enzyme-catalyzed organic synthesis with in situ cofactor regeneration[10] and should be applicable to the synthesis of many novel biologically important sialosides and oligosaccharides starting from unactivated monosaccharides.

Acknowledgment. We thank Dr. J. C. Paulson (Cytel Corp., La Jolla, CA) for providing us with α(2,6)sialyltransferase.

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Surface-Enhanced Raman Spectroscopy of C_{60} on Gold: Evidence for Symmetry Reduction and Perturbation of Electronic Structure in the Adsorbed Molecule

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Received February 20, 1991

The recent discovery of methods for preparing and purifying C_{60} in significant yield[1-3] has facilitated new studies of its structure and photophysical properties. Recent electrochemical studies reveal that C_{60} and C_{70} have very similar pyracylene-type electronic character,[4] in apparent contradiction to the theoretical prediction of quite different highly delocalized excited-state orbitals in the two molecules.[5] This behavior, along with the recently reported observation that salts of the C_{60} radical anion behave as semiconductors,[6] prompts questions of whether the C_{60} structure and electronic properties will be perturbed at interfaces. Low-resolution STM images of C_{60} reveal spheroidal molecules that are mobile on gold surfaces, indicating that they are not strongly bound.[7,8] The detailed interpretation of the STM results remains specious, however, as it is not clear to what extent the STM probe tip perturbs the electronic structure of the adsorbed molecule.[7] We have therefore used surface-enhanced Raman (SER) spectroscopy to obtain a clearer picture of the surface interactions and structure of C_{60} on gold. Differences between the SER and Raman spectra provide evidence for both a loss of symmetry and a change in the electronic structure of C_{60} upon adsorption.

C_{60} was prepared as described previously.[2] The IR[1] and Raman[9,10] spectra of bulk C_{60} confirm that it has an icosahedral structure. Only four of 174 normal modes are IR active, and 10 or 11 bands are observed in the Raman spectrum (see footnote *d*, Table I).[9-11] In the SER spectrum of pure C_{60} on gold with no applied potential (Figure 1a), we can clearly identify 22 bands,[12] which are compared with bands in the Raman spectra of bulk C_{60} and C_{70} in Table I. In addition to bands similar to those in the bulk C_{60} Raman spectrum, we observe a new band at 340 cm^{-1} that may correspond to a metal–molecule vibration. The other new bands in the C_{60} SER spectrum agree closely with bands in the C_{70} Raman spectrum.[10,11,13] [C_{70} is predicted to have 53 Raman-active modes, 21 of which have been observed (Table I).]

Table I. SER and Raman Bands (cm^{-1}) of C_{60}

SER	Raman[b]	
C_{60}[a]	C_{60}	C_{70}
175 w		
256 sh		261 (28, 4)
270 s	273 (20, 10)	
340 m		
398 w		400 (sh, 0)
419 m		411 (7, 0)
	437 (9, 3)	
		459 (7, 0)
488 s	496 (43, 3)	501 (6, 0)
510 w–m		
551 w		
575 w		573 (6, 0)
700 m, br	710 (6, 2)	704 (11, 2)
730 m		739 (12, 4)
766 m	774 (10, 3)	770 (5, 0)
962[c] w, br	~970[d] (~2)	
		1062 (19, 5)
1088 w		
1186 w	1099 (2, 0)	1186 (46, 8)
1235 w		1231 (51, 8)
	1250 (2, 0)	1260 (5, 0)
1307 vw		1298 (sh, 0)
		1317 (sh, 0)
		1336 (13, 0)
		1370 (13, 0)
1393 w		
1422 w–m	1428 (14, 3)	
1452 vs		1448 (52, 9)
	1470 (100, 6)	1471 (25, 0)
		1517 (18, 8)
1559[c] s	1575 (9, 3)	1569 (100, 19)

[a] Abbreviations: w = weak, m = medium, s = strong, v = very, br = broad, sh = shoulder. [b] Raman data for C_{60} and C_{70} from ref 10. Intensities for (parallel, perpendicular) polarizations are relative to the 1470-cm^{-1} band for C_{60} and to the 1569-cm^{-1} band for C_{70}. [c] Reassigned in this work. [d] Observed in the reported spectrum[10] but not tabulated or included in the analysis.

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(11) The substantial intensity of the ~1568-cm^{-1} band in the Raman spectrum of C_{60}/C_{70} reported in ref 10, even with only ~8% C_{70}, and the intensity of the 1559-cm^{-1} band in our pure C_{60} SER spectrum argue for its assignment as a C_{60} as well as a C_{70} band. This reassignment has also been suggested in ref 9, submitted shortly before the present work.

(12) The surface cleaning procedure, spectrochemical cell, and Raman spectrometer are described in the following: Garrell, R. L.; Beer, K. D. *Langmuir* **1989**, *5*, 452–458. The electrode was roughened by 20 oxidation/reduction cycles between −0.600 V and +1.200 V at a scan rate of 0.500 V/s, with pauses of 8 s at −0.600 V and 1.2 s at +1.200 V. The electrode was removed from the roughening cell and rinsed with doubly distilled water to ensure the removal of residual chloride ion. To obtain spectrum 1a, 1 μL of 1.1 × 10^{-4} M C_{60} in CCl_4 was deposited on the electrode surface. This corresponds to a surface coverage of 1–2 monolayers on a 4-mm-diameter smooth surface. For spectra 1b and 1c, ~0.3 monolayer was deposited. The C_{60}-coated electrode was immersed in N_2-purged water (which served as a heat sink to minimize laser heating of the adlayer) or in N_2-purged aqueous 0.1 M KCl supporting electrolyte, and the solution was blanketed with N_2 throughout the experiment. Single-scan spectra (scan rate 1 cm^{-1}/s, 2-cm^{-1} band-pass) were obtained with 20 mW of 676.4-nm radiation (Lexel RamanIon krypton ion laser). Repeat scans were identical, indicating that no laser-induced degradation was occurring. Spectra 1b and 1c have been smoothed with a five-point polynomial smoothing function.

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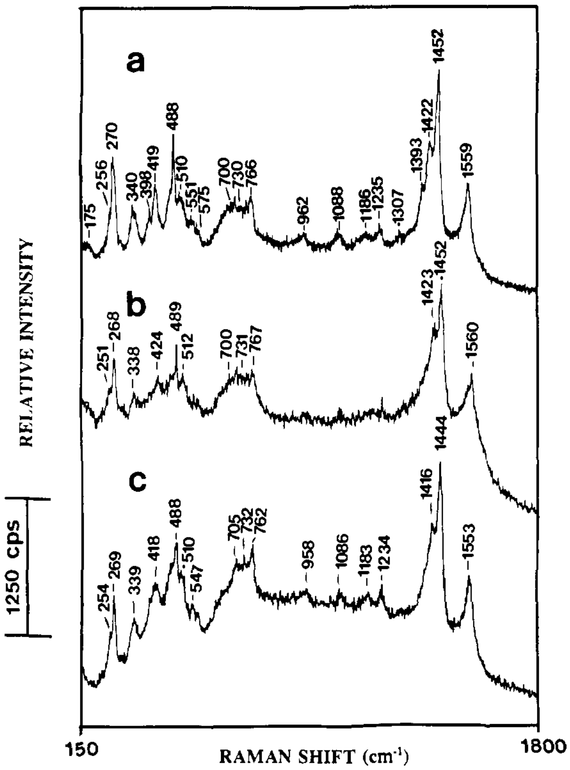

Figure 1. Surface-enhanced Raman spectrum of C_{60} coated on a gold electrode immersed (a) in pure water with no applied potential, (b) in 0.1 M aqueous KCl at +0.200 V vs SCE, and (c) in 0.1 M KCl at −0.600 V vs SCE. No SER scattering is observed above 1800 cm^{-1}.

This is not to suggest that C_{60} has been transmuted to C_{70} on the gold surface! Rather, we propose that C_{60} in the interfacial environment has decreased symmetry, which causes new modes to become Raman active. The chemical similarity between C_{60} and C_{70} leads us to predict that many of the normal modes and vibrational frequencies of these spheroidal carbon clusters will be similar. The higher frequency modes will be dominated by bond-stretching motions (changes in edge lengths), while the lower frequency modes are expected to involve radial distortions to a more ellipsoidal shape.[14] We have obtained a preliminary SER spectrum of C_{70}, and indeed the band positions in the 1000–1600-cm^{-1} region are similar to those observed in the SER spectrum of C_{60}, although the relative intensities more closely match those of the bulk C_{70} spectrum.[15] We cannot yet say whether adsorbed C_{60} distorts to a C_{70}-like ellipsoidal shape, or whether the symmetry is reduced to C_{5v} or even lower due to adsorbate–surface interactions. We are currently performing a more detailed analysis of the C_{60} and C_{70} SER spectra and normal modes.

The seven strongest bands in the C_{60} Raman spectrum (at 1575, 1470, 1428, 774, 496, 437, and 273 cm^{-1}) have analogues of comparable relative intensity in the SER spectrum, but the SER bands are shifted to lower frequency. (Some of the weaker Raman bands are also shifted slightly, and some have different relative intensities in the SER spectrum.) The frequency shifts are similar to those observed for other aromatic molecules upon adsorption on gold[16] and are interpreted as evidence for a change in the electronic structure of the adsorbate. Donation of π electron density to the metal, or back-donation from the metal d orbitals to the molecular π^* orbitals, results in a decrease in the adsorbate C–C bond strength, and thus a decrease in the molecular force constants and vibrational frequencies. In the case of C_{60}, its high electron affinity[17] suggests that metal-to-molecule back-donation may be the more important of the two mechanisms.

Spectra b and c of Figure 1 are SER spectra obtained with 0.1 M KCl as the electrolyte at +0.200 and −0.600 V. The similarity of spectra b and a shows that Cl^- does not perturb the adsorbed C_{60}. Applying a more negative potential (Figure 1c) causes the three highest frequency bands, which arise from normal modes involving bond stretching,[14] to shift downward significantly, as expected if metal-to-molecule back-donation contributes to the adsorbate–substrate interactions. Similar negative frequency shifts are observed for these bands in the Raman spectra of C_{60}^- and alkali-metal-doped C_{60} films.[18] A potential of −0.600 V is not sufficient to reduce C_{60} in water with KCl as the electrolyte (no current is passed).[4,19] Applying a more negative potential is likely to result in the formation of the fulleride anion on the surface. This may provide a method for fabricating metal–semiconductor Schottky barriers that can exploit the unique electronic properties of the fulleride salts.[6] The electrochemical data also suggest that the C_{60} anion undergoes Jahn–Teller distortion,[4,5] which may make its symmetry and vibrational spectrum quite similar to those of neutral C_{60} on gold at negative applied potentials, shown here. Further vibrational spectroscopic studies of adsorbed neutral C_{60} and fulleride salts are under way.

Acknowledgment. This work was supported by NSF Grants CHE89-21133 (to F.N.D. and R.L.W.) and DMR84-51962 (to R.L.G.) and NIH Grant GM42977 (to R.L.G.). We thank Lexel Laser, Inc., for use of the RamanIon laser.

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NMR Observation of Trimethyloxonium Formation from Dimethyl Ether on Zeolite HZSM-5

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Received May 9, 1991

The reaction of methanol to gasoline (MTG) on zeolite HZSM-5 is central to what is probably the most successful synthetic fuels process.[1] This process accounts for a substantial part of New Zealand's gasoline supply. Despite extensive study of the methanol/HZSM-5 system, the mechanism for the formation of the first C–C bond is still disputed.[1,2] The most popular[1] of the proposed reaction mechanisms involves the formation of trimethyloxonium (**1**) followed by deprotonation by an unspecified basic site to yield methylenedimethyloxonium ylide (**2**). The ylide is then assumed to either abstract a methyl group to form dimethylethyloxonium, which undergoes β-elimination to yield ethylene and dimethyl ether, or to undergo a Stevens-type rearrangement to form methyl ethyl ether (Scheme I).[3,4] A detailed

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