Gas-Phase Photoemission Study of 2-Mercaptobenzothiazole

G. Contini*

C.N.R., Institute of Mineral Processing, Via Bolognola 7, 00138 Roma, Italy

V. Di Castro

Dipartimento di Chimica, ed INFM, Università di Roma "La Sapienza", P.le Aldo Moro 5, 00185 Roma, Italy

S. Stranges

Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro 5, 00185, Roma, Italy, and TASC-INFM, Area Science Park, 34012 Basovizza, Trieste, Italy

R. Richter

Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy

M. Alagia

TASC-INFM, Area Science Park, 34012 Basovizza, Trieste, Italy

Received: September 6, 2001; In Final Form: January 15, 2002

2-Mercaptobenzothiazole ($C_7H_5NS_2$) has been investigated by synchrotron radiation photoelectron spectroscopy (PES) in the gas phase. The valence region, C 1s and S 2p photoemission spectra have been measured. Comparison of the experimental results with theoretical ab initio calculations, performed for two possible tautomeric forms of the molecule, shows that only the thione form is present in the gas phase. Vibrational structure has been clearly observed in the valence photoemission spectra. In the C 1s spectrum the seven components due to the inequivalent carbon atoms in the molecule have been assigned on the basis of ab initio calculations. S 2p components have also been assigned. The photoemission results have been compared with previously reported photoemission measurements for 2-mercaptobenzoxazole.

Introduction

The adsorption of 2-mercaptobenzothiazole (in the following MBT) on metals and metal sulfides has been widely investigated[1−4] because this compound forms hydrophobic complexes with many metals and therefore is used as a corrosion inhibitor or collector for mineral flotation. Moreover, this molecule is interesting for the formation of self-assembled monolayers on metals[5−7] due to the growing interest in these interfacial structures based upon the spontaneous adsorption and orientation of molecules with a reactive group which binds chemically to the substrate and an organic part which interacts with the other molecules.

A prerequisite for better understanding the interaction and bond formation between the adsorbed molecules and the substrate is the detailed knowledge of the electronic structure of the free molecule, thus it is crucially important to identify and study the species in the vapor phase, this being the entity interacting with the substrate. Moreover, in the case of MBT two tautomeric forms may exist in the vapor phase: the thione (NH) and the thiol (SH) forms, the former with a C═S double bond and the latter having the endocyclic double bond C═N and the hydrogen atom bonded to the sulfur atom instead of the nitrogen (see Figure 1). The electronic structure of the free molecule is sensitive to the difference in the chemical structure and allows differentiation between the two tautomers.

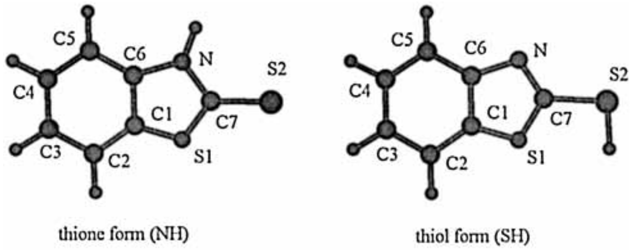

Figure 1. 2-Mercaptobenzothiazole (MBT) tautomers: thione form (NH) (left) and thiol form (SH) (right). The numbering of the carbon and sulfur atoms is used in the text.

In this paper we report results of the first gas-phase photoelectron investigation of MBT vapor. Valence photoelectron spectra obtained at different photon energies are presented and the assignment of the observed features is given on the basis of ab initio calculations. C 1s and S 2p photoelectron spectra are reported and discussed in comparison with previously reported data on 2-mercaptobenzoxazole (C_7H_5NOS, in the following MBO), a similar molecule with an oxygen instead of the endocyclic sulfur.[8]

Experimental Section

The experiment was carried out using the ARPES end-station of the Gas-Phase beamline at Elettra. Details of the beamline and the experimental station have been given elsewhere.[9]

---

* Corresponding author. Fax: +39 068804463. E-mail: continig@iasi.rm.cnr.it.

10.1021/jp013423b CCC: $22.00

Photoelectron spectra were recorded using a hemispherical photoelectron energy analyzer (VSW, 50 mm mean radius) operating in the constant pass energy mode. In this mode, the electrons are decelerated to a constant kinetic energy in the analyzer, which in turn gives a constant energy resolution. The position of the spectrometer with respect to the polarization vector of the synchrotron radiation could be rotated under vacuum and was kept at the "magic angle" (54.7°) throughout the experiment. The kinetic energy scale of the analyzer was calibrated by introducing suitable gases (Ar, SF_6) into the ionization region together with the sample and recording a photoelectron spectrum at the same photon energy. MBT (Aldrich Chemical Co., Inc.), purified by repeated sublimation cycles before use, was introduced into the ionization region by vaporizing the solid sample under vacuum. The temperature of the oven during the vaporization was kept constant at 90 °C. To ascertain that at the temperature used no molecule decomposition occurs, infrared spectroscopy measurements on sublimated MBT were carried out, showing no modification upon sublimation. Mass spectra showed no peaks with masses higher than the molecular one. To prevent contamination of the analyzer, the lenses were heated and the interaction region was surrounded by a liquid nitrogen shield.

The ground-state equilibrium geometry and the total energy of the neutral MBT tautomers, the thione (NH) and the thiol (SH) forms (see Figure 1), were computed by ab initio full-electron calculations at the MP2 level (Möller−Plesset second-order perturbation theory) with a 6-31G* basis set using the Gaussian 94 program.[10] The SCF eigenvectors and eigenvalues were also obtained for both molecules at the equilibrium geometry.

The Levenburg−Marquardt nonlinear minimization algorithm with nonapproximated Voigt functions was used in the fit of both valence and C 1s PE spectra. The two valence spectra recorded at different photon energies were fitted simultaneously using the following procedure. For each valence PE spectrum five sum functions were used to fit the five peaks. The Voigt width parameters (Gaussian and Lorentzian) and the energy separations between the Voigt components (vibrational progression) were used as unconstrained fitting parameters. The Voigt width parameters were assumed equal for all components of each sum function. The amplitudes of each Voigt peak and the ionization energy (IE) of the first Voigt component of the sum function were left free to change. For the two valence spectra recorded at a different photon energy (fitted at the same time), only the total amplitude of each of the five sum functions was allowed to change.

Results and Discussion

Valence Photoelectron (PE) Spectrum. The experimental valence PE spectrum of MBT vapor recorded at 21.8 and 35.0 eV photon energy is reported in Figure 2, together with the calculated vertical ionization energies ($-\epsilon_{MO}$) for the outermost occupied molecular orbitals of both MBT tautomers (crosses). These values, according to Koopmans' theorem[11] and its use in the case of the ionization of closed shell systems,[12] are derived as the negatives of the molecular orbitals eigenvalues of the HF−SCF eigenvectors obtained for the neutral molecule at the equilibrium geometry. The energy scale was calibrated against the argon $3p_{3/2}$ ionization peak at 15.759 eV.[13] The spectrum shows five resolved photoelectron bands at 7.91 (highest occupied molecular orbital, HOMO), 8.28, 9.07, 9.94, and 11.01 eV, which have been recorded at 60 meV energy resolution at both photon energies and in the spectrum measured at 35.0 eV photon energy a group of unresolved bands at IE higher than 11 eV, recorded at lower energy resolution (100 meV).

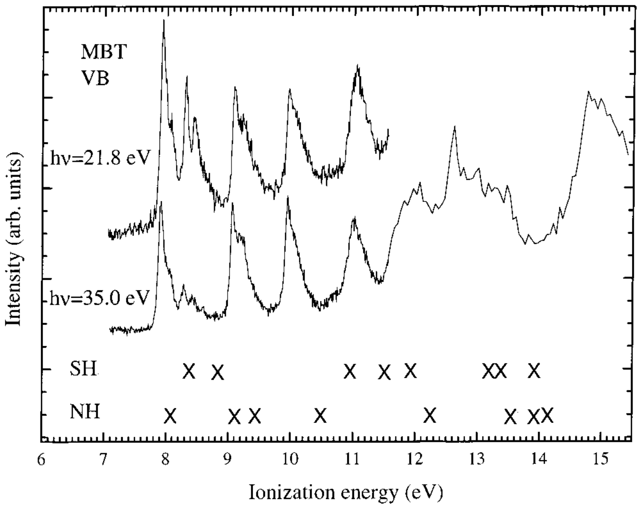

Figure 2. Valence PE spectrum of MBT vapor obtained at 21.8 and 35.0 eV photon energy. The calculated orbital energies for the outermost MOs of both thione (NH) and thiol (SH) tautomers are reported in the bottom part as crosses.

TABLE 1: MBT Valence Photoemission Ionization Energies (IE)[a]

MO (NH)	$-\epsilon_{MO}$ (NH) (eV)	MO (SH)	$-\epsilon_{MO}$ (SH) (eV)	exp. IE (eV)	exp. relative intensity	exp. area ratio at $h\nu = 35.0$ eV vs $h\nu = 21.8$ eV
8a″	8.04	8a″	8.33	7.91 (v)	100	0.63
				8.05	46	
				8.18	9	
35a′	9.07	7a″	8.79	8.28 (v)	100	0.27
				8.42	79	
				8.57	35	
				8.72	10	
7a″	9.42	6a″	10.96	9.07 (v)	100	1.00
				9.19	73	
				9.32	41	
				9.44	17	
				9.57	3	
6a″	10.50	5a″	11.47	9.94 (v)	100	1.08
				10.05	63	
				10.16	35	
				10.27	15	
				10.38	1	
5a″	12.23	35a′	11.91	10.90 (a)	52	0.89
				11.01 (v)	100	
				11.12	62	
				11.23	35	
				11.34	20	
34a′	13.50	34a′	13.19			
4a″	13.88	4a″	13.35			
33a′	14.10	33a′	13.91			

[a] Theoretical IE values in eV obtained by MP2/6-31G* for vertical transitions ($-\epsilon_{MO}$) with the number and symmetry of the corresponding molecular orbital (MO) are reported for NH and SH tautomers, together with the experimental IE values in eV and the relative intensity of the vibrational components (a and v in brackets mean adiabatic and vertical, respectively). The area ratio between the experimental peaks recorded at $h\nu = 35.0$ eV and those recorded at $h\nu = 21.8$ eV are also reported.

Comparison of the experimental PE spectrum with the theoretical ionization energies (Figure 2 and Table 1) of the two tautomers shows better agreement of the experimental data with the thione form (NH) than with the thiol form. In fact the first five experimental photoemission peaks are almost evenly distributed in energy as expected for the thione form, while for the thiol (SH) form two groups of photoemission bands

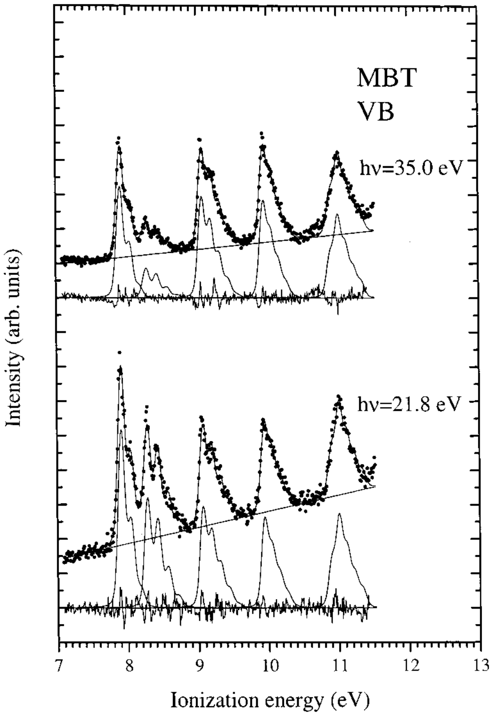

Figure 3. Outer-valence PE spectrum of MBT vapor obtained at 21.8 and 35.0 eV photon energy. The experimental curves (points) are shown together with the best fit (see text for details). The residual between the experimental data and the fit is shown below each spectrum.

separated by an energy gap are predicted. Further information can be obtained comparing the relative intensities of the photoemission peaks at 21.8 and 35.0 eV. As can be clearly observed, there is a strong decrease of the relative intensity of the photoionization cross sections of the first and second band in changing the photon energy from 21.8 to 35.0 eV (the intensity ratios of the first five bands measured at 35.0 and 21.8 eV are reported in Table 1). The photoionization cross section of the S 3p atomic orbitals is expected to have a Cooper minimum[14] at about 35 eV and it decreases from 4.37 to 0.52 Mb on going from 21.2 to 35.0 eV photon energy.[15] All other valence atomic orbital cross sections, C (2s, 2p), O (2s, 2p), and N (2s, 2p), decrease monotonically as the photon energy increases. The first and the second occupied MOs of the thione form have a large contribution of the S 3p atomic orbitals (34.2 and 54.3%, respectively), with respect to the third MO (14.1%). In the case of thiol form (SH) the largest S 3p atomic orbital contributions are found in the third and forth MOs (47.0 and 42.8%, respectively) while the S 3p atomic orbital contributions in the first and second MOs are 13.7 and 21.3%, respectively. Therefore, the observed strong decrease in relative intensity of the first and second PE bands, intensity ratios 0.63 and 0.27, respectively (see Table 1) is indicative of the presence of the thione tautomer in the vapor phase. This result is also consistent with the C 1s and the S 2p spectra discussed below.

A previous photoemission study has shown that the analogous MBO molecule in the gas phase is also present only in the thione form.[8] In both cases the calculated MP2 energy of the thione ground-state neutral molecule is lower than the one obtained for the thiol form. The difference in energy is 1.32 hartree for MBO and 1.24 hartree for MBT.

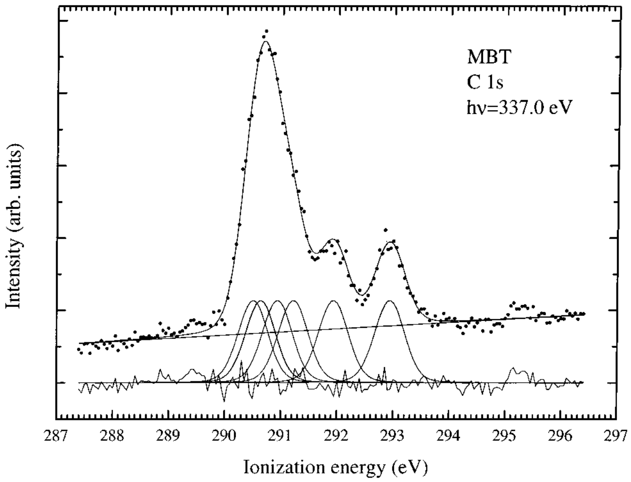

Figure 4. Carbon 1s PE spectrum of MBT vapor obtained at 337.0 eV photon energy. The experimental spectrum (points) is shown together with the best fit obtained using seven Voigt functions (see text for details). The residual between the experimental data and the fit is also reported. It should be noted that two of the Voigt functions obtained by the fit present very close ionization energy values (290.63 and 290.64 eV).

To investigate the vibrational structure of the valence spectrum we have fitted the experimental peaks considering only one vibrational progression and using the procedure described in the experimental section. The results are shown in Figure 3 and reported in Table 1. The fit of the HOMO peak has been obtained using a sum of three Voigt components, whereas four components have been used for the second peak and five for the third, fourth, and fifth bands. The vibrational energy separations obtained by the fit are 0.136 eV (1097 cm^{-1}) for the first peak (HOMO), 0.146 eV (1177 cm^{-1}) for the second peak, 0.125 eV (1008 cm^{-1}) for the third peak, 0.109 eV (879 cm^{-1}) for the fourth peak, and 0.110 eV (887 cm^{-1}) for the fifth peak. These values are systematically lower (0.11−0.14 eV) than the ones measured for the MBO molecule,[8] according to the substitution of the oxygen atom with the heavier sulfur atom. Because of the large number of delocalized vibrational modes it does not seem possible to give even a tentative assignment for the vibrational progression of the PE bands using the simple approach; a calculation is needed to give an exact attribution.

C 1s PE Spectrum. The experimental C 1s spectrum obtained at 337.0 eV photon energy is reported in Figure 4 together with the best fit of the data. The experimental spectrum shows three main peaks with an intensity ratio 5:1:1. These signals, which are due to the ionization of the seven inequivalent carbon atoms of the molecule, have been fitted using seven Voigt functions whose ionization energies, width, and amplitude were considered free parameters, but the width and amplitude assumed equal for all components. The sum of the seven Voigt functions is in good agreement with the experimental data, confirming the presence of only one tautomeric form of MBT in the gas phase (it should be noted that two of Voigt functions obtained by the fit present very close ionization energy values at 290.63 and 290.64 eV). The ionization energies of the seven components are reported in Table 2 and compared with the values obtained by ΔSCF[16] and by HF ab initio calculations. The experimental data are in good agreement with the ΔSCF theoretical results both for IE values (0.2−0.5% error) and energy distribution. Therefore, it is possible to derive a reliable attribution of the seven components. The carbon atoms in the benzene ring not bonded to the heteroatoms (C_2, C_3, C_4, C_5) show ionization energies close to each other and in good agreement with the value measured for the carbon atoms in benzene (290.42 eV).[17] Larger shifts are expected for the carbons bound to the heteroatoms. The peaks at highest energies can be attributed to

TABLE 2: C 1s Experimental and Theoretical Ionization Energies (IE) Are Reported in eV. The Theoretical IE Have Been Calculated for the Thione Form by ΔSCF[16] and HF MP2/6-31G*. The Energy Shift Relative to the Lowest Value Is Shown in Parentheses[a]

	exp. IE (fit results)	theor. IE (ΔSCF)	theor. IE (HF MP2/6-31G)
C_1	291.22 (0.71)	291.85 (0.72)	307.33 (0.99)
C_2	290.94 (0.43)	291.45 (0.32)	306.72 (0.38)
C_3	290.51 (0.00)	291.13 (0.00)	306.34 (0.00)
C_4	290.63 (0.12)	291.33 (0.20)	306.53 (0.19)
C_5	290.64 (0.13)	291.38 (0.25)	306.61 (0.27)
C_6	291.93 (1.42)	292.81 (1.68)	307.95 (1.61)
C_7	292.93 (2.42)	294.38 (3.25)	309.82 (3.48)

[a] For the numbering of the seven carbon atoms see Figure 1.

the carbon atoms bound to the nitrogen atom, which is the most electronegative atom in the molecule. In particular, by comparison with the theoretical IE, the component at 292.93 eV can be correlated with the ionization of the C_7 carbon atom bonded to the sulfur and nitrogen heteroatoms, while the peak at 291.93 can be attributed to the C_6 atom of the benzene ring bound to the nitrogen atom. As regards the HF calculations, the IE values are systematically overestimated, as expected for Koopmans' approximation. Nevertheless the IE difference between the carbon components are in good agreement with the experimental data and the ΔSCF calculations.

It is interesting to compare the C 1s photoemission spectrum of MBT with that obtained for the similar MBO molecule,[8] where oxygen instead of sulfur is present in the pentatomic ring. The calculated and experimental IE of the carbon atoms (C_2, C_3, C_4, C_5) of the benzene ring unconnected to any substituent and the carbon atom (C_6) bonded to the nitrogen are only slightly affected by the substitution of the oxygen atom with a less electronegative sulfur atom, and show a maximum shift of 0.13 eV toward lower IE. The main effect is observed on the C_1 and C_7 atoms directly bound to the exchanged heteroatom. In these cases shifts of 1.10 eV for C_7 and 1.12 eV for C_1 toward lower IE are observed. By comparison of these two molecules, the strong electron attractive effect of the oxygen is highlighted, whereby the O atom withdraws electronic charge mainly from the nearest atoms, and to a lesser extent from the rest of the molecule.

S 2p PE Spectrum. The experimental S 2p PE spectrum of MBT taken using 190.0 eV photon energy is reported in Figure 5. The energy scale was calibrated against the S $2p_{3/2}$ signal of SF_6 at 180.27 eV.[18] The experimental spectrum displays four components at 167.6 eV, 168.8, 170.0, and 171.2 eV. The four features can be assigned to the photoionization of the two sulfur atoms split by spin−orbit interaction.

The lower IE doublet can be attributed to the photoionization of the exocyclic sulfur atom (S_2) by comparison with the MBO S 2p spectrum. In fact, in the MBO molecule there is only the exocyclic sulfur atom and in the S 2p spectrum two components have been observed at 167.7 and 168.9 eV. The features at 170.0 and 171.2 eV are therefore due to the photoionization of the sulfur atom in the pentatomic ring. This attribution is in agreement with the ΔSCF calculation which predict a shift of 2.8 eV toward higher energy for the 2p ionization energy of the endocyclic sulfur with respect to the exocyclic one.[16] The shift of 2.2 eV between the photoemission signals of the two sulfur atoms was also observed in the solid MBT molecule.[2,4] The experimental values of the S $2p_{1/2}$ signals of the two sulfur atoms in the molecule 168.9 and 171.1 eV can be compared with literature data on other sulfur-containing molecules in the gas phase: 171.0 eV in CS_2,[19] 171.56 eV in H_2S,[20] 171.92 eV in OCS,[21] 175.98 eV in SO_2,[22] and 181.48 eV in SF_6.[18] It can be observed that the exocyclic sulfur shows a very low ionization value indicative of a high electron density on this atom as already observed for MBO,[8] while the endocyclic sulfur has a ionization value similar to the one observed in CS_2 and H_2S indicative of an almost neutral sulfur atom.

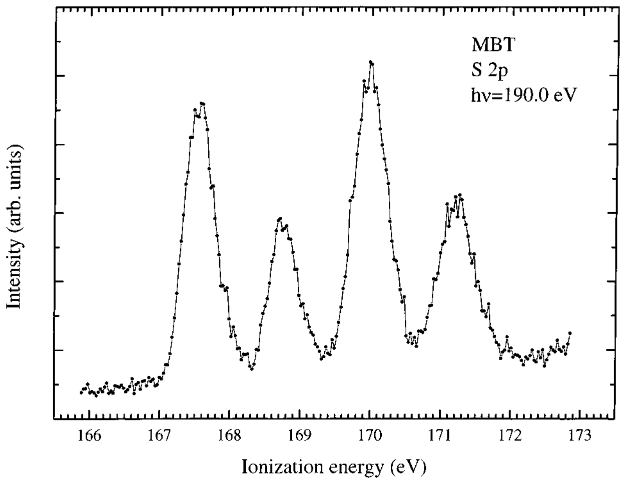

Figure 5. Sulfur 2p PE spectrum of MBT vapor obtained at 190.0 eV photon energy.

The four peaks in the S 2p spectrum show an asymmetric shape with a full width at half-maximum (fwhm) of 0.54 eV, that is much larger than the total instrumental broadening which is estimated to be less than 0.24 eV. A similar intrinsic peak broadening was observed also for MBO (fwhm = 0.59 eV) and ascribed to various effects, mainly the vibrational excitation, and the molecular field splitting. In MBT the molecular field splitting calculated by ΔSCF are 0.09 eV for S_1 (the endocyclic sulfur) and 0.12 eV for S_2 (the exocyclic sulfur)[16] and are smaller than that calculated for MBO (0.15 eV).[23] Unresolved vibrational excitations probably give the largest contribution to the broadening and asymmetry of the photoemission peaks as already suggested for the MBO molecule, and reported for small molecules.[19,21]

Conclusions

The synchrotron radiation photoelectron spectra of MBT vapor were measured for the first time and assigned on the basis of ab initio calculations. The valence photoemission spectrum was in agreement with the MO calculation for the thione form, both for the MO energies and the sulfur 3p contribution to the outermost orbitals. The vibrational structure clearly observed for the outermost valence bands was characterized in terms of a single progression. In the C 1s photoemission spectrum the components due to the seven inequivalent carbon atoms in the molecule were identified and attributed by comparison with ΔSCF ab initio calculations. Two sulfur components were clearly identified in the S 2p photoemission spectrum and have been ascribed to the two sulfur atoms in the molecule by comparison with the theoretical results and previous literature data.

Acknowledgment. Two of the authors (G.C. and V.D.C.) acknowledge the financial support by "Istituto Nazionale di Fisica della Materia, I.N.F.M." for the measurements at the ELETTRA laboratory. One of the author (G.C.) acknowledges financial support by "CINECA" (Bologna, Italy) for the calculations. The authors thank the ELETTRA staff.

References and Notes

(1) Contini, G.; Ciccioli, A.; Cozza, C.; Barbaro, M.; Marabini, A. M. *Int. J. Mineral. Process.* **1997**, *51*, 283.

(2) Szargan, R.; Uhlig, I.; Wittstock, G.; Rosbach, P. *Int. J. Mineral. Process.* **1997**, *51*, 151.

(3) Hallmeir, K. H.; Mayer, D.; Szargan, R. J. *Electron Spectrosc. Relat. Phenom.* **1998**, *96*, 245.

(4) Szargan, R.; Schaufus, A.; Rosbach, P. J. *Electron Spectrosc. Relat. Phenom.* **1999**, *100*, 357.

(5) Zerulla, D.; Uhlig, R.; Szargan, R.; Chasse, T. *Surf. Sci.* **1998**, *402−404*, 604.

(6) Whelan, C. M.; Smyth, M. R.; Barnes, C. J.; Brown, N. M. D.; Anderson, C. A. *Appl. Surf. Sci.* **1998**, *134*, 144.

(7) Whelan, C. M.; Smyth, M. R.; Barnes, C. J. *J. Electroanal. Chem.* **1998**, *441*, 109.

(8) Contini, G.; Di Castro, V.; Stranges, S.; Richter, R.; Alagia, M. *J. Phys. Chem. A* **2000**, *104*, 9675.

(9) Blyth, R. R.; Delaunay, R.; Zitnik, M.; Krempasky, J.; Krempaska, R.; Slezak, J.; Prince, K. C.; Richter, R.; Vondracek, M.; Camilloni, R.; Avaldi, L.; Coreno, M.; Stefani, G.; Furlani, C.; de Simone, M.; Stranges, S.; Adam, M. Y. *J. Electron Spectrosc. Relat. Phenom.* 1**999**, *101−103*, 959.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, V.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision C.3; Gaussian, Inc., Pittsburgh, PA, 1995.

(11) Koopmans, T. A. *Physica* **1933**, *1*, 104.

(12) Richards, W. G. *Int. J. Mass. Spectrom. Ion Phys. (Proc.)* **1969**, *2*, 419.

(13) Lloyd, D. R. *J. Phys. E, Sci. Instrum.* **1970**, *3*, 629.

(14) Cooper, J. W. *Phys. Rev.* **1962**, *128*, 681.

(15) Yeh, J. J. Atomic calculation of photoionisation cross-sections and asimmetry parameters; Gordon and Breach Science Publisher: Langhorne, 1993.

(16) Contini, G.; Carravetta, V.; Di Castro, V.; Stranges, S.; Richter, R.; Alagia, M. *J. Phys. Chem. A* **2001**, *105*, 7308.

(17) Thomas, T. D.; Shaw, R. W. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *5*, 1081.

(18) Hudson, E.; Shirley, V.; Domke, M.; Remmers, G.; Puschmann, A.; Mandel, T.; Xue, C. *Phys. Rev. A* **1993**, *47*, 361.

(19) Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Wermer, L. O.; Manne, R.; Bear, Y. *Esca Applied to Free Molecules*, 2nd ed; North-Holland Publishing Company: Amsterdam, 1971.

(20) Hudson, E.; Shirley, D. A.; Domke, M.; Remmers, G.; Kaindl, G. *Phys. Rev. A* **1994**, *49*, 161.

(21) Brems, V.; Nestmann, B. M.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1998**, *287*, 255.

(22) Gedat, E.; Puttner, R.; Domke, M.; Kaindl, G. *J. Chem. Phys.* **1998**, *109*, 4471.

(23) Carravetta, V.; Contini, G.; Plashkevych, O.; Agren, H.; Polzonetti, G. *J. Chem. Phys. A* **1999** *103*, 4641.