CF$_2$Cl$_2$, and C$_2$H$_6$ being limited to $n = 1$ and $n = 2$ complexes and smaller molecules such as CH$_4$ yielding up to $n = 4$. For all of these species, the addition of *subsequent* van der Waals complexing partners results in only a diffuse continuum under moderate cooling, but yields sharper substructure with more intense cooling conditions. Hence, it is important that the complexing gas not be used for cooling itself, otherwise clustering of the complexing species will result in a rapid appearance of a continuum and hence obscure the sharp spectral structure of the higher n complexes.

The effects of rare gas complex formation on radiative lifetimes are qualitatively similar to arenes such as tetracene,[1] but quantitatively different in that the external heavy atom effect is much larger. This is further confirmed in the $n = 2$ CF$_2$Cl$_2$ complex. It is interesting that for all other complexing species CH$_4$, C$_2$H$_6$, and C$_2$H$_4$ the radiative lifetimes are slightly increased and there are no structural effects either from the complexing molecule or the geometry of the cluster.

With care in cooling conditions in the expansion, it is possible to spectrally resolve excited-state vibrational progressions. Hence, these systems offer interesting possibilities for dynamical studies of energy transfer, once the exact identity of the vibrational progressions can be confirmed by laser-ionization mass spectrometry.

In summary, we have explored many new types of van der Waals complexes with large organic molecules. We have obtained novel and useful spectroscopic information which, when supplemented by radiative lifetime data, has permitted spectral assignments for a diverse range of van der Walls species. This is an important first step in beginning dynamical studies of such phenomena as excited-state proton transfer and other isomerization effects in van der Waals clusters, designed to mimic the effect of the condensed phase.

Charge Transfer from Tetrathiafulvalene to Silver and Gold Surfaces Studied by Surface-Enhanced Raman Scattering

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Vibrational spectra of tetrathiafulvalene (TTF) adsorbed on silver and gold surfaces have been observed via surface-enhanced Raman scattering (SERS). When adsorbed onto silver and gold island films at room temperature and pressure, TTF exists primarily as the radical cation TTF$^+$. This appears to be the first SERS observation of an adsorbed cation in a nonelectrochemical environment. The oxidation of TTF to TTF$^+$ is probably promoted by surface impurities which raise the work function of the metal surface. Some support for this idea comes from kinetic measurements of TTF adsorption onto colloidal gold surfaces; at short times TTF exists predominantly as the partially oxidized species TTF$^{0.3+}$, which converts slowly in time to TTF$^+$, consistent with an increased work function due to slow deposition of impurities onto the gold surface. Since the oxidation state of many charge-transfer compounds can be *quantitatively* determined by Raman spectroscopy, SERS spectra of TTF and related molecules provide a means to explore the nature of charge transfer between metal surfaces and adsorbates. We discuss some potential applications, including the relationship between charge transfer and the SERS mechanism itself.

Introduction

Charge transfer is probably the most general chemical interaction occurring between metal surfaces and adsorbates; hence, a calibrated molecular probe for measuring the extent of charge transfer to a metal surface would be a great boon. In this paper, we show that tetrathiafulvalene (TTF) is an ideal adsorbate for this purpose. TTF was adsorbed on various silver and gold surfaces and its vibrational spectrum obtained by virtue of surface-enhanced Raman scattering (SERS).[1] Adsorption-induced shifts in the frequencies of several vibrational modes could then be used to determine the extent of charge transfer between the metal surface and adsorbed TTF.

Low-dimensional organic materials containing TTF, TTF derivatives, or TTF analogues as electron-donating moieties have been examined extensively.[2] Especially interesting are the highly conducting organic "metals" that can be synthesized from TTF (or kindred charge donors) and an appropriate charge acceptor (e.g., TCNQ). Studies of these bulk conducting salts have revealed a *quantitative* relationship between the amount of charge transferred from TTF and shifts in the Raman frequencies of characteristic TTF molecular vibrations.[3,4] Accordingly, the

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(1) For a recent review see: Chang, R. K., Furtak, T. E., Eds. "Surface Enhanced Raman Scattering"; Plenum Press: New York, 1982.
(2) One of many reviews of these systems is: Keller, H. J., Ed. "Chemistry and Physics of One-Dimensional Metals"; Plenum Press: New York, 1977.

SERS spectra of adsorbed TTF offer a well-calibrated probe for gleaning details about charge transfer to surfaces. Among other factors, the extent of charge transfer between an adsorbate and a metal surface depends on the adsorbate ionization potential and the metallic work function. Thus, the great variety of TTF derivatives and analogues (having different ionization potentials) and the differing work functions of the SERS metals (e.g., Ag, Cu, and Au) provide a rich material storehouse for understanding the detailed mechanism of charge transfer between metals and adsorbates. The potential of TTF (or related compounds) to probe charge-transfer processes at interfaces is underscored by the relatively strong adsorption exhibited by TTF, which allowed SERS studies to be carried out under a wide variety of experimental conditions.

Finally, we note that there is still considerable controversy concerning the detailed mechanism of SERS. In particular, there has been much speculation recently about the possible role of new electronic states which form due to charge transfer between the metal and adsorbed molecule.[5-9] Examination of TTF adsorption, where both the enhancement and the degree of charge transfer can be quantitatively measured, may allow such theories to be tested.

Experiments

SERS spectra of adsorbed TTF were obtained from silver and gold surfaces deposited onto silica substrates as island films. The full details of the preparation and optical properties of silver island films have been discussed elsewhere.[10] Briefly, we deposit a mass thickness of 50 Å of silver at $\sim$1 Å/s onto a polished silica surface heated to 150 °C in a cryopumped evaporator operated at $\sim$10^{-7} torr. This produces a film of Ag islands of approximately circular cross section, roughly 200 Å in diameter and covering 30–40% of the surface. The absorption profile of these films is highly reproducible and has a large peak at $\sim$440 nm. The films give excellent SERS spectra, with optimum excitation around 500 nm where the enhancement of the Raman scattering cross section is $\sim$10^5 per adsorbed molecule.

The gold films used were deposited in a similar fashion, and their optical properties were optimized by using the absorption profiles as a guide. We found that films with mass thickness of 75 Å evaporated at $\sim$1 Å/s onto silica substrates heated to 150 °C had the optimum absorption profiles as determined by the sharpness and magnitude of the absorption peak. High-resolution electron micrographs showed the morphology of the gold islands to be similar to the silver islands. Their absorption profiles exhibited a large, relatively narrow peak at $\sim$575 nm, and excellent SERS spectra of adsorbates were obtained with excitation wavelengths in the red. We also attempted to use copper island films, but were unable to see SERS spectra from TTF, or any other adsorbate, despite the fact that the absorption profiles showed a well-defined resonance peaked at $\sim$340 nm. We believe that this was due to the relatively thick oxide coating that was formed very
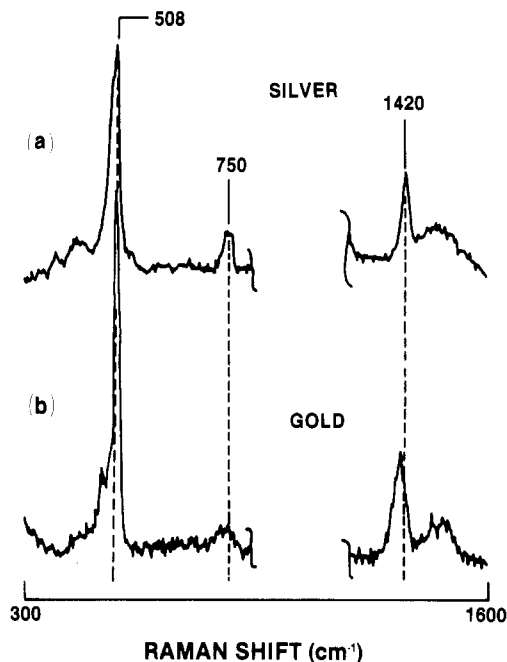

Figure 1. SERS spectra of TTF adsorbed on (a) silver and (b) gold island films, as deposited from 1 × 10^{-4} M acetone solutions. Frequencies of the most prominent bands indicate formation of the cation TTF$^+$ (cf. Table I).

rapidly upon exposure to air. Corroboration of this hypothesis is obtained from our observation that SERS spectra from aqueous copper colloids can only be obtained upon addition of excess reducing agent.[11]

The TTF (Aldrich) was recrystallized from a cyclohexane (20%)/hexane (80%) mixture before use and was applied to the island films from solutions of acetone. The island films were spun at high speed after the TTF solution was applied to remove excess TTF and solvent, assuring an even coating of adsorbate, whose coverage was controlled by the concentration of TTF in solution. Other solvents, including methanol and methylene chloride, were also used, but no solvent-dependent effects were found.

SERS spectra from island films were obtained from a backscattering geometry, using a double monochromator equipped with holographic gratings to disperse the scattered light. Standard photon counting electronics were used and the system was controlled with a microcomputer. Excitation was supplied with Ar$^+$ or Kr$^+$ ion laser radiation which was focused to a 0.1 × 3 mm^2 line at the sample. The total power level was maintained below 10 mW and the substrates were spun to reduce laser-induced damage of either the island film or the adsorbate. Excellent SERS spectra were obtained with signal levels among the highest that we have measured for adsorbates on island films.

Experiments with TTF adsorbed on the surface of gold colloids were also conducted. The aqueous gold sols were prepared according to Creighton's prescription[12] and aggregated by the addition of pyridine. Upon aggregation (which caused the initially red sol to turn blue–gray) strong SERS signals from adsorbed pyridine could be detected. Pyridine was then displaced from the gold surface by the addition of TTF, and the SERS spectrum of the latter recorded. The kinetics of the surface displacement reaction as well as the kinetics of subsequent processes involving adsorbed TTF were monitored with an optical multichannel analyzer. These kinetic studies will be re-

(3) Kuzmany, H.; Stolz, H. J. *J. Phys. C* **1977**, *10*, 2241.

(4) Siedle, A. R.; Candela, G. A.; Finnegan, T. F.; VanDuyne, R. P.; Cape, T.; Kokoszka, G. F.; Woyciejes, P. M.; Hashmall, J. A. *Inorg. Chem.* **1981**, *20*, 2635.

(5) Demuth, J. E.; Sanda, P. N. *Phys. Rev. Lett.* **1981**, *47*, 57.

(6) Avouris, Ph.; Demuth, J. E. *J. Chem. Phys.* **1981**, *75*, 4783.

(7) Schmeisser, D.; Demuth, J. E.; Avouris, Ph. *Chem. Phys. Lett.* **1982**, *87*, 324.

(8) Otto, A. *J. Electron Spectrosc. Relat. Phenom.*, submitted.

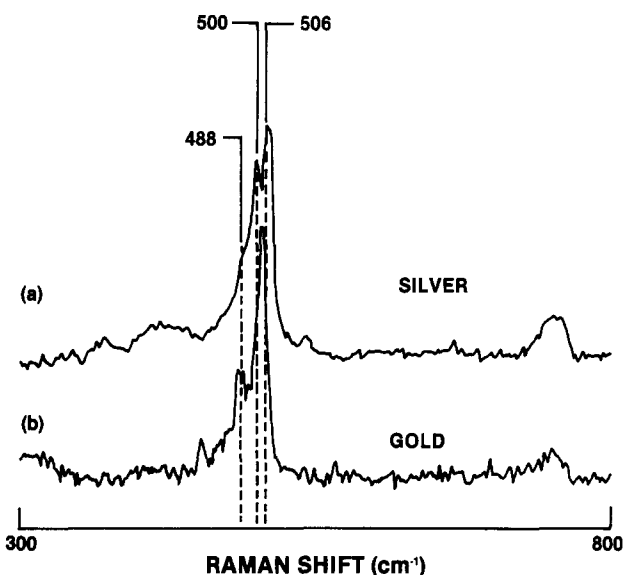(9) Adrian, F. J. *J. Chem. Phys.* **1982**, *77*, 5302.

(10) Weitz, D. A.; Garoff, S.; Gramila, T. *J. Opt. Lett.* **1982**, *7*, 168.

(11) Alvarez, M. S.; Creighton, J. A.; Weitz, D. A.; Garoff, S.; Kim, M. W. *Bull. Am. Phys. Soc.*, submitted.

(12) Creighton, J. A., In ref 1.

TABLE I: Comparison of Some Raman Frequencies (cm^{-1}) in TTF^0, TTF$^+$, and Adsorbed TTF

a_g modes[a]	bulk TTF^0	bulk TTF$^+$	TTF on Ag	TTF on Au
ν_3	1512	1416	1420	1418
ν_5	796	758	750	748
ν_6	468	506	508	506
			500	488

[a] See ref 4.

Figure 2. Detail of low-frequency region of Figure 1 revealing the doublet structure of the ν_6 band. The lower frequency component of ν_6 has a larger Raman shift on silver than on gold.

ported in fuller detail in a separate publication.

Results

Figure 1a displays the SERS spectrum obtained from TTF as deposited onto a silver island film from a 1×10^{-4} M solution in acetone. Most prominent are the bands at 1420, 750, and 508 cm^{-1}, having no counterparts in the Raman spectrum of TTF^0,[13,14] the neutral TTF molecule. In TTF^0, the most intense Raman band occurs at 1518 cm^{-1}, and bands of moderate intensity at 735 and 474 cm^{-1} most closely correspond to the 750- and 508-cm^{-1} features seen in the SERS spectrum. The large disparity between the observed frequencies and those of TTF^0 suggests that the adsorbed molecule is no longer in its neutral state.

In donor–acceptor organic salts, Raman scattering has identified TTF in many different oxidation states; for example, TTF$^{0.5+}$ (in TTF-TCNQ),[3] TTF$^+$ (in (TTF)-Br$_{1.0}$),[14] and TTF^{2+} (in TTF(AuCl$_4$)$_2$).[4] In several compounds where TTF exists as the singly charged cation,[4] assignments of totally symmetric a_g modes have been made at 1416 (ν_3), 758 (ν_5), and 506 (ν_6) cm^{-1}. The ν_3 band is especially sensitive to the oxidation state of TTF since the ν_3 frequency decreases by nearly 100 cm^{-1} as TTF goes from its neutral state to TTF$^+$. The excellent agreement between the bulk TTF$^+$ values for ν_3, ν_5, and ν_6 and the frequencies for TTF adsorbed on silver island films clearly indicates that TTF has become completely oxidized on the silver surface to form the radical cation TTF$^+$.

To test the generality of this charge-transfer process, analogous experiments were conducted on gold surfaces.

(13) Bozio, R.; Girlando, A.; Pecile, C. *Chem. Phys. Lett.* **1977**, *52*, 5031.
(14) Bozio, R.; Zanon, I.; Girlando, A.; Pecile, C. *J. Chem. Phys.* **1979**, *71*, 2282.
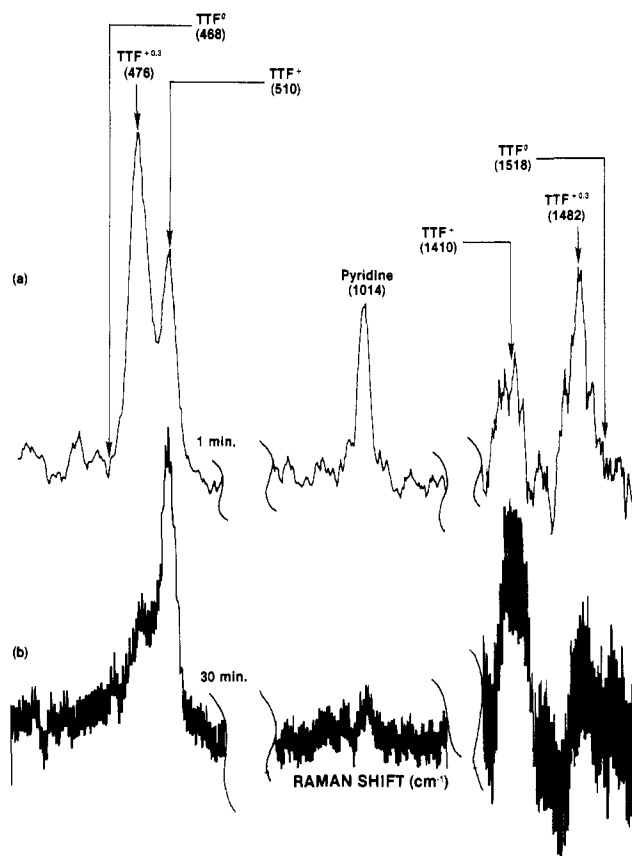

Figure 3. Kinetics of TTF adsorption onto colloidal gold particles showing two distinct TTF species. At shorter times (a), when little pyridine has been displaced by TTF, TTF exists predominantly as the partially oxidized TTF$^{0.3+}$. At longer times (b), this partially oxidized species is converted to TTF$^+$.

Figure 1b shows a typical SERS spectrum of TTF adsorbed on gold island films. In its essential features this spectrum virtually duplicates the results for TTF on silver. Thus, under ambient conditions, TTF is oxidized to its radical cation on both silver and gold surfaces. Table I compares the observed Raman frequencies for TTF adsorbed on these metal island films with the corresponding values for bulk TTF^0 and TTF$^+$.

The expanded SERS spectra in Figure 2 show the ν_6 band of adsorbed TTF$^+$ to be a doublet with the components on silver at 500 and 508 cm^{-1}, considerably closer in frequency than their gold counterparts at 488 and 506 cm^{-1}. More about the origin of this doublet feature was learned from a kinetic study of TTF adsorption onto colloidal gold surfaces. The results of this study rest in Figure 3. The temporal evolution of the TTF$^+$ SERS spectrum was followed as TTF first displaced previously adsorbed pyridine and then as the adsorbed TTF$^+$ underwent further changes. Spectra were recorded at intervals of several minutes, and each spectrum represents roughly 30 s of data collection. On colloids, it can be seen that the relative intensities of the bands comprising the ν_6 doublet eventually reach the value observed on island film surfaces, but only long after TTF has displaced pyridine from the gold surface.

To explore the effects of increased adsorbate concentration on the extent of charge transfer, we compared the SERS spectra from optically equivalent island films with different TTF$^+$ coverages. Different surface coverages were achieved by changing the concentration of TTF^0 in solutions used for deposition. Figure 4 displays typical spectra corresponding to increased TTF$^+$ surface coverage. Clearly, increased surface coverage of TTF$^+$ on silver and
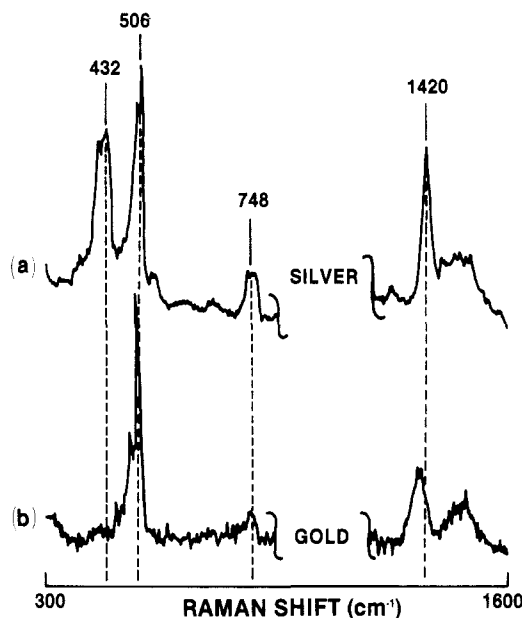
Figure 4. SERS spectra as in Figure 1 except that TTF was deposited from a 1×10^{-2} M acetone solution. Note new band at 432 cm^{-1} appearing on silver surface.
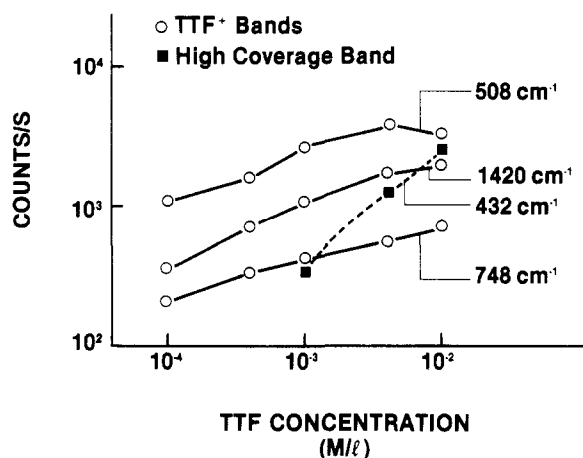

TTF CONCENTRATION (M/ℓ)

Figure 5. Variation of SERS intensity with TTF solution concentration on silver island films for most prominent Raman bands. The TTF$^+$ bands show a different concentration dependence than the 432-cm^{-1} band. Where TTF$^+$ intensities plateau (between 10^{-3} and 10^{-2} M), coverage is presumed to be on the order of a monolayer.

gold has little effect on the extent of charge transfer: the intensities of the characteristic TTF$^+$ bands increase with increasing solution concentration of TTF^0, suggesting higher TTF$^+$ surface coverage, but the frequencies of these bands, which are proportional to extent of charge transfer, remain unchanged. Also remaining unchanged in the course of increasing TTF$^+$ coverage is the relative intensity ratio of the bands comprising the ν_6 doublet.

Most striking in Figure 4 is the appearance of an intense Raman line at 432 cm^{-1}. This feature has no counterpart in the high-coverage SERS spectrum on gold island films. The depolarization ratio of the new band at high coverage was different from those from TTF$^+$: the ratio was 0.6 for the 432-cm^{-1} band and 0.4 for the 506- and 1420-cm^{-1} bands.

Figure 5 summarizes the variation of SERS intensity with coverage of TTF on silver island films. The bands characteristic of TTF$^+$ (1420, 748, and 508 cm^{-1}) display similar behavior, and the slope of the count rate vs. TTF^0 solution concentration is near 0.5 for all three Raman lines. In sharp contrast to this, the slope for the 432-cm^{-1} line is about unity. Coverage-dependent studies were also
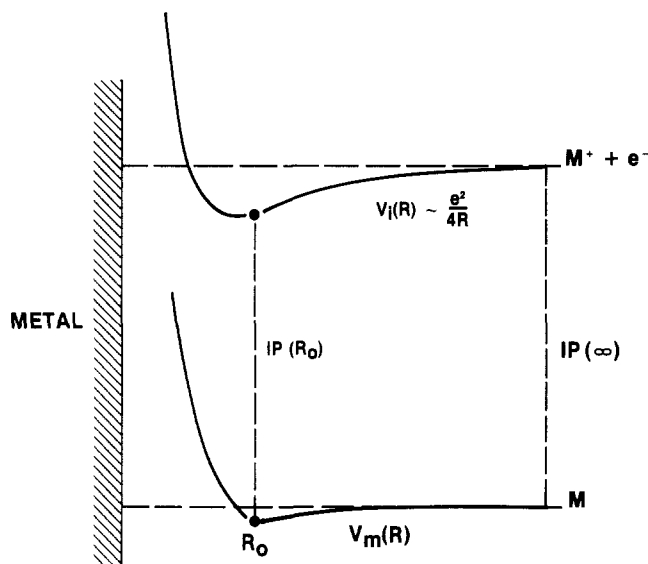

Figure 6. Schematic potential energy curves for interaction of a neutral molecule M and its cation M$^+$ with a metal surface. The molecule approaches to a distance R_0 at which its ionization potential is lowered below the free-molecule value by an amount given approximately by the image force contribution at that distance, so $IP(R_0) \simeq IP(\infty) - e^2/4R_0$.

performed on gold island films. Except for the absence of the high-coverage feature at 432 cm^{-1}, the results for gold were similar to those for silver.

Discussion

The SERS spectra for TTF adsorbed on silver or gold surfaces display three characteristic vibrational bands that indicate complete oxidation of TTF to the radical cation TTF$^+$. This observation of a positively charged surface species contrasts with the usual case found for SERS; formation of negatively charged adsorbates that produce stable salts with Ag$^+$ is the general rule. In fact, we know of no other nonelectrochemical SERS study that unambiguously identifies organic cations adsorbed on a coinage metal surface. In what follows we discuss the mechanism of the charge transfer, the nature of the adsorbed TTF species, and the potential use of charge-transfer compounds as probes to study adsorbate–metal interactions.

Charge-Transfer Mechanism. Surface ionization of an adsorbed molecule to produce an adsorbed cation

$$M(\text{adsorbed}) \rightarrow M^+(\text{adsorbed}) + e^-(\text{in metal})$$

is subject to an energetic constraint: the work function (ϕ) of the surface must exceed the ionization potential (IP) of the adsorbed molecule. As illustrated in Figure 6, this IP can be appreciably lower than that for the free molecule, because the adsorbed cation is stabilized by a Coulombic interaction with the image charge induced in the metal. For TTF, the IP of the free molecule is about 6.9 eV.[15] The image stabilization[16] is approximately $3.6/R$ eV, where R denotes distance of the molecule from the surface in angstroms. TTF seems likely to be "lying flat" on the surface, for reasons given in the next section. Thus, a lower bound for R is the van der Waals radius of a sulfur atom,[17] or $R_0 > 2.0$ Å. The corresponding upper bound for the

(15) Gleiter, R.; Schmidt, E.; Cowan, D. O.; Ferraris, J. P. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 207. Klots, C. E.; Compton, R. N.; Raaen, V. F. *J. Chem. Phys.* **1974**, *60*, 1177.

(16) Purcell, E. M. "Electricity and Magnetism"; McGraw-Hill: New York, 1965; p 106.

(17) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

image contribution is $e^2/4R_0 < 1.8$ eV, so the estimated ionization potential of adsorbed TTF is $\gtrsim 5.1$ eV. This lower bound is higher than the work function of a clean Ag or Au surface ("preferred value" 4.7 or 4.8 eV, respectively[18]). However, in our experiments, the metal films are likely contaminated by adsorbed oxygen[19] and other species.[20] The work function is thus expected to be larger by up to ~ 0.8 eV, for at least some adsorption sites.[21] At such sites, the energetic criterion for complete ionization of TTF can be fulfilled.

The treatment above serves as a qualitative physical guide to the energetics of charge-transfer processes on metal surfaces. For the ambient pressures where our experiments were conducted, it was not possible to identify surface impurities or determine their coverages. Hence, the values of such germane charge-transfer parameters as ϕ and R_0, and how those values depend on adsorbate and adsorbate coverage, cannot be stated precisely. For adsorption experiments conducted under ultrahigh vacuum, a more optimistic state of affairs might prevail, and the use of TTF (or similar compounds) as a calibrated spectroscopic probe of charge transfer could help in the general understanding of work function changes induced by adsorbates. In particular, on clean silver or gold surfaces, we would not expect extensive charge transfer to occur upon adsorption of TTF; the work functions are simply too low compared to the IP of TTF. As impurities (oxides or sulfides, for example) were coadsorbed along with TTF, charge transfer would become more and more complete. On metals with larger work functions, like platinum, considerable charge transfer is likely even on the clean metal.

Nature of the Adsorbed TTF$^+$. The electron which is removed from TTF resides in a molecular orbital which divides most of the charge density evenly among the sulfur atoms.[22] It is likely, then, that the adsorbed TTF$^+$ is lying flat with each of its four sulfur atoms resting on the metal surface. This configuration was also suggested by SERS results for ethylene adsorbed on silver.[23] TTF, with its D_{2h} symmetry and central C=C bond, can be thought of as a sulfur analogue of ethylene and thus might be expected to assume the same configuration upon adsorption. The adsorption of TTF is evidently quite strong; in competitive adsorption experiments from solution, we found that TTF readily displaced organic sulfide compounds chemisorbed on silver as mercaptides. Yet, the SERS spectra show no evidence for surface-induced decomposition of TTF as seen for other organic sulfides.[24] This strong, nondissociative adsorption seems consistent with a model where the delocalized charge in TTF$^+$ results in strong electrostatic attraction to the surface without the formation of strong covalent bonds between the metal atoms and sulfur. This surmise is in accord with the low nucleophilicity of the sulfur atoms in TTF and difficulty in forming bonds between the sulfurs of TTF and transition-metal atoms.[4]

The doublet structure seen in the ν_3 and ν_6 bands of TTF$^+$ adsorbed on colloidal gold surfaces may elucidate further the adsorption process, as illustrated by our preliminary kinetic experiments (Figure 3). These doublets do not result from surface-induced lowering of the TTF$^+$ molecular symmetry. Such symmetry lowering can split originally degenerate modes or make "allowed" originally "forbidden" transitions, or both. For TTF, with or without the surface present, all modes are nondegenerate, and there are no forbidden modes near ν_3 or ν_6. Rather, the kinetic experiments suggest that there are two distinct adsorbed species. One corresponds to complete charge transfer (lower frequency component of ν_3 and higher frequency component of ν_6). The other exhibits frequency shifts corresponding to about 30% charge transfer (TTF$^{0.3+}$). On a time scale of minutes, the relative intensity of both doublet pairs changes in favor of complete charge transfer. These dynamic changes may be attributable to the slow oxidation of the gold surface. As outlined in the previous section such oxidation would be expected to increase the metallic work function, thereby facilitating complete charge transfer. The relative intensities observed for the ν_6 doublet on gold island films is also consistent with a chemical oxidation mechanism. On gold island films the (coverage-independent) doublet ratio is roughly equal to that for TTF$^+$ on the colloids after long times. Since the island films are exposed to air for hours after the TTF deposition, one expects them to have adsorbed the amounts of oxygen (or other impurities) necessary to promote complete charge transfer.

Island-film spectra of adsorbed TTF$^+$ reveal that the lower frequency components of the ν_6 doublet, indicative of partial charge transfer, have substantially different Raman shifts on silver (500 cm^{-1}) than on gold (488 cm^{-1}), suggesting more complete charge transfer in the former. This difference contrasts sharply with the higher frequency ν_6 components, indicative of total charge transfer, which exhibit virtually identical Raman shifts on the two metals. These results suggest that the impurities adsorbed on the silver surface are considerably stronger oxidizing agents than those adsorbed on gold.

We note in passing that unlike the ν_6 band, the ν_3 band of TTF, which is even more sensitive to the degree of charge transfer, shows no strong evidence of a doublet on gold island films. That a well-resolved doublet appears in the ν_3 regions in gold colloid spectra may be indicative of a strong solvent effect, and is worthy of further investigation.

Another feature inviting further study is the intense band at 432 cm^{-1} which appears at high coverages on silver but not on gold (Figure 4). Although the origin of this band is puzzling, we note a possible spectroscopic assignment in the infrared-active ν_{18} mode of the neutral TTF molecule.[13] This mode appears as a strong absorption at 427 cm^{-1} in solutions of TTF^0 and at 434 cm^{-1} in the solid powder,[13] whereas the ν_{18} mode of TTF$^+$ occurs at 460 cm^{-1}. Interestingly, the atomic displacements in the infrared-active ν_{18} mode (with b_{1u} symmetry) are very similar to those in the Raman-active ν_6 mode (with Ag symmetry).[14] Reducing the symmetry group from D_{2h} to C_{2v} on adsorption converts both a_g and b_{1u} modes to a_1 modes. Since ν_6 is the most intense band in the SERS spectrum of adsorbed TTF$^+$, a strong contribution from the ν_{18} mode might be expected, but it is strange that this should come from TTF^0 and not TTF$^+$ and appear on silver but not on gold.

Utility as Probe of Charge Transfer. By virtue of the unusually low ionization potential of TTF^0 and the large

(18) Lerner, R. G.; Trigg, G. L., Eds. "Encyclopedia of Physics"; Addison-Wesley: Reading, MA; p 1112.

(19) Dorain, P. B.; VonRabin, K. U.; Chang, R. K.; Laube, B. L. *Chem. Phys. Lett.* **1981**, *84*, 405.

(20) Raman spectra of bare silver island films, for instance, contain features probably attributable to carbon species (Tsang, J. C.; Demuth, J. E.; Sanda, P. N.; Kirtley, J. R. *Chem. Phys. Lett.* **1980**, *76*, 54) and perhaps organic sulfides. Most of these bands disappear after adsorption of TTF, indicating that these surface impurities, being more weakly adsorbed, are displaced by TTF.

(21) Engelhardt, H. A.; Menzel, D. *Surf. Sci.* **1976**, *57*, 591.

(22) Metzger, R. M.; Bloch, A. N. *J. Chem. Phys.* **1975**, *63*, 5098.

(23) Moskovits, M.; Dilella, D. P. *Chem. Phys. Lett.* **1980**, *73*, 500.

(24) Sandroff, C. J.; Herschbach, D. R. *J. Phys. Chem.* **1982**, *86*, 3277.

shifts in vibrational frequency which accompany its ionization, the SERS technique (and presumably other surface vibrational spectroscopies) permits us to quantify the extent of charge transfer from TTF to metal surfaces. Thus, one of the most appealing applications of adsorbed charge-transfer compounds would be to deduce the relationship between charge transfer and the SERS mechanism itself. Indeed, some direct relationship between Raman cross-section enhancements and charge transfer is hinted at in the data already presented.

Several charge-transfer mechanisms have been invoked recently which may account for a factor between 10 and 100 in the Raman cross-section enhancement of molecules adsorbed on noble metal surfaces. Most of these mechanisms involve dynamic charge transfer. For example, the amount of charge transferred between the adsorbate and the molecule can be modulated by molecular vibrations, causing changes in the metal island plasma frequency and increasing the Raman cross section.[25] Alternatively, an exciting laser field capable of promoting an electron from the metal or adsorbate to a new state associated with the chemisorbed molecule can give rise to a type of resonance enhancement.[9,26]

However, on our island films we find relatively little evidence that dynamic charge transfer plays a major role in the enhancement, and find instead that electromagnetic effects are dominant. The excitation spectrum of TTF^+ on silver island films shows no evidence of an additional resonance contribution from a new electronic state induced by chemisorption, but rather the excitation profile has the shape of the measured island-film absorption, in accord with electromagnetic models.[10] Furthermore, the SERS spectra of TTF^+ on silver and gold are remarkably similar despite the different excitation wavelengths used, an observation also suggesting the absence of an important role played by a resonant contribution to the Raman process by new electronic states formed during molecule–metal bonding.

Nevertheless, charge transfer—of a static type—does contribute in a measurable way to the SERS spectra of TTF. SERS intensities from TTF^+ are among the largest that we have measured on island films. Furthermore, relative intensities in the SERS spectra of TTF^+ are significantly different from their bulk values, a difference which may be attributable to static charge-transfer effects.

In the SERS spectrum of TTF^+ adsorbed on silver (Figure 1) the ν_6 band at 508 cm^{-1} (essentially a stretch of the ethylene carbon–sulfur bond)[13] is substantially *more* intense than the ν_3 band at 1420 cm^{-1} (the ethylenic double-bond stretch).[13] These relative intensities obtain for the full range of TTF^+ coverage. The Raman spectrum of TTF^+ in solution, obtained with the same 5145-Å excitation wavelengths used for SERS experiments on silver, showed ν_6 to be significantly *less* intense than ν_3.[14] The origin of the reversal in the ν_6/ν_3 intensity ratio is not well understood but it is evidently associated with charge transfer rather than a surface- or metal-specific process. The latter can be safely ruled out since a ν_6/ν_3 intensity ratio similar to that on silver was found on gold despite the vastly different excitation wavelength (6471 Å) used to obtain the SERS spectra on gold.

In addition, although the origin of the ν_6/ν_3 ratio remains uncertain, the persistence of its high value with change of surface and coverage can also be taken as evidence for the role of charge transfer in the enhancement mechanism for

SERS. In TTF^+, since most of the charge density is localized on the sulfur atoms,[22] the molecular vibrations with the largest sulfur displacements are likely to be most strongly affected by any charge-transfer contribution to the enhancement. Thus, ν_6, the C—S stretch, might be expected to exhibit a larger enhancement than ν_3, the ethylenic C=C stretch, in agreement with the large ν_6/ν_3 intensity ratio observed.

We believe that a very rough qualitative model involving static charge transfer may account for much of the observed behavior. The result of the static process is to transfer an electron from a relatively localized electronic orbital on TTF into the metal, where presumably it attains some free-electron character and becomes less localized. Hence, the resulting electronic orbital is predominantly metallic in character, while still retaining some molecular characteristics. The resulting orbital increases the volume sampled by the electron and hence increases its contribution to the total polarizability which, in turn, increases the Raman scattering cross section. A similar argument, proposed to account for the strong Raman scattering from organic charge-transfer complexes, has been extended to the SERS mechanism itself.[27]

If we assume that the electronic orbital samples a volume of metal comparable to that of TTF^+ along with the volume separating the metal from the surface, we estimate that the increase in volume sampled by the transferred electron is more than a factor of 3, resulting in a Raman enhancement of nearly 1 order of magnitude. We note that this effect might be expected to be rather general, occurring to some degree whenever a static charge transfer between the molecule and the metal occurs. Furthermore, it would not have any resonant behavior in its excitation dependence. We note in addition that many molecules studied with SERS using island films have involved some degree of static charge transfer. Thus, this mechanism might account for some of the enhancement in some of these cases. The characteristics of the mechanism would include a nonresonant contribution to the excitation profiles, a contribution whose magnitude depends somewhat on the degree of charge transfer, and a contribution that would emphasize modes strongly coupled to the transferred charge. All of these are consistent with our observations. This effect may be viewed as a "chemical" contribution to the enhancement of the Raman scattering cross section by about 1 order of magnitude due to the change in polarizability of an adsorbed molecule. Nevertheless, we emphasize the qualitative nature of this hypothesis which clearly must be put on a more quantitative footing before more detailed comparisons with experiment can be made. Perhaps, future experiments in which TTF derivatives with larger molecular volumes are adsorbed onto silver and gold surfaces will help in making such comparisons.

There are several areas aside from SERS where TTF and related charge-transfer compounds could find widespread use. Codeposition of TTF with other materials (including many celebrated charge acceptors such as TCNQ) should provide spectra that reveal the competition between the metal surface and other electron acceptors for the charge available from the donor. Also, since the TTF spectrum affords a quantitative measure of the amount of charge transferred to a metal surface, studies of the effects of charge donation on coadsorbate bond weakening now appear feasible. Finally, because the extent of charge transfer depends on the metallic work function (which can increase due to adsorbed impurities), it may be possible

(25) Abe, H.; Manzel, K.; Schulze, W.; Moskovits, M.; DiLella, D. P. *J. Chem. Phys.* **1981**, *74*, 792.

(26) Billman, J.; Otto, A. *Solid State Commun.* **1982**, *44*, 105.

(27) Aussenegg, F. R.; Lippitsch, M. E. *Chem. Phys. Lett.* **1978**, *59*, 214.

to identify reactive, oxidizing species in catalytic systems. Since silver catalysts are widely used in the selective oxidation of ethylene,[28] where charge transfer could play a very important role,[29] the results reported here may be directly relevant.

(28) Verykios, E.; Stein, F. P.; Coughlin, R. W. *Catal. Rev. Sci. Eng.* **1980**, *22*, 197.
(29) Haul, R.; Hoge, D.; Neubauer, G.; Zeeck, U. *Surf. Sci.* **1982**, *122*, L622.

Registry No. TTF, 31366-25-3; Au, 7440-57-5; Ag, 7440-22-4; TTF+, 35079-56-2.

Collision-Induced Resonances in Radio-Frequency Spectroscopy Inside the Cavity of an Infrared Laser

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The extremely high sensitivity of the infrared–radio-frequency double resonance inside the cavity of a CO_2 laser enables us to observe collision-induced satellites on various kinds of radio-frequency resonances such as the pure quadrupole resonance, and the K-doubling and l-doubling resonances. These collision-induced resonances are produced through three-step processes composed of (1) a velocity-selective collisional process which transfers molecules from the pumped levels to the collisionally coupled levels *without* much variation of velocity, (2) radio-frequency pumping between collisionally coupled levels, and (3) a second velocity-selective collisional process which transfers molecules back to the pumped levels again without variation of velocity. Observation of such collision-induced double resonance signals in the pure quadrupole spectrum of CH_3I and CH_3Br, in the K-doubling spectrum of formic acid, and the l-doubling spectrum of CH_3Br is reported. The observed characteristics of the collision-induced signals confirms the mechanism given above and provides additional evidence for the efficiency of the rotational resonance in which two molecules exchange energy but the total internal energy is conserved.

I. Introduction

The technique of radio-frequency spectroscopy inside the cavity of a laser made it possible to observe radio-frequency transitions with a sensitivity several orders of magnitude greater than the straightforward absorption method. This very high sensitivity has proven useful to measure the frequencies of "forbidden transitions".[1] More recently, it has been applied to observation of transitions between doublet levels split by the molecular asymmetry (K-type doublets)[2] and transitions between multiplet levels due to the interaction of the nuclear quadrupole moment and the gradient of the molecular electric field at the nucleus position ("pure" nuclear quadrupole spectrum).[3]

The sensitivity of this rf spectrometer is so high that, besides the main resonances due to double resonance on the three-level systems, weaker signals are often observed, due to levels which are not directly pumped by the laser but are affected by collisional transfer.

In fact several recordings show, beside the main resonances in the states $(J',K') \leftrightarrow (J'',K')$ pumped by the laser radiation, other resonances with a smaller intensity and distributed in the frequency range over both sides of the principal resonances. From an analysis of the resonance

frequencies they have been identified as connected to states $(J' \pm n,K')$ and $(J'' \pm n,K'')$. These satellite resonances are clearly related to collision-induced processes since their relative intensity tends to zero as the pressure decreases.

A preliminary report of these resonances in the case of "pure" quadrupole resonances of CH_3I has already been given[3] and the purpose of this paper is to summarize the results about these collision-induced resonances observed in radio-frequency spectroscopy inside the laser cavity. In particular, the basic processes and the various systems for which collision-induced resonances have been investigated will be presented in more detail.

It is essential for collision-induced signals to be observed that there exist preferred channels for collisional population transfer. The "selection rules" for such transfers were experimentally studied by microwave–microwave double resonance (MMDR)[4] and a theoretical calculation of collisional transition probabilities has been given by Rabitz and Gordon.[5] An important difference between the MMDR experiments and those reported here is that in MMDR, because of a small Doppler width in the microwave region ($\Delta\nu \sim$ 20–100 kHz), all velocity groups are

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(1) T. Oka, "Molecular Spectroscopy: Modern Research", Vol. II, K. Narahari Rao, Ed., Academic Press, New York, 1976, p 229.
(2) P. Glorieux and G. W. Hills, *J. Mol. Spectrosc.*, **70**, 459 (1978).
(3) E. Arimondo, P. Glorieux, and T. Oka, *Phys. Rev. A*, **17**, 1375 (1978).
(4) T. Oka, *Adv. At. Mol. Phys.*, **9**, 127 (1973), and references therein.
(5) H. Rabitz and R. G. Gordon, *J. Chem. Phys.*, **53**, 1815, 1831 (1970).