylene.



It was of obvious interest to see if the decomposition route for silylketenes could be extended to other heterocumulenic systems. To this end we have examined, and preliminarily report here, the thermolysis of silylthioketenes.

FVP of bis(trimethylsilyl)thioketene[3] (**5**) at 768 °C resulted in 47% conversion and the formation of the seemingly complex mixture of products **6**–**11** for which the yields have been corrected for unreacted **5**.[4]



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