Improved microwave-discharge source for uv photoemission

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A microwave-discharge uv light source has been improved to yield significant photon fluxes at 26.9 and 40.81 eV. In order to optimize the 26.9-eV (NeII) and 40.81-eV (HeII) radiation, the discharge was operated at ~2.5 Pa (0.019 Torr) in an external constant magnetic field of ~0.070 T (700 G), which, together with the oscillating electric field of the cavity, produces electron cyclotron resonance. When the discharge conditions were optimized for production of 40.81-eV photons, features near the Fermi energy in the photoemission distribution from W(100) for 40.81-eV photons are approximately 6% as intense as the corresponding features in the distribution for 21.22-eV photons. We estimate that under these conditions the flux of 40.81-eV photons is roughly 50% of the flux of 21.22-eV photons. Photoemission energy distributions with $h\nu = 16.85$, 21.22, 26.9, and 40.81 eV have been measured for saturated exposures of CO on W(100) at a temperature of ~80 K. The variation in these data with photon energy is important for making orbital assignments to the energy levels of adsorbed molecular CO.

I. INTRODUCTION

It has been demonstrated by many groups working in ultraviolet photoemission spectroscopy (UPS) that the capability of varying the photon energy is important for making orbital assignments to energy states of gas phase molecules,[1] bulk solids,[2] and surface complexes,[3] as well as for distinguishing direct and nondirect transitions in solids.[4] Much of the early UPS work was done at photon energies less than ~11.6 eV, a limit imposed by the transmission edge of LiF windows.[5] The energy range was greatly extended with the increased use of synchrotron radiation which provides a continuous spectrum of photons into the x-ray region[6] and, alternatively, with the development of windowless spectrometers[7] operating in conjunction with rare gas resonance line sources.[5] The two types of these line sources most widely used for UPS have been the dc cold-cathode discharge[5] and the Evenson cavity microwave discharge.[8] In this paper we describe the optimization of a microwave-discharge source for the production of several resonance lines of uv radiation up to 40.81 eV, the energy of HeII resonance radiation.

The microwave discharge has several attractive characteristics as a source of photons[8]: (1) Since there are no internal electrodes which can be sputtered, the source is less subject to damage and contamination, (2) it produces little electrical interference, and (3) the source can be constructed fairly inexpensively. Microwave discharges have been successfully operated as strong sources of photons with energies up to 21.22 eV (HeI radiation),[9,10] but the discharges become unstable and extinguish at the lower gas pressures (≤15 Pa or ~0.11 Torr) required for producing significant amounts of radiation from the decay of more highly ionized species such as HeII.[10] To overcome this problem, we use the effect of electron cyclotron resonance[11,12] to maintain stable lamp discharges at pressures as low as 2.5 Pa (0.019 Torr).

Most microwave-discharge sources used for UPS are similar to the design shown in Fig. 1.[8] Gas is passed through Vycor tubing of about 10 mm diam at a pressure of about 250 Pa (1.88 Torr) under typical operating conditions. 50–100 W of microwave power at 2.45 GHz are fed into a resonant cavity[8] external to the vacuum system, and a discharge is produced inside the tube yielding uv radiation.

In order to operate the discharge at low pressure, an external magnetic field is applied parallel to the axis of the tubing. The effect on the discharge is twofold. First, the electrons are constrained to spiral around the magnetic field lines between collisions and hence the diffusion loss to the walls of the capillary is reduced. Second, when the magnetic field B is tuned to the cyclotron resonance,[11,12] the electrons are accelerated to much higher energies between collisions than they would be at zero magnetic field, provided that the electron–atom collision frequency is small compared with the cyclotron frequency, i.e., that the gas pressure is low. The condition for resonance is satisfied when the microwave angular frequency is equal to the cyclotron frequency $\Omega\,[=(e/m)B$, where e/m is the charge-to-mass ratio of the electron]. Cyclotron resonance produces an enhancement in the rate of energy transfer from the electric field to the discharge and a consequent improvement in the stability of the discharge at low pressures.

II. EXPERIMENTAL DETAILS

The magnet is constructed of Armco iron. It has the shape shown in Fig. 1 with overall dimensions 14.3 cm

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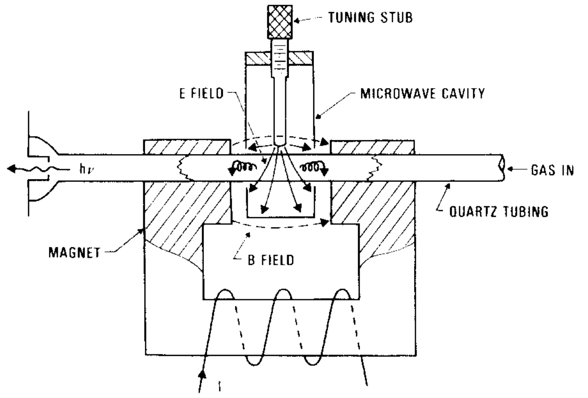

FIG. 1. Schematic of the discharge lamp. The edges of the visible glow shown by the jagged lines may extend about 20 cm along the tube.

long × 9.1 cm high × 3.1 cm wide and a square cross section 3.1 cm on a side. (The pole pieces have a slightly smaller cross section with dimensions 2.5 × 2.8 cm.) The windings consist of about 1550 turns of 17-gauge Formvar-coated Cu wire on a brass spool with dimensions 9.5 cm o.d., 3.8 cm i.d., and 7.6 cm long. 12-mm-wide slots in the pole faces allow the magnet to be raised into position around the tubing. Armco iron caps are then fitted into the slots to give a low reluctance around the magnetic circuit. With a microwave frequency of 2.45 GHz, the resonance condition requires that the magnetic field be approximately 0.087 T (870 G); however, the present magnet provides a rather inhomogeneous magnetic field. The power absorbed by the cavity is optimized when the field is about 0.065 T in the center of the gap and about 0.095 T close to the pole faces.

Only the component of the microwave electric field perpendicular to the magnetic field is effective in producing cyclotron resonance. Since the field configurations of both the cavity and the magnet are not well known, the optimum choice for the direction of the magnetic field was not clear. Figure 1 shows that the magnetic field is generally parallel to the Vycor tubing in the region of the discharge. This choice of geometry enables the electrons in the extremities of the discharge as well as those in the cavity itself to experience an appreciable magnetic field. In fact, however, the discharge was sustained at pressures as low as ~5 Pa (0.038 Torr) when the magnet was oriented perpendicular to the tubing.

The cavity and microwave generator are available commercially. In addition, we have incorporated a current regulating circuit discussed by Brandenberger,[13] which stabilizes the output power of the microwave generator.

III. LAMP PERFORMANCE

The spectral distribution of the uv radiation produced by the lamp was evaluated by measuring the photoelectron emission spectrum from a tungsten single crystal oriented in the (100) direction. The radiation passes through a series of 1.5-mm-diam capillaries into an uhv system and is incident on the tungsten sample at a polar angle of ~45°. The sample is located 38 cm from the center of the microwave cavity. The photoemitted electrons pass into a hemispherical retarding energy analyzer, which intercepts a cone of emission ±45° about the sample normal, and are then detected by a microchannel plate and fluorescent screen.[14] The electron energy analyzer effectively serves as a uv monochromator since it can measure and distinguish emission features near the Fermi cutoff for each of the various resonance lines in the source. Photoemission electron energy analysis has also been used in previous tests[15–17] on dc discharge uv sources to distinguish unambiguously the contributions from the various resonance lines in He. When the present source is operated with He gas, the only significant features in the emission spectrum are those due to the He I 21.22-eV line and the He II 40.81-eV line. The contributions from other principal lines in He are negligible, e.g., the features in the emission spectrum for 48.37-eV radiation are ≲10% as intense as the corresponding features for 40.81-eV radiation.

Figure 2 shows the variation of the W *d*-band photoemission signal measured ~2 eV below the Fermi level for He I and He II radiation. The data are normalized so that the signal is equal to unity under the high-pressure conditions ordinarily used for producing He I radiation. In the case of He I, one sees at first a decrease with pressure from 200 Pa (1.5 Torr) down to approximately 40 Pa (0.3 Torr). Then the cyclotron resonance effect takes hold and the photon flux increases. The final decrease in intensity with pressure is probably due to the decrease in the atom number density as well as the changing characteristics of the discharge. In this low pressure range, however, the signal from He II radiation increases to a maximum as the pressure decreases down to approximately 2.5 Pa (0.019 Torr). Below this pressure the discharge becomes unstable. At the He II maximum the intensity of the emission from the *d*-band feature for He II radiation is about 1/16 of that for He I and about 1/55 of that for He I at a lamp pressure of 250 Pa (1.88 Torr).

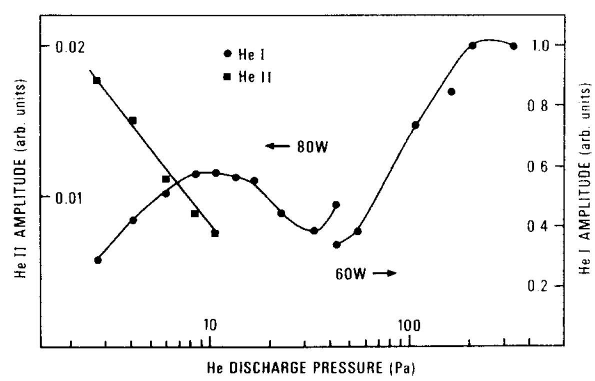

FIG. 2. He I and He II photon flux intensities monitored as the pressure in the lamp was reduced from 250 Pa (1.88 Torr) to 2.5 Pa (0.019 Torr). The break in the He I curve indicates where the microwave power was raised from 60 to 80 W.

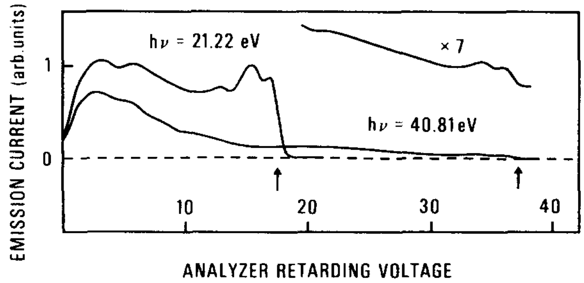

FIG. 3. HeI and HeII photoemission spectra at a lamp pressure of ~2.5 Pa (0.019 Torr). The arrows indicate the respective Fermi cutoffs.

By contrast, when the microwave discharge is operated with zero external magnetic field, the lowest attainable stable pressure is ~25 Pa (0.19 Torr). The ratio of HeII to HeI emission features measured at this pressure is only 1/200.

Figure 3 shows photoelectron energy spectra for HeI and HeII radiation produced at a source pressure of 2.5 Pa (0.019 Torr). In the energy range between the vacuum level and the Fermi cutoff for photoelectrons from HeI radiation, the measured spectrum is the sum of the HeI and HeII components shown in Fig. 3. The spectrum has been decomposed into its HeI and HeII contributions by normalizing a pure HeI emission spectrum to the HeI Fermi edge and *d*-band peak shown in Fig. 3. This pure HeI emission spectrum is generated at a pressure of ~250 Pa (1.88 Torr) where there is no HeII component.

We now calculate an order of magnitude estimate for the ratio of HeI to HeII photon fluxes under the optimum conditions discussed above. The area of each curve in Fig. 3 is proportional to the emission into the cone of the detector, which has a half-angle of 45°. If we assume that the detector collects the same fraction of the total emission from W(100) for both HeI and HeII radiation, the ratio of total HeI to HeII photoelectron currents, calculated from Fig. 3, is ~2 to 1. In order to achieve an estimate of the relative photon fluxes, we must know the quantum yield of emitted electrons per incident photon. Although there are no data on the quantum yield of clean W at 40.81 eV, data by Cairns and Samson[18] on 16 metals including untreated W show that the ratio of the HeII to HeI quantum yields for normally incident light is less than unity in every case. Furthermore, data by Waclawski and Hughey[19] on W which had been heated to 2400 K suggest that the quantum yield is maximum for a photon energy of approximately 21 eV. If we conservatively estimate that the quantum yield at 40.81 eV is approximately equal to that at 21.22 eV, we get the result that the ratio of HeI to HeII photon fluxes is about 2 to 1 which implies that the ratio of the optimum HeI flux at 250 Pa (1.88 Torr) to the optimum HeII flux at 2.5 Pa (0.019 Torr) is approximately 7 to 1. Since the optimum HeI flux striking the sample in our apparatus is about 3–5 $\times$ 10^{11} photons/sec,[14] we estimate to within an order of magnitude that the optimum HeII flux striking the sample is several times 10^{10} photons/sec.

When a discharge in Ne is used as a source of photons, the variation with pressure of the NeII flux is similar to that for HeII. The flux reaches a maximum at a pressure of ~2.5 Pa (0.019 Torr), and the ratio at this pressure of the W *d*-band photoemission signals measured at 2 eV below the Fermi level for NeI and NeII radiation is approximately 7 to 1.

Although this work describes a preliminary design of a cyclotron resonance microwave source, our estimate of 2:1 for the HeI to HeII photon flux ratio compares favorably with results for dc cold cathode discharges.[15–17] Unfortunately, Refs. 15–17 do not give values for the HeII photon flux with which our order of magnitude estimate of several times 10^{10} photons/sec may be compared. It may be possible that decreasing the diameter of the tubing or increasing the region of homogeneity of the magnetic field will improve the lamp performance considerably.

IV. RESULTS

The light source has been used to study the photoemission spectra for saturated adsorption of CO on W(100) at 80 K, conditions under which the virgin state of adsorbed CO is populated.[20] Figure 4 gives the results for photon energies of 16.85, 21.22, 26.9, and 40.81 eV. Each curve is a difference curve, i.e., the spectrum for clean W(100) has been subtracted from the spectrum taken after saturation exposure of CO. The data span an energy range from +1

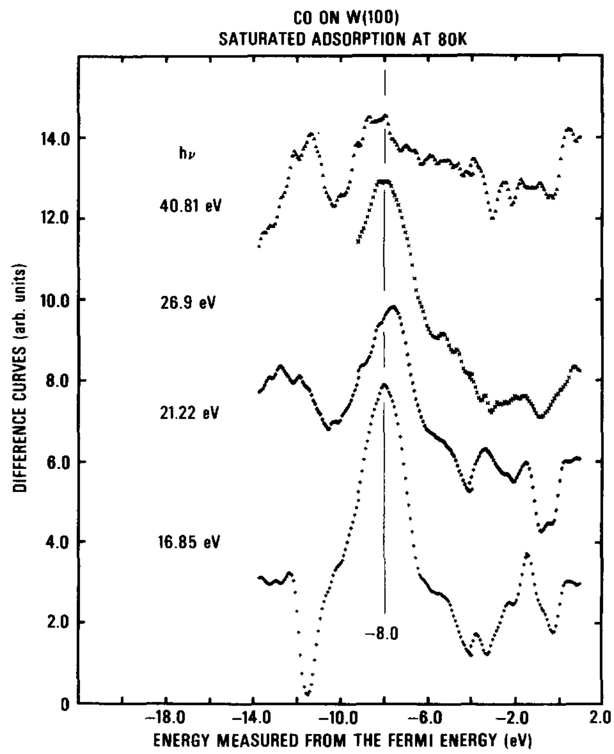

FIG. 4. Difference curves at four photon energies for saturated adsorption of CO on W(100) at 80 K. (For $h\nu$ = 40.81 eV, adsorption took place over a range of temperature between 145 and 85 K.) The curves are normalized so that the emission from the *d*-band peak between 2 and 3 eV below the Fermi level for the clean surface is given a value of 5 (arbitrary units).

eV with respect to the Fermi level to about −14 eV. Previous data by Baker and Eastman[21] and Plummer *et al.*[14] for this system at ~300 K with $h\nu = 21.22$ eV have shown that the presence of β-CO on W(100) yields a peak in the difference curve at ~−5.6 eV and the presence of α-CO yields a peak at ~−8.7 eV. The results for adsorption at 80 K with $h\nu = 21.22$ eV are similar except that the peak at −8.7 eV is shifted upward in energy to −7.7 eV indicating adsorption of virgin CO. In addition, the HeI data show a small peak at −11.4 eV, which is much stronger for HeII radiation. Additional data do not reveal any other levels down to ~17 eV below the Fermi energy. This two-level structure and the $h\nu$ dependence of the lower-lying level[1,3] are consistent with the interpretation that the −11.4-eV level of virgin CO is derived from the 4σ level of gaseous CO, whereas the −7.7-eV level is derived from the 5σ and 1π levels of gaseous CO.

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[1] A. Katrib, T. P. Debies, R. J. Colton, T. H. Lee, and J. W. Rabalais, Chem. Phys. Lett. **22,** 196 (1973).

[2] D. E. Eastman and M. Kuznietz, J. Appl. Phys. **42,** 1396 (1971).

[3] See, for example, D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. **27,** 1520 (1971); J. C. Fuggle, T. E. Madey, M. Steinkilberg, and D. Menzel, Phys. Lett. A **51,** 163 (1975); T. Gustafsson, E. W. Plummer, D. E. Eastman, and J. L. Freeouf, Bull. Am. Phys. Soc. **20,** 304 (1975); and unpublished data.

[4] See, for example, C. N. Berglund and W. E. Spicer, Phys. Rev. **136,** A1030 (1964); **136,** A1044 (1964); D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. **28,** 1327 (1972).

[5] J. A. R. Samson, *Techniques of Vacuum Ultraviolet Spectroscopy* (Wiley, New York, 1967), Chaps. 5 and 6.

[6] C. Gahwiller, F. C. Brown, and H. Fujita, Rev. Sci. Instrum. **41,** 1275 (1970).

[7] J. K. Cashion, J. L. Mees, D. E. Eastman, J. A. Simpson, and C. E. Kuyatt, Rev. Sci. Instrum. **42,** 1670 (1971).

[8] F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, Rev. Sci. Instrum. **36,** 294 (1965).

[9] J. E. Rowe, S. B. Christman, and E. E. Chaban, Rev. Sci. Instrum. **44,** 1675 (1973).

[10] J. A. Kinsinger, W. L. Stebbings, R. A. Valenzi, and J. W. Taylor, Anal. Chem. **44,** 773 (1972).

[11] A. D. MacDonald, *Microwave Breakdown in Gases* (Wiley, New York, 1966), p. 134.

[12] E. H. Holt and R. E. Haskell, *Foundations of Plasma Dynamics* (MacMillan, New York, 1965), p. 237.

[13] J. R. Brandenberger, Rev. Sci. Instrum. **42,** 1535 (1971).

[14] The ultraviolet photoemission system is fully described by E. W. Plummer, B. J. Waclawski, T. V. Vorburger, and C. E. Kuyatt, in *Progress in Surface Science*, edited by S. G. Davison (to be published).

[15] C. R. Brundle, M. W. Roberts, D. Latham, and K. Yates, J. Electron Spectrosc. **3,** 241 (1974).

[16] R. T. Poole, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, J. Electron Spectrosc. **5,** 773 (1974).

[17] F. Burger and J. P. Maielg, J. Electron Spectrosc. **5,** 783 (1974).

[18] R. B. Cairns and J. A. R. Samson, J. Opt. Soc. Am. **56,** 1568 (1966).

[19] B. J. Waclawski and L. R. Hughey, J. Opt. Soc. Am. **59,** 1494 (1969).

[20] T. Engel and R. Gomer, J. Chem. Phys. **50,** 2428 (1969).

[21] J. M. Baker and D. E. Eastman, J. Vac. Sci. Technol. **10,** 223 (1973).