distribution we obtain for our LCVD films is determined by the properties of gas-phase clusters produced using laser chemistry of organometallics.

To attain the number densities needed to produce substantial quantities of gas-phase clusters for synthesis and reactivity studies or for film deposition, the vacuum chamber or substrate must be in contact with a relatively high ambient gas pressure. Any previously well-characterized substrate is quickly contaminated. High temperatures must be avoided for all surfaces to avoid thermal background chemistry. The rate of LCVD is limited by the rate of mass transport from the gas/mobile phase to the growing film and by the gas/mobile phase chemistry which occurs before the gas phase condenses on the substrate. Similarly, film morphology is also a direct consequence of the diffusion-limited deposition conditions.[28]

Laser chemistry of organometallics is "nonlinear" in the sense that (1) multiphoton processes can be used to generate the reactants for subsequent chemistry and also (2) because the net chemistry involves reactions between products of earlier stages

with those of the later stages. Using FT-IR spectroscopy in reflectance and transmission, we have shown[29] in the present case that at least some of the allyl and cyclopentadienyl ligands are incorporated in the film as intact entities. In a previous paper,[8] we demonstrated how to remove these impurities so as to obtain nearly bulk platinum electrode characteristics from transparent platinum films. Laser chemistry of organometallics would seem to be a unique and novel type of synthetic chemistry.[30]

Conclusions

Cluster films of metals can be produced using laser chemistry of organometallics. The log-normal distribution can be used to categorize gas-phase cluster distributions produced by different synthetic methods.

(28) In addition to a variety of fractal growth schemes (see for examples: Zumofen, G.; Blumen, A.; Klafter, J. *New J. Chem.* **1990**, *14*, 189–196 and references therein), we have found the following reference useful; Mader, S. *Thin Solid Films* **1964**, *2*, 35–41.

(29) Casey, M. J.; Citra, M.; Chaiken, J. *J. Am. Chem. Soc.*, submitted.
(30) There very well might be a connection between the type of chemistry we describe in this article and the sonochemistry described by: Suslick, K. *Nature* **1991**, *353*, 414–416.

Vibrational Population Inversion in Aniline following Trapping/Desorption from Fullerene Surfaces

Y. Paz, M. S. de Vries,[†] D. J. Elloway,[†] and R. Naaman*

Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel
(Received: December 3, 1991; In Final Form: February 24, 1992)

Aniline molecules were state selectively detected using multiphoton ionization following trapping/desorption from amorphous C_{60} and C_{70} films, and from single-crystal C_{60} surfaces. Vibrational population inversion was observed in all three cases in the inversion mode of the NH_2 group. The vibrational excitation was much less efficient for scattering from a LiF single-crystal surface. A charge-transfer model rationalizes the observations and indicates that the fullerene surfaces strongly interacts with molecules with low ionization potentials.

In general, vibrational excitation upon collision of a molecule with a surface is not an efficient process. When it occurs, it is attributed to coupling to an electron–hole deexcitation in the metal surface.[1] In this process an electron is transferred from the metal surface to a colliding molecule having a high electron affinity. The mechanism has been discussed theoretically,[2] and formation of the anion was also found to be important for rationalizing the vibrational excitation in associative molecular desorption[3–5] and dissociative scattering.[6] It has been demonstrated that when the surface is nonmetallic, no vibrational excitation is observed.[7]

The chemical and physical properties of fullerenes have been the subject of many investigations.[8] Crystals of C_{60} have been probed by various techniques. It has been established that the crystal is a molecular one, and most of its electronic characteristics are well described by those of the isolated molecule.[9] Despite the importance of the surface properties of the solid for the understanding of its chemical stability, not much information is available on the subject because few experimental methods can be applied for the investigation of surfaces of nonconducting solids.

Here we present a study on aniline emerged from amorphous C_{60} and C_{70} films and from single-crystal C_{60} surfaces. The

molecules were state selectively detected using resonant ionization. Vibrational population inversion was observed in all three cases which can be rationalized by the specific surface–molecule interaction.

Aniline was chosen for this investigation because of its relatively low ionization potential (7.7 eV) and its well-documented spectroscopy. In addition, comparison is possible with previous studies in which the energy content in aniline scattered from various nonmetal surfaces has been documented.[10]

(1) Rettner, C. T.; Fabre, F.; Kimman, J.; Auerbach, D. J. *Phys. Rev. Lett.* **1985**, *55*, 1904.
(2) See, for example: Gadzuk, J. W. *J. Chem. Phys.* **1987**, *86*, 5196.
(3) Thorman, R. P.; Anderson, D.; Bernasek, S. L. *Phys. Rev. Lett.* **1980**, *44*, 743.
(4) Bernasek, S.; Leone, S. R. *Chem. Phys. Lett.* **1981**, *84*, 401.
(5) Kubiak, G. D.; Sitz, G. O.; Zare, R. N. *J. Chem. Phys.* **1985**, *83*, 2538.
(6) Kolodney, E.; Amirav, A.; Elber, R.; Gerber, R. B. *Chem. Phys. Lett.* **1984**, *111*, 366.
(7) Kolodney, E.; Baigh, D.; Powers, P. S.; Reisler, H.; Wittig, C. *Chem. Phys. Lett.* **1988**, *145*, 177.
(8) An extensive bibliography is available from the following electronic address: bucky@sol1.lrsm.upen.edu.
(9) Shen, Z.-X.; Cao, R.; Dessau, D. S.; Yang, X.; Pianetta, P.; Marshall, D. S.; Wells, B.; King, D.; Elloway, D.; Wendt, H. R.; Brown, C. A.; Hunziker, H.; de Vries, M. S. submitted to *Phys. Rev. Lett.*
(10) Paz, Y.; Naaman, R. *J. Chem. Phys.* **1991**, *94*, 4921.

†Permanent address: IBM Almaden Research Center, San Jose, CA 94120-6099.

The experimental setup has been described before.[11] It consisted of a two-stage differentially pumped beam machine. A pulsed nozzle (Jordan Inc.) with a nozzle diameter of 0.5 mm was used for producing 100-μs long pulses of aniline seeded in various gases. Ar, He, and H_2 were used as carrier gases in order to vary the aniline velocity. The scattering chamber was pumped by a liquid nitrogen trapped 6-in. diffusion pump, and in addition a cold trap surrounded the sample holder. The pressure in the chamber during the experiment was in the low 10^{-7} Torr range. Single-crystal C_{60} or amorphous C_{60} or C_{70} surfaces were held by a sample holder that was temperature controlled in the range 70–500 K with an accuracy of 1 K. In a separate study we found that aniline sticks to any of the three surfaces at a surface temperature below 260 K. Therefore, all the experiments described here were performed with surface temperatures in the range 320–380 K. An unfocused laser beam was used for the resonance-enhanced two-photon ionization (RETPI) process, and a michrochannel plate monitored the resulting ions.

The fullerenes were produced with the carbon arc method,[12] followed by chromatographic separation. Amorphous surfaces were produced by sublimation of the purified material onto aluminum substrates, to create 1000-Å films. Crystals of C_{60} about 1 mm in size were grown from a supersaturated vapor, after successive sublimation steps. Crystals grown in this way have been investigated by high-resolution transmission electron microscopy (TEM) and electron diffraction,[13] angularly resolved photoemission,[9] differential scanning calorimetry (DSC), and NMR.[14] Their structure is fcc, with stacking faults giving rise to local hcp structure.

Figure 1 shows the RETPI spectra of the cold aniline in the molecular beam (a), aniline scattered from a LiF single-crystal surface (b) and aniline that emerged from a C_{60} single-crystal surface (111) (c). Two spectral features are especially important for our discussion, the origin and the $I_1{}^1$ bands. The I mode is the $-NH_2$ inversion mode which has a frequency of 40.9 cm^{-1} in the ground electronic state. Since the Franck–Condon factors for exciting the origin and the $I_1{}^1$ transition are about the same,[15] the ratio (R) of the relevant two lines in the spectra represents the relative population of the $I_1{}^1$ state versus the ground state. For all fullerene surfaces investigated, the ratio, after correction for the laser intensity, was found to be 1.7 ± 0.5. For comparison, R is less than 1 for a LiF single-crystal surface. No change in the ratio could be observed when the incident collision energy was varied from about 100 up to 800 meV, or when the surface temperature was changed between 260 and 360 K. Furthermore, the ratio did not depend on the flight time of the emerged molecules, as measured by changing the delay between the molecular beam pulse and the detection laser pulse. In the time-of-flight studies it was found that all molecules are emerged with a translational temperature identical to the surface temperature and independent of the collision energy. Some of the molecules may reside on the surface for up to 10 μs. These observations, as well as the independence of the vibrational population on the collision energy and scattering velocity, imply that the molecules have time to fully accommodate with the surface. It must also be noted that the experimental geometry was such that a large solid angle was probed by the detection laser; therefore any possible dependence of the ratio on scattering angle would not be observed. The large error bar for the ratio R results from the need to integrate the band contour in order to obtain the J-independent ratio. The congestion of the spectral lines at the $I_1{}^1$ region did not allow a more precise evaluation of the ratio. The ratio of 1.7 is a conservative lower limit for the population ratio, deduced after all
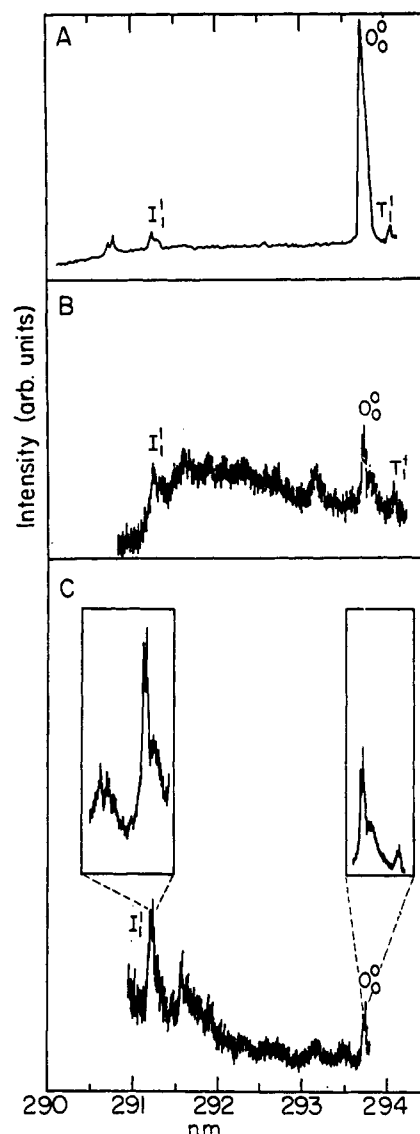

Figure 1. Resonance enhanced two photon ionization spectrum of aniline in (A) the cold beam, (B) aniline scattered from a LiF surface, and (C) aniline desorbed from C_{60} single-crystal surface. The origin and the $I_1{}^1$ regions are expanded.

the experimental difficulties were taken into account.

The results can be rationalized assuming a charge-transfer process. Because of the relatively low ionization potential of aniline and the large electron affinity of the fullerene surfaces (e.g., for C_{60} $EA_{surface} = EA_{molecule} = 2.62$ eV)[16] a crossing between the covalent and the ionic interaction potentials can occur at a distance of about 3 Å from the surface. From this point in its approach, the molecule can transfer charge to the surface. The aniline cation is planner with a $^2B_1$ ground state,[17] while the neutral species electronic ground state is A_1. Its inversion (I) mode has a symmetry of b_1 with a double minimum in the ground electronic state. Therefore conservation of symmetry requires that the ground-state neutral will become an vibrationally excited ion, upon electron transfer to the surface. For the same reason, an ion in its ground state will produce a vibrationally excited neutral (in the $v = 1$ state) when neutralized.

When the colliding species leaves the surface, a second potential crossing occurs and neutrals are formed. If we assume that when colliding with the surface the vibrationally excited ions are quenched and return mainly to their ground state, then on the second crossing, the neutrals are formed in the vibrationally excited

(11) Cohen, S. R.; Naaman, R.; Sagiv, J. *J. Chem. Phys.* **1988**, *88*, 2757.

(12) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(13) Geiss, R. H.; Brown, C. A.; Chapa-Perez, O.; Savoy, R. J.; Wendt, H. R.; Elloway, D.; de Vries, M. S. Submitted to *Philos. Mag. Lett.*

(14) Siemens, R. L.; Johnson, R. D.; Dorn, H. C.; Bethune, D. S.; Brown, C. A.; Lyerla, J.; Yannoni, C. S.; Wendt, H. R.; de Vries, M. S.; Taylor, L.; Nguyen, D.; Salem, J. R.; Elloway, D. Submitted to *J. Thermal Anal.*

(15) Quack, M.; Stockburger, M. *J. Mol. Spectrosc.* **1972**, *43*, 87.

(16) Yang, F. H.; Pettiette, C. L.; Conceicao, J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233.

(17) Meek, J. T.; Sekreta, E.; Wilson, W.; Viswanathan, K. S.; Reilley, J. P. *J. Chem. Phys.* **1985**, *84*, 1741.

state. If the only effect of the surface is reversal of momentum, leaving the internal energy intact, then the initial vibrational population formed upon the first curve crossing remains when the molecule is leaving the surface. In that case, on reneutralization, occurring on the way out from the surface, the neutral aniline is formed in the ground vibrational state.

The probability for charge transfer P_c may depend on the orientation of the aniline relative to the surface. However if the molecule resides on the surface for a long time, relative to its rotational time, this probability approaches unity.

Regarding the electronic transition between the neutral aniline and its cation, we denote the probability for the transition between the covalent vibronic state, c, and the vibronic state of the ion, as a_{cf}. For simplicity we shall focus only on the vibrational ground state and the $I(v = 1)$ mode, denoted as 0 and i, respectively. In what follows, f represents the fraction of excited cations that undergo vibrational relaxation to the ground state at the surface. The ratio between the population in the two modes can now be written as

$$R = \frac{P_c[a_{0i}a_{ii}(1 - f) + a_{i0}(a_{00} + fa_{0i})]}{1 + P_c[a^2_{00} + a^2_{0i}(1 - f) + a_{0i}a_{00}f - 1]} \quad (1)$$

Since $P_c \approx 1$ and $a_{00} \approx a_{ii} < a_{0i} \approx a_{i0}$ and if $f \approx 1$, then the expression for R becomes

$$R \approx \frac{a_{0i}^2 f}{a_{0i}^2(1 - f) + a_{0i}a_{00}f} \approx \frac{a_{0i}}{a_{00}} > 1 \quad (2)$$

The above description indicates that even those molecules that are fully accommodated with the surface can come out vibrationally excited. In fact, with small a_{ii}, accommodation would be a prerequisite for excited products. That, in turn, implies that in the present experiment, the fraction f, of accommodated molecules is the same for all incident energies, as well as for all scattered velocities. This suggests a strong interaction between the fullerene surface and the aniline ion.

The present work indicates a new mechanism that may result in extensive vibrational excitation in molecules desorbed or scattered from surfaces. This nonthermal vibrational population is counterintuitive and provides an indication for a strong interaction between the generally inert fullerene surfaces and molecules that are good electron donors.

Solvent-Induced Proton Transfer in Strongly H-Bonded Complexes: An Adiabatic Dynamical Simulation Study

D. Borgis,* G. Tarjus, and H. Azzouz

Laboratoire de Physique Théorique des Liquides,† Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France (Received: December 9, 1991; In Final Form: February 24, 1992)

We study, by an adiabatic dynamical simulation technique, a mixed classical–quantum model for strongly H-bonded complexes in polar solvents. The solvent influence on the adiabatic proton dynamics is considered and its consequences on proton-transfer rate constant are discussed. In particular, we show that, for large enough coupling to the solvent, the system passes from a "vibrational" to a "reactive" behavior.

I. Introduction

Considerable attention has been paid in the past decades to the properties of H-bonded systems[1,2] and as well as to those of proton-transfer reactions in solution for which the characteristic features of the H-bond interaction play an important role.[3] In the past few years, there has been an increasing number of theoretical works on proton and hydrogen transfers in condensed phases from a molecular perspective. Microscopic formulations for computing the rate constant have been developed for this purpose.[4-6] The most advanced application is the study of hydrogen diffusion in bulk metal[7] and on metal surfaces.[8] Most theoretical[6,9] and simulation[10] works on proton-transfer reactions in solution have been focused on the nonadiabatic limit in which the reactive process is dominated by the tunneling of the proton. This limit applies to molecules and complexes in which the H-bond interaction between donor and acceptor atoms is relatively weak and for which there is a substantial potential energy barrier along the proton coordinate.

An interesting case which has not yet been studied at a molecular dynamics level is that of strongly H-bonded complexes in solution. For these complexes, the barrier in the proton potential may be small or even absent. In many cases, the vibrational energy

levels of the proton are well separated and the proton transfer can be considered as being in the adiabatic limit.

In this Letter, we present the preliminary results of an adiabatic dynamical simulation of a mixed quantum–classical system modeling a strongly H-bonded complex in a polar solvent. We focus on the influence of the solvent on the proton dynamics and do not treat the influence of the low-frequency vibrational modes of the complex which may be coupled to the proton. The solvent

(1) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond: Recent Developments in Theory and Experiments;* North Holland: Amsterdam, 1976.

(2) Bratos, S.; Ratajczak, H.; Viot, P. In *Hydrogen-Bonded Liquids;* Dore, J. C., Texeira, J., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1991.

(3) Bell, R. P. *The Proton in Chemistry;* Chapman and Hall: London, 1973. Caldin, E. F.; Gold, D. *Proton Transfer Reactions;* Chapman and Hall: London, 1975.

(4) Gillan, M. *J. Phys. C* **1987,** *20,* 3621.

(5) Voth, G. A.; Chandler, D.; Miller, W. H. *J. Phys. Chem.* **1989,** *93,* 7009; *J. Chem. Phys.* **1989,** *91,* 7749.

(6) Borgis, D.; Lee, S.; Hynes, J. T. *Chem. Phys. Lett.* **1989,** *162,* 19.

(7) Gillan, M. *Phys. Rev. Lett.* **1987,** *58,* 563.

(8) Haug, K.; Wahnström, G.; Metiu, H. *J. Chem. Phys.* **1990,** *92,* 2083.

(9) Cukier, R. I.; Morrillo, M. *J. Chem. Phys.* **1989,** *91,* 857.

(10) Borgis, D.; Hynes, J. T. *J. Chim. Phys. (Paris)* **1990,** *87,* 819; *J. Chem. Phys.* **1991,** *94,* 3619.