Low-Temperature Resonance Raman Scattering from Iodide Adsorbed on Nanostructured Silver Surfaces

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An overtone progression was observed in Raman scattering spectra from iodide-modified, electrochemically roughened silver surfaces at low temperatures. Spectral intensities of the bands were found to vary with the degree of surface roughening, whereas vibrational frequencies remained highly conserved. Both surface-enhanced and resonance scattering phenomena contribute to observed band intensities when excited in the spectral region between 406 and 415 nm. It is suggested that the progression originates from I_2-like species that are formed on small silver clusters at low temperatures under irradiation. This complex can be viewed as a supermolecule in which the electronic resonance is determined by the size of the cluster and I−I stretch represents a normal mode of the molecule.

Introduction

Adsorption of halides, in particular iodide, on nanostructured silver surfaces such as colloidal suspensions and two-dimensional arrays of particles has been shown to form an Ag_s−I complex (where Ag_s represents the Ag surface) that is capable of reducing a variety of molecules in solution.[1,2] It was suggested that each iodide ion donates charge to the particle that remains localized near the Ag_s−I complex affecting the surface potential of the system. The nature of the silver−iodide bond or, in other words, the degree of ionic and covalent character determines the extent of charge transferred.

An extensive amount of literature exists regarding the adsorption of iodide on silver metal including single crystals. Infrared, high-resolution electron energy loss and X-ray photoelectron spectroscopies, low-energy electron diffraction,[3−5] electrochemical measurements,[6,7] and scanning tunneling and atomic force microscopies[8−10] were employed to quantify the adsorption and to determine the binding state, structure, and dynamics of iodine atoms on the surface at sub- and monolayer coverage. The results can be summarized as follows: (i) iodide is spontaneously adsorbed on silver forming a strong surface bond; (ii) the bond is mainly covalent with little or no ionic character; (iii) monolayers of iodine on silver are likely to exhibit $(\sqrt{3} \times \sqrt{3})$R30° structure, however more complex structures were also observed; (iv) interactions between adjacent iodine atoms are negligible with respect to the I_s−metal bond.[4]

Surface-enhanced Raman scattering (SERS) spectroscopy also provides a convenient tool for probing the interactions of various molecules with metal surfaces.[11] SERS spectra of halides adsorbed on silver surfaces are dominated by a broad, low-frequency band assigned to the metal−halide stretch.[12] It was suggested and demonstrated experimentally on silver colloids that the frequency of this band is coverage dependent because of vibrational coupling of dipoles formed between halide ion and the metal surface.[13,14] Halides form a covalent bond with silver and gold surfaces; however the degree of bond covalency is greater for gold and increases from chloride to iodide as was

determined from a potential dependence of the frequency of the metal−halide band in SERS spectra.[6] Electrooxidation of iodide at the gold aqueous interface combined with SERS spectroscopy revealed formation of polyiodide species and molecular iodine.[15]

In the present paper, a new phenomenon is described—the observation of a strong vibrational progression in low-temperature, SERS spectra of iodide adsorbed on electrochemically roughened silver surfaces. The results reveal the formation of a new type of a surface complex and provide further insight into optical and chemical properties of nanostructured metal surfaces. In a related paper, the detailed resonance Raman scattering study of these surface complexes is presented.[16]

Experimental Methods

Chemicals and Materials. Solutions of reagent grade potassium iodide were made using high-purity water (resistivity 18 MΩ cm) from a Millipore-Milli Q system. Solution of I_3^- was prepared by addition of KI to I_2 solution. Thin films of silver (99.99%, Aesar (Johnson Matthey)) were prepared by vapor depositing approximately 1 μm equivalent mass thickness of the metal on glass substrates which were first coated with chromium as an adhesion layer. Solutions were purged with high-purity nitrogen (99.995%) prior to measurements. All sample manipulations were completed under an inert argon (99.996%) atmosphere.

Iodide Modification. Thin films of silver were first treated in a plasma cleaner for 2 min to remove any organic deposits that might occur from the atmosphere. After being rinsed in water, the film was then subjected to an electrochemical roughening procedure using double-potential step oxidation−reduction cycles performed in the dark and under an argon gas atmosphere. Either 0.10 M of Na_2SO_4 or 0.1 M of $NaClO_4$ was used as an electrolyte. A platinum foil and a saturated-calomel electrode (SCE) were employed as the auxiliary and the reference electrodes, respectively. All potentials are reported with respect to the SCE reference. Three cycles of the following sequence were performed: the potential was initially stepped to +0.55 V at which 25 mC/cm^2 of charge was allowed to pass,

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† In memory of our friend and colleague Therese M. Cotton.

and then the potential was stepped to -0.60 V until the current reached a minimum. The roughened Ag film was rinsed under a stream of water and then immersed into a 1.0 mM KI solution for 2 s. The iodide-modified film was rinsed under a stream of water to remove excess KI and then dried under a stream of nitrogen gas before transfer to the cryostat. The electrolyte solution was purged with high-purity nitrogen gas for at least 20 min prior to experiments.

Cryogenic System. The modified Ag films were mounted in a copper holder in a closed cycle helium cryogenic system (APD cryogenics) with variable temperature control from room temperature (ca. 295 K) to 8.2 K. The sample temperature was obtained from a calibrated chromel−gold (iron 0.07%) thermocouple that provided ±0.1 K precision.

Raman Spectroscopy. Raman scattering and surface-enhanced Raman scattering spectra were excited using the 406.7, 413.1, 415.4 or 647.1, 752.5 nm lines of a Kr$^+$ laser (Coherent, Innova 100) or the 363.8 or 457.9 nm lines of an Ar$^+$ laser (Coherent, Innova 200). The laser power at the sample was typically less than 1 mW. The laser beam was focused with a cylindrical lens providing ca. 0.1×1.5 mm sampling spot. The scattered light was collected by an f/1.5 fused silica lens in a 180° backscattering geometry and analyzed by a triple spectrograph (Spex, Triplemate 1877) equipped with a back-thinned CCD detector (Princeton Instruments, LN 1100x330). Accumulation times varied between 10 and 400 s. The spectra were calibrated using either a low-pressure argon lamp or a mixture of chloroform and bromoform in combination with the laser line. Spectral resolution was 0.046 nm (e.g., 2.7 cm^{-1} at 413.1 nm).

Spectral data were processed and figures were prepared using the program Spectra Solve for Windows (LasTek Pty. Ltd.).

Results

Adsorption of iodide on the Ag surface results in the formation of a nearly covalent bond to the metal characterized at room temperature by a single broad vibrational band at 113 cm^{-1} in the surface-enhanced Raman spectrum (Figure 1a). In a previous study, this vibration was assigned to an Ag$_s$−I complex (Ag$_s$ represents the silver surface) which is different from chemically prepared bulk AgI.[1] The latter displays two resolved vibrational modes at 83 and 105 cm^{-1} and rapidly photodecomposes under laser irradiation to form Ag$_s$−I. At liquid nitrogen temperature and with red excitation, the broad band at 113 cm^{-1} somewhat sharpens, shifts to ca. 117 cm^{-1}, and exhibits unresolved structure (Figure 1b). This behavior can be attributed to a decrease in the homogeneous and inhomogeneous contributions to the line width at low temperatures. A similar trend was observed for all excitation wavelengths across the visible and near-ultraviolet spectral range, except for the wavelengths between 400 and 440 nm.

When excited with 413.1 or 415.4 nm at liquid nitrogen temperature, a new Raman spectrum containing a strong vibrational progression emerged from the iodide-modified, electrochemically roughened Ag surface (Figure 2a,b). Up to six overtones with a regular spacing equal to the fundamental frequency of 123 cm^{-1} were present in the spectra. It should be noted that the bands at 1050, 1002, 619, and 220 cm^{-1} in Figure 2 are from polystyrene used as an internal standard. A transparent polystyrene plate of 0.8 mm thickness was sandwiched with the modified Ag film in the cryostat. Both the progression and the polystyrene spectra were recorded simultaneously, and all bands were normalized to the 1002 cm^{-1} band.
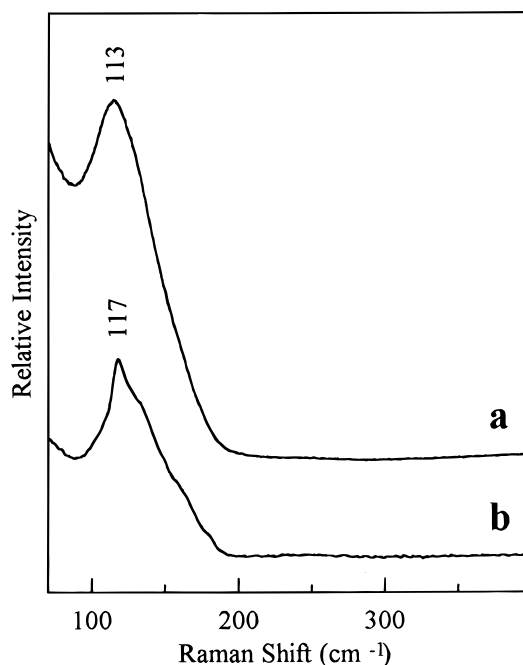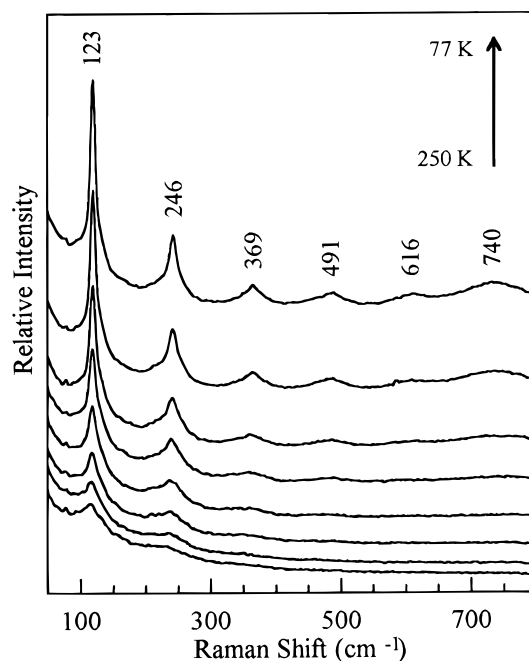

Figure 1. Surface-enhanced Raman spectra of an iodide-modified, electrochemically roughened Ag film at the temperatures (a) 295 K and (b) 77 K. Excitation wavelength was 752.5 nm.
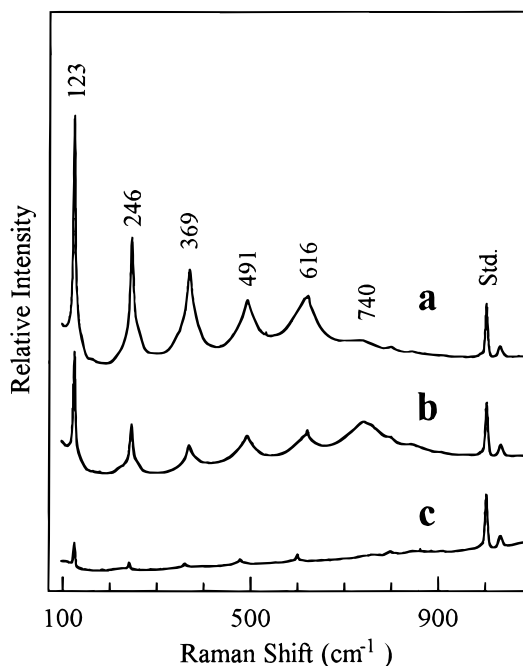
Figure 2. Surface-enhanced Raman spectra of an iodide-modified, electrochemically roughened Ag film at 77 K excited at the wavelengths (a) 415.4 nm, (b) 413.1 nm, and (c) 406.7 nm. Bands at 1050, 1002, 619, and 220 cm^{-1} are from the polystyrene internal standard (Std).

The existence of the strong vibrational progression in the Raman spectrum implies a highly symmetric mode as the origin of the scattering.

The number of overtone bands in the progression as well as overall and their relative intensities depended on the excitation wavelength. With 406.7 nm excitation, as shown in Figure 2c, the overall intensity of the progression was ca. 10 times weaker than that at 415.4 nm. No progression was detected with 457.9 and 363.8 nm excitations. These facts suggest the presence of a resonance electronic transition in this spectral region. A detailed characterization of the ground and excited states of the

Figure 3. Temperature dependence of the surface-enhanced Raman spectra of an iodide-modified, electrochemically roughened Ag film over the range 250−77 K. Excitation wavelength was 413.1 nm.
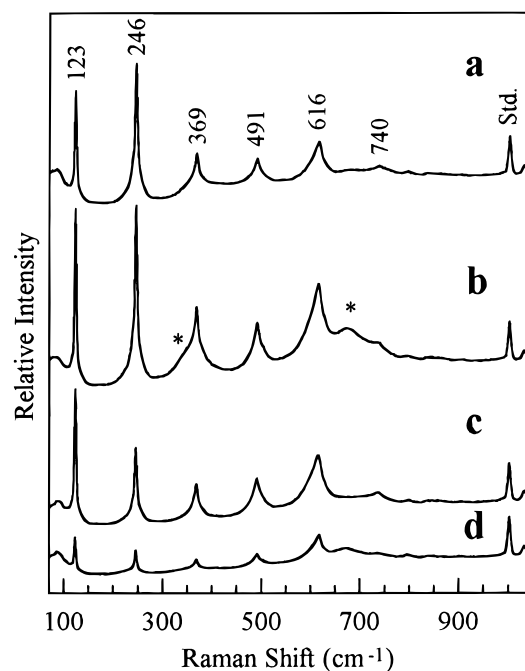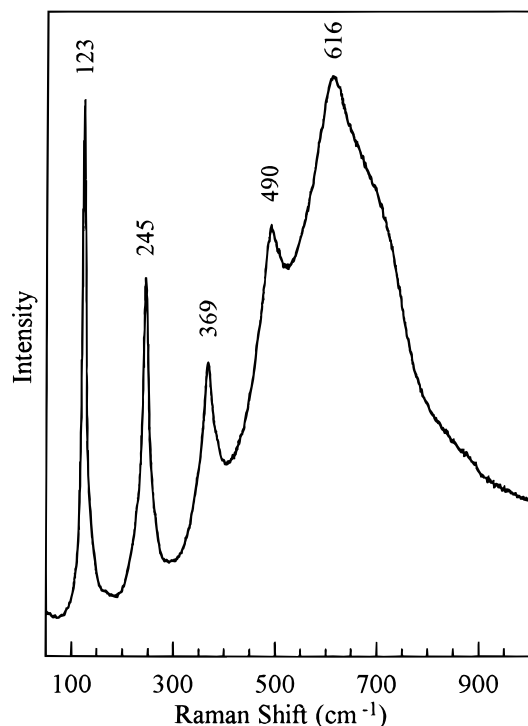

Figure 4. Surface-enhanced Raman spectra obtained at different spots on an iodide-modified, electrochemically roughened Ag film at 77 K. Excitation wavelength was 415.4 nm. Broad underlying bands noted by (∗) were assigned to resonance fluorescence emission (see ref 16).

transition based on a Raman excitation profile was recently reported.[16] The profile was reconstructed from 77 different excitation wavelengths in the spectral range from 409 to 433 nm.

The Raman progression was observed only at low temperatures. Figure 3 depicts the evolution of the Raman signal as the temperature was lowered from 250 to 77 K.

A further lowering of the temperature to 8.2 K resulted in an increase by a factor of 2 in the signal. The appearance of the spectrum and its intensity was highly reversible as the temperature was cycled between 295 and 8.2 K. No photobleaching of the signal was detected at low temperatures and at the low laser powers employed. However, a noticeable photobleaching under laser irradiation was evident above 100 K. The temperature also affected the width of the band in the progression. Decreasing the temperature caused the bands to sharpen. At the same time, the integrated peak areas increased suggesting that the species which gives rise to the Raman progression are preferentially formed at low temperatures.

Significant variations of the SERS signal were noted across the Ag surface. Both the overall intensities of the spectra and the relative intensities of individual bands changed as the laser probed different spots on the metal, as illustrated in Figure 4. However, the vibrational frequencies of the fundamental and overtone bands were highly conserved. In other words, when the progression was present the bands always appeared at the same frequencies. Such behavior represents the electronic heterogeneity of the electrochemically roughened surface as is discussed below.

It is important to emphasize that the Raman progression was observed on an electrochemically roughened silver surface. Both sulfate and perchlorate electrolytes yield the same results. Attempts to detect this phenomenon on surfaces chemically etched by nitric acid were unsuccessful, even though such surfaces are known to be SERS active.[17] A weak progression was also observed on freshly prepared, vacuum-deposited thick Ag films, but having an intensity 2 orders of magnitude less than that of electrochemically roughened surfaces.

The characteristic Raman progression from the iodide-modified Ag surface could be detected at less than monolayer coverage. The typical experiment was to immerse the electrochemically roughened Ag film into 1.0 mM iodide solution for 2 s. Because iodide adsorbed on the Ag surface exists in a zerovalent state,[4,18] formation of multilayers is very unlikely. Furthermore, when the iodide concentration was reduced to 1.0 μM, a proportionally weaker signal was still obtained. It was assumed that, due to the limitations of diffusion, there was no physical possibility for multilayer formation under these conditions. Additional experiments with iodide at submonolayer coverage which exhibit the Raman progression were performed using suspensions of silver particles. Previous studies demonstrated that monolayer coverage can be accurately determined by spectroscopic measurements of the intensity of a charge-transfer band (iodide to solvent) at 226 nm.[1] The fact that the strong Raman progression can be observed at less than monolayer coverage further emphasizes the role of surface-enhanced phenomena. As anticipated, the surface-enhanced Raman progression was completely depolarized, whereas the normal Raman scattering would be expected to be polarized for a highly symmetric vibrational mode.

When the Ag films were exposed to higher concentrations of iodide for longer periods of time or an excess of iodide was added to the colloidal silver, a strong, broad emission appeared along with the Raman progression. The wavelength maximum of the broad emission was around 425 nm and can be attributed to exciton recombination in bulk AgI.[2] A typical spectrum in which both the Raman progression and the broad emission are present is shown in Figure 5 for colloidal silver in the presence of excess iodide.

Discussion

To explain the origins of the unusual Raman progression observed at low temperatures for the iodide-modified, electrochemically roughened Ag surface, two hypotheses were con-

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Figure 5. Surface-enhanced Raman spectra from a suspension of Ag particles in the presence of excess iodide at 77 K. Excitation wavelength was 413.1 nm.

Figure 6. Raman spectra of the I_3^- ion in methanol excited at the wavelengths: (a) 363.8 nm, (b) 413.1 nm, (c) 457.9 nm, and (d) 647.1 nm.

sidered. First, the progression might arise from small clusters of the semiconductor AgI, formation of which was evident in the experiments with high concentrations of iodide. Several similarities point toward this possibility. When excited near the band gap or in the exciton levels, resonance multiphonon Raman scattering from phonons of the semiconductor crystal can occur. Strong progressions with up to nine overtones have been reported for several crystals including CdS, GaP, ZnTe, ZnSe, InAs, and CdSe.[19-21] A dependence of the relative intensities of the overtone bands upon the excitation wavelength was explained by Scott and co-workers in terms of resonance enhancement when the frequency of a scattered photon coincides with an exciton level in the crystal.[19,20] A temperature dependence of the Raman intensities was rationalized as a change with temperature of the exciton and band gap energies in the crystal. A fundamental at 123 cm^{-1} and one overtone at 244 cm^{-1} have been also observed in the resonance Raman spectrum of wurtzite-type AgI crystals measured with 442 nm excitation.[22] However, several other bands much stronger than the 123 cm^{-1} band were also present in the region between 100 and 130 cm^{-1}. All these bands reflect the complex phonon structure of the crystal.

It seems very unlikely that the characteristic Raman progression in the current study originates from the semiconductor AgI. Only a single vibration and its overtones were present in the Raman spectrum; no other bands pointing toward the expected complex phonon structure of AgI were noted. Moreover, the relative intensities in the AgI progression would be expected to vary with temperature, as stated above. In the present experiments, the relative intensities of the bands in the progression remained unchanged through the entire temperature range for which the progression was observed.

In the second hypothesis, it was considered that the progression might originate from a polyiodide molecule such as I_2, $I_2^\pm$, I_3^-, etc. It is known that these molecules produce characteristic Raman progressions under resonance excitation.
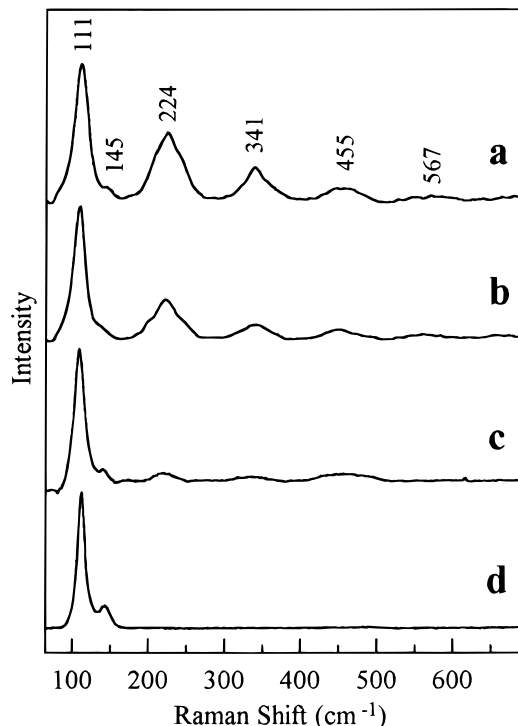
Raman spectra of I_3^- in methanol obtained with different excitation wavelengths are shown in Figure 6. When excited in resonance with an electronic transition, a progression appeared with a fundamental band at 111 cm^{-1} and several overtones previously assigned to the symmetric I−I stretch (Figure 6a,b).[23] In addition, a band at 145 cm^{-1} is attributed to the asymmetric vibration of the solvent-distorted I_3^- molecule.[24] This band becomes more prominent in the spectra excited under preresonant and nonresonant conditions (Figure 6c,d). The presence of an asymmetric mode in the Raman spectrum would be expected for any polyiodide species other than $I_2^{(\pm)}$ adsorbed on the Ag surface. Interactions of the strongly adsorbing I_3^- species with the metal are expected to cause the necessary distortion for the appearance of the asymmetric mode in the Raman spectrum. In the current experiments with iodide-modified Ag surfaces, only a single band and its overtones characteristic for a symmetric vibration were detected. No other bands that can be reliably assigned to an asymmetric vibration were determined with any excitation. These facts strongly suggest an I_2-like species adsorbed on the Ag surface as the origin for the Raman progression. Note that the surface adsorbed I_2 species has a characteristic vibrational frequency of 123 cm^{-1}, which is different from the frequencies of 215, 238, and 114 cm^{-1} previously reported for I_2, I_2^+, and I_2^-, respectively.[25-27]

The question that should be addressed is whether I_2 species are *spontaneously* formed on the silver surface at low temperature. As was mentioned in the previous section, low temperatures facilitate the appearance of the Raman progression. The role of temperature can be viewed as a stabilizing factor. If I_2 is spontaneously formed and stabilized on the Ag surface at low temperatures, then at higher temperatures it will be spontaneously dissociated by kT resulting in the disappearance of the progression. Because the progression was observed to disappear at ca. 120 K, the dissociation energy of I_2 should correspond to the kT energy equivalent to 150 cm^{-1}. The excitation of the first overtone (246 cm^{-1}) in the Raman

spectrum is already beyond the dissociation limit, and one would expect that under steady-state irradiation, photodissociation of the I_2 species would lead to fast disappearance of the progression. That is not the case, however, because up to six vibrational overtones were indefinitely observed in the spectrum.

Two hypotheses can be involved for explanation of this discrepancy. First, the dissociation energy of the I_2 species on the silver surface is actually larger than the energy of the largest observable overtone and, consequently, larger than kT at which the progression disappears. This means that formation and dissociation of the I_2 species cannot spontaneously occur as temperature varies from 77 to 300 K. Second, photodissociation does appear but, because the monolayer of iodide on the silver surface is tightly packed inhibiting two-dimensional diffusion, spontaneous re-formation of the I_2 species immediately takes place. (Note, that Raman scattering occurs on the time scale much shorter than that required for dissociation. For example, resonance Raman spectra of molecules in the ground state can be measured by exciting into the electronic state from which dissociation results.) It is not clear, however, what is the role of temperature in these processes. In addition, iodide is adsorbed on the Ag surface in a zerovalent state[4,18] so that there is no possibility for spontaneous formation of a bond between neighboring I atoms without disturbing the covalency of the Ag_s–I bond. The latter would require energy for the shift of electron density from the metal to the adsorbed I atom. On the basis of the above arguments, it is unlikely that the surface adsorbed I_2 is spontaneously formed from two nearby Ag_s–I species at low temperatures.

Another peculiar feature of the observed phenomenon is a strong variation of the intensity of the Raman progression on different sampled areas of the electrochemically roughened Ag film. This variation is directly associated with the heterogeneity of the Ag surface and was found to depend on the roughening procedure. There are fundamental differences between chemical roughening, after which the progression was never observed, and electrochemical roughening that always yielded a strong progression. In the chemical roughening procedure, the silver metal is etched away by nitric acid leaving behind cavities on the surface. This roughened surface is sufficient for generating surface-enhanced Raman scattering via surface plasma waves, as was reported by Rupérez and Laserna.[17] In the electrochemical roughening procedure, the silver is first anodically stripped away and then cathodically redeposited back onto the surface. This results in the formation of silver clusters of varying size which cannot be produced by chemical roughening. The heterogeneity in the electrochemical roughening across the silver surface will generate a distribution of sizes for the clusters. Because the electronic and, consequently, the optical properties of the small Ag clusters are strongly influenced by their size,[28,29] it is expected that the local absorption band will appear at slightly different wavelengths for different spots on the silver surface. Probing the surface at different spots with a single excitation wavelength is thus equivalent to exciting resonance Raman scattering in different absorption bands with slightly shifted wavelength maxima, which is essentially the same as tuning the excitation wavelength across a single absorption band. As was recently demonstrated from a detailed excitation profile, tuning the excitation wavelength across a single absorption band resulted in a strong variation in the relative and overall intensities of the bands in the Raman progression from iodide adsorbed on the Ag surface.[16]

The model proposed to explain the origin for the Raman progression is depicted in Figure 7. The SERS spectrum arises
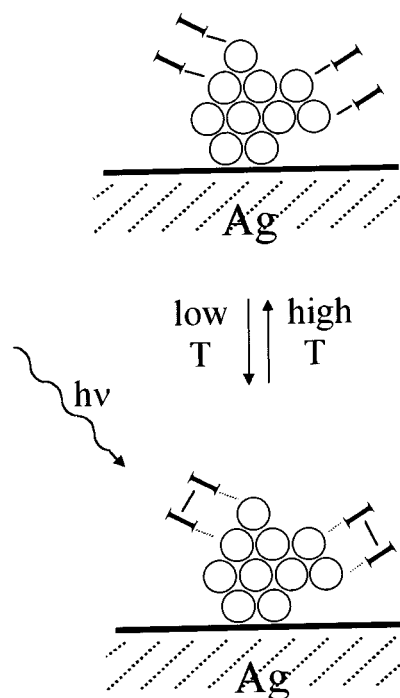
Figure 7. Model for the photoinduced formation of an I_2-like species adsorbed on the surface of a small Ag cluster at low temperatures.

from an I_2 species that forms a complex with a small Ag cluster. This complex can be envisioned as a "supermolecule" that is composed of several I_2 species electronically coupled to the same Ag cluster, producing a delocalized electronic state. The fundamental frequency of 123 cm^{-1} represents an I–I stretch, which is a normal mode of the supermolecule. The characteristic absorption band and, therefore, the prerequisites for resonance Raman excitation strongly depend on the size of the cluster. Our current data are not sufficient to determine what is the precise nature of the electronic transition that gives rise to the surface-enhanced resonance Raman scattering. It can be only emphasized that the electronic states for this transition are delocalized states involving both adsorbed iodide and electron density of the Ag cluster. Note that different cluster sizes will affect the electronic properties of the I_2–Ag complex rather than the vibrational frequency of the I–I stretch. This is consistent with the fact that the same 123 cm^{-1} fundamental frequency was always observed, independent of the variations in relative intensities of the bands from the different spots on the Ag surface.

As was described above, the I_2-like species cannot be spontaneously formed on the Ag surface. Formation of this species requires the adsorbed I atoms to be in a nonzerovalent state, which necessitates, in turn, electron density to be shifted toward the iodine atom. It is believed that, upon irradiation, a photoinduced electron transfer occurs from silver to the adsorbed iodide. The role of temperature is to stabilize this charge transfer state in order to form an I–I bond. A similar phenomenon was recently reported in which a methyl viologen cation radical was produced on an electrochemically roughened Ag surface after a photoinduced electron transfer from the metal.[30] Low temperatures (77 K) appeared to stabilize the charge transfer state so that the cation radical was observed indefinitely in the SERS spectra. At room temperature, the back-reaction neutralized the cation radical and no characteristic spectrum was observed under steady-state irradiation. Similarly, in the current study, charge from iodide is transferred back to the metal at higher temper-

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atures resulting in a breaking of the I−I bond on the surface and thus in the disappearance of the Raman progression.

The following experiments provide additional support for the formation and dissociation of an I−I bond on the Ag surface. When the iodide-modified, electrochemically roughened Ag surface was overcoated with silicone oil prior to lowering the temperature, only a very weak Raman progression was observed. It is known from other experiments that silicone oil does not displace adsorbed species from the silver surface and does not affect their SERS intensities. In the case of iodide, it was concluded that silicone oil interferes with the formation of I_2 on the surface.

Finally, it is important to emphasize that the vibrational frequency of I_2 adsorbed on the Ag surface (123 cm^{-1}) is downshifted from that of the I_2 molecule in solution (215 cm^{-1}). This downshift results from a weakening of the I−I bond because some electron density is required to maintain the Ag_s−I bond (reduction of the force constant) as well as from an increase in the effective mass of the surface bound I atoms.

Conclusions

The experimental data presented here suggest the presence of small Ag clusters on the electrochemically roughened silver surface. Modification of the surface with a monolayer of iodide results in formation at low temperatures and under laser irradiation of adsorbed I_2-like species. This species generates a strong Raman progression with the fundamental at 123 cm^{-1} when excited with 406, 413, and 415 nm laser lines. However, no progression was observed with 458 and 364 nm excitations. Relative intensities of bands in the progression vary at different spots on the electrochemically roughened surface thereby reflecting electronic inhomogeneity of the surface. This inhomogeneity results from different sized Ag clusters present at different spots on the surface that originated from nonuniformity of the electrochemical procedure.

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