

LETTER | NOVEMBER 01 1992

Surface plasmon enhanced photochemistry: $\text{Mo}(\text{CO})_6$ -Al-quartz

M. Wolf; X.-Y. Zhu; J. M. White; T. H. Koschmieder; J. C. Thompson



J. Chem. Phys. 97, 7015–7016 (1992)

<https://doi.org/10.1063/1.463211>



View
Online



Export
Citation

CrossMark



The Journal of Chemical Physics

Special Topic: Algorithms and Software for Open Quantum System Dynamics

Submit Today

Surface plasmon enhanced photochemistry: Mo(CO)₆-Al-quartz

M. Wolf, X.-Y. Zhu, and J. M. White

Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712

T. H. Koschmieder and J. C. Thompson

Department of Physics, University of Texas, Austin, Texas 78712

(Received 15 May 1992; accepted 16 July 1992)

Electrons at a metal boundary can oscillate collectively (surface plasmons) and produce mixed transverse and longitudinal electromagnetic (EM) fields which decay exponentially normal to the surface.¹ Surface EM field enhancement due to resonant excitation of surface plasmon modes has been found to be important in surface enhanced Raman scattering (SERS).² Model calculations predict similar enhancements in the photochemistry of adsorbates.³ While surface photochemistry has attracted considerable interest in the last few years, direct experimental evidence for surface plasmon induced processes leading to bond cleavage is quite rare.⁴ Recent studies have shown that desorption of metal atoms can be stimulated by excitation of collective oscillations in small metal clusters⁵ and smooth metal films.⁶ The detailed mechanism, however, is still under discussion.⁷

We report here the enhanced photodissociation ($h\nu = 3.5$ eV) of Mo(CO)₆ adsorbed on thin Al films under resonant surface plasmon (SP) excitation. Using *p*-polarized light, resonant excitation can be achieved by scanning the angle of incidence in Kretschmann's configuration for attenuated-total-reflection (ATR).⁸ The photodissociation of Mo(CO)₆, adsorbed on various substrates, closely resembles the optical absorption spectrum of the free molecule, supporting the dominance of a *direct excitation* mechanism.⁹ Consistent with this we find that direct excitation is responsible for photon-driven Mo(CO)₆ dissociation in the absence of Al. Thus, we expect the strong evanescent surface plasmon fields at the Al-adsorbate interface to enhance the photolysis of weakly held Mo(CO)₆. To study these enhancement effects we chose an excitation wavelength (351 nm) close to the 360 nm cutoff of the optical absorption spectrum of Mo(CO)₆.¹⁰

The experiments were performed in a UHV chamber (2×10^{-10} Torr) with a 10×10 mm rectangular quartz prism, which could be cooled with liquid nitrogen to 120 K and heated via IR irradiation to ~ 550 K.¹¹ The Al films were freshly evaporated in UHV at room temperature; the thickness was determined by a quartz crystal microbalance. Under these conditions, a continuous film with a roughness (surface height variance) of a few nm will be formed.¹² With the sample at 120 K, Mo(CO)₆ was dosed through a tube, which faced the front surface (film side) of the prism at a distance of ~ 3 mm (3L dose in all experiments; estimated coverage 2 ML). The prism was irradiated through its hypotenuse with polarized light of an excimer laser ($h\nu = 3.5$ eV, pulse energy 1.7 mJ/cm², spot diameter 4 mm) [see Fig. 1(a)]. The incident angle (azi-

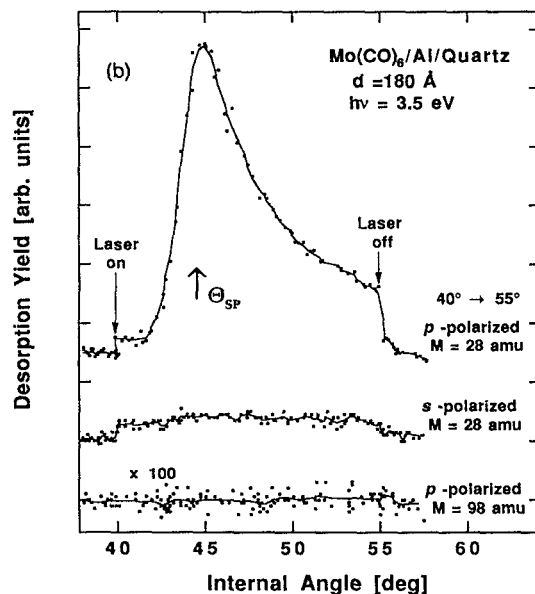
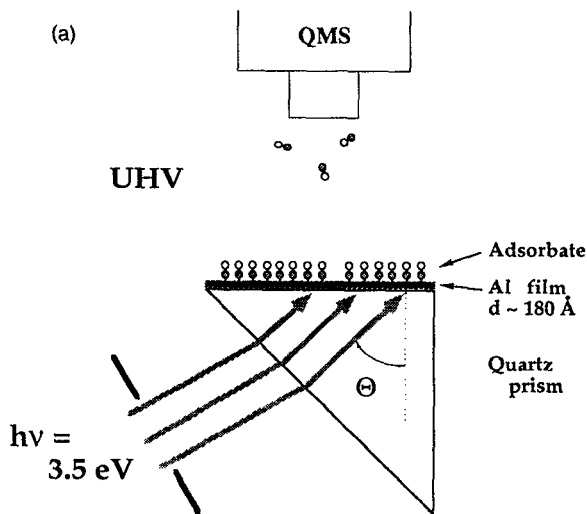


FIG. 1. (a) Schematic illustration of the experimental configuration: Mo(CO)₆ is adsorbed on a quartz prism covered with a 180 Å Al-film. The light enters through the prism hypotenuse at the internal angle θ . The desorption yield is monitored with a quadrupole mass spectrometer (QMS). (b) Top traces: CO desorption yield (28 amu) during photolysis of Mo(CO)₆ at 351 nm as a function of the internal angle θ for *p*- and *s*-polarization, respectively. Bottom trace: Mo(CO)₆ cracking signal at 98 amu ($\times 100$ sensitivity) during photolysis.

mouth of the prism) was recorded and converted to the internal angle Θ . A quadrupole mass spectrometer (QMS) was used for time-of-flight (TOF) mass spectroscopy and to monitor the yield of desorption products during irradiation (integrated TOF spectra).

Surface plasmons can be excited with p -polarized, but not s -polarized, light. We have, therefore, measured the CO desorption yield from $\text{Mo}(\text{CO})_6$ preadsorbed on a 180 Å Al film as a function of the internal angle [Fig. 1(b), top traces]. For p polarization, starting from a low level at 40° the CO signal rises sharply at the critical angle ($\Theta_c = 42.6^\circ$) and peaks at 45°. ¹³ The results are independent of the scanning direction. Comparing the signal below Θ_c with its peak value, an *enhancement ratio of 32* is obtained. During these measurements, the total coverage was depleted by less than 10%. For s polarization, however, the CO signal stays nearly constant (middle trace). The observed peak in the CO yield for p polarization must therefore result from surface plasmon excitation.

At the surface plasmon resonance the absorbance in the Al film is close to unity and might lead to thermal desorption. Figure 1(b) (bottom trace) shows that there is no thermal desorption of the parent molecule [no fragmentation signal of $\text{Mo}(\text{CO})_6$ at 98 amu in the QMS ionizer]. This proves that the observed CO originates from the dissociation of adsorbed $\text{Mo}(\text{CO})_6$. From TOF measurements (not shown), we obtain the same mean translational energy $\langle E_{\text{trans}} \rangle / 2k = 100 \pm 20$ K for CO desorption from both $\text{Mo}(\text{CO})_6$ -Al-quartz and $\text{Mo}(\text{CO})_6$ -quartz, i.e., thermal accommodation is realized. This is consistent with studies of the gas phase dynamics which show that photodissociation occurs through an excited state whose average lifetime is long compared to that required for intramolecular vibrational energy transfer. ¹⁴

The results suggest that the photolysis of $\text{Mo}(\text{CO})_6$ on Al under resonant surface plasmon excitation is driven by direct excitation. The enhancement effect can simply be explained by the EM field enhancement at the SP resonance. The calculated electromagnetic field strength at the vacuum interface of a perfectly smooth 180 Å Al film on quartz peaks at $\Theta = 44.3^\circ$; the enhancement ratio of ~ 70 is twice that of the experimentally observed enhancement in CO yield. The corresponding ratio of the optical absorbance in the Al film of ~ 8 cannot account for the observed enhancement. However, above Θ_{SP} , the measured CO yield falls off slower than the calculated EM field, assuming a

perfect film. An effective dielectric constant for the adsorbate layer will account for some, but not all, of the discrepancy. For the most part, the slower falloff can be accounted for in terms of surface roughness, which enhances photon-SP coupling. Roughness has been shown to broaden and shift the SP resonance by several degrees to higher internal angles. ¹⁵

In summary, we have demonstrated that surface plasmon oscillations, excited at an adsorbate covered metal-vacuum interface, can effectively couple to the electronic system of an adsorbed molecule. For p -polarized light incident at the surface plasmon resonant angle in an ATR configuration, we observe a strong enhancement ($32\times$) of the photodissociation rate of $\text{Mo}(\text{CO})_6$ adsorbed on a thin Al film. This is attributed to a direct excitation by the enhanced evanescent electromagnetic fields.

This work was supported by National Science Foundation Grant No. CHE-90-15600 and by the Robert A. Welch Foundation. M.W. acknowledges a Feodor-Lynen research fellowship of the Alexander-von-Humboldt Society.

¹H. Raether, in *Surface Plasmons* (Springer, Berlin, 1988).

²*Surface Enhanced Raman Scattering*, edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982); M. Moskovits, *Rev. Mod. Phys.* **57**, 783 (1985).

³P. C. Das, A. Puri, and T. F. George, *J. Chem. Phys.* **93**, 9106 (1990); A. Nitzan and L. E. Bruns, *ibid.* **75**, 2205 (1981).

⁴X.-L. Zhou, X.-Y. Zhu, and J. M. White, *Surf. Sci. Rep.* **13**, 73 (1991).

⁵W. Hoheisel, U. Schulte, M. Vollmer, and F. Träger, *Appl. Phys. A* **51**, 271 (1990).

⁶E. T. Arakawa, I. Lee, and T. A. Callcott, in *Springer Lecture Notes in Physics*, edited by J. C. Miller and R. F. Huglund, Jr. (Springer, Berlin, 1991), Vol. 389.

⁷W. Hoheisel, T. Götz, M. Vollmer, and F. Träger, in *Desorption Induced by Electronic Transition, DIET V*, edited by E. B. Stechel, A. R. Burns, and D. R. Jennison (Springer, Berlin, in press).

⁸E. Kretschmann, *Z. Phys.* **241**, 313 (1971).

⁹W. Ho, in *Desorption Induced by Electronic Transition, DIET IV*, edited by G. Betz and P. Varga (Springer, Berlin, 1990).

¹⁰D. S. Alderdice, *J. Mol. Spectrosc.* **15**, 509 (1965).

¹¹M. Wolf, X.-Y. Zhu, and J. M. White, *Chem. Phys. Lett.* (submitted).

¹²L. L. Levenson, A. Yahashi, H. Usui, and I. Yamada, *Thin Solid Films* **193-194**, 951 (1990); I. J. M. M. Raaymakers and M. J. Verkerk, *Appl. Opt.* **25**, 3610 (1986).

¹³For oxidized Al films in air ($\lambda = 541$ nm) an ATR minimum at 44.7° was observed.

¹⁴S. A. Buntin, R. R. Cavanagh, L. J. Richter, and D. S. King, *J. Chem. Phys.* **94**, 7937 (1991).

¹⁵D. Hornauer, H. Kapitza, and H. Raether, *J. Phys. D* **1**, L100 (1974); R. Orłowski and H. Raether, *Surf. Sci.* **54**, 303 (1976).