Title

High-Resolution Results from the LBL 55-Meter SGM at SSRL near the K-Edge of Carbon and Nitrogen

Authors

Heimann, P.A.
Senf, F.
McKinney, W.
et al.

Publication Date

1989-07-17

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

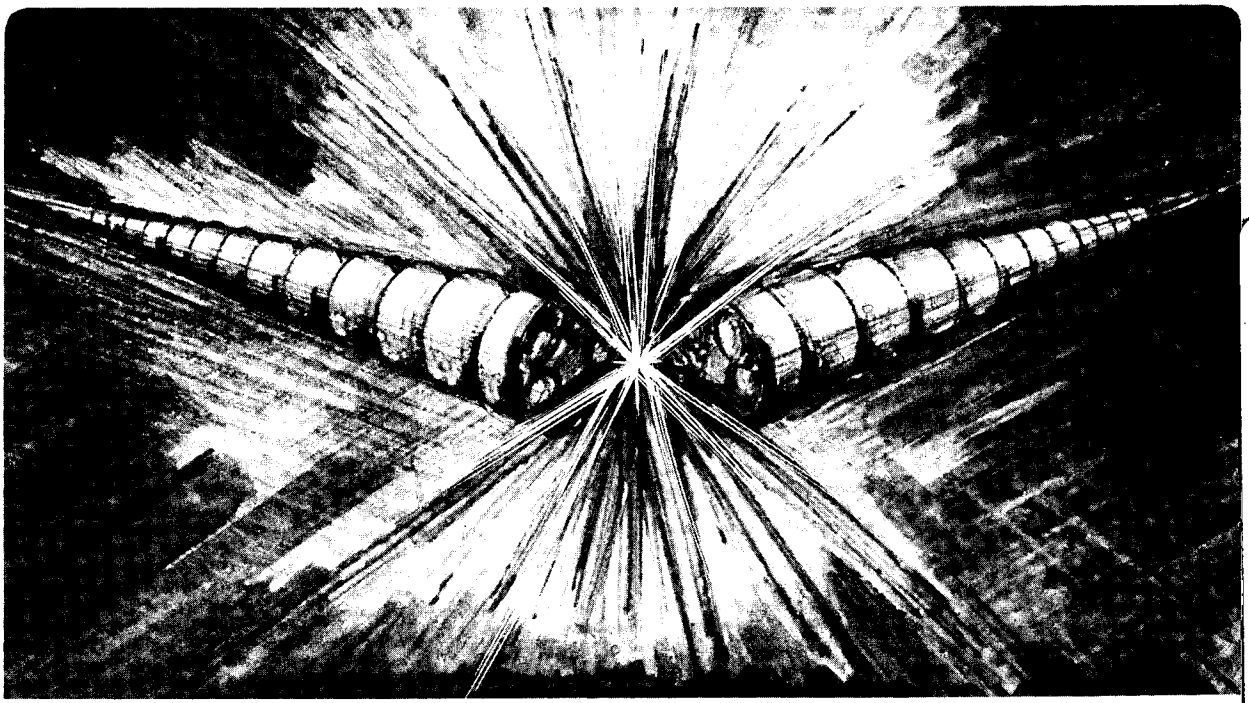
Accelerator & Fusion
Research Division

Presented at the 9th International Conference
on Vacuum Ultraviolet Radiation Physics,
Honolulu, HI, July 17–21, 1989, and
to be published in the Proceedings

High-Resolution Results from the LBL 55-Meter SGM at SSRL near the K-Edge of Carbon and Nitrogen

P.A. Heimann, F. Senf, W. McKinney, M. Howells,
R.D. van Zee, L.J. Medhurst, T. Lauritzen, J. Chin,
J. Meneghetti, W. Gath, H. Hogrefe, and D.A. Shirley

July 1989



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

LBL-28635

HIGH-RESOLUTION RESULTS FROM THE LBL 55-METER SGM AT SSRL NEAR THE K–EDGE OF CARBON AND NITROGEN

P.A. Heimann,† F. Senf,§ W. McKinney,‡ M. Howells,‡ R.D. van Zee,†
L.J. Medhurst,† T. Lauritzen,* J. Chin,* J. Meneghetti,* W. Gath,*
H. Hogrefe,‡ and D.A. Shirley†

†Materials & Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720
§Stanford Synchrotron Radiation Laboratory, Stanford, CA 94305
‡Accelerator and Fusion Research Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720
*Engineering Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

July 17, 1989

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical and Material Sciences Divisions of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 to Lawrence Berkeley Laboratory. In addition, the work was partially done at the Stanford Synchrotron Radiation Laboratory, and supported by the Department of Energy under Contract No DE-AC03-82ER13000, Office of Basic Energy Sciences, Division of Chemical Sciences.

HIGH-RESOLUTION RESULTS FROM THE LBL 55-METER SGM AT SSRL NEAR THE K-EDGE OF CARBON AND NITROGEN

P.A. Heimann,† F. Senf,§ W. McKinney,‡ M. Howells,‡ R.D. van Zee,†
L.J. Medhurst,† T. Lauritzen,* J. Chin,* J. Meneghetti,* W. Gath,*
H. Hogrefe,‡ and D.A. Shirley†

†Materials & Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720
§Stanford Synchrotron Radiation Laboratory, Stanford, CA 94305
‡Accelerator and Fusion Research Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720
*Engineering Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

Abstract

The performance of a 55-meter Spherical Grating Monochromator (SGM) is described. A resolution of 60 MeV has been achieved at 400 eV, inferred from the linewidths of the nitrogen 1s-π^* resonance. With 0.5 eV resolution, a photon flux of 4×10^{10} photons/sec has been observed at 440 eV. An initial experiment has studied the core-shell resonances of gas-phase ethylene, C_2H_4. Vibrational fine structure was resolved both for the carbon 1s-π^* and carbon 1s-Rydberg excitations. Comparison with the vibrational frequencies of ground state ethylene implies that the ν_1 (C-H stretch) and ν_2 (C-C stretch) or ν_3 (H-C-H bend) are excited. It is suggested that the lower Rydberg orbitals, 3s and 3pσ, have molecular, anti-bonding character.

Spherical Grating Monochromator (SGM) Performance

A Spherical Grating Monochromator (SGM) was designed at Lawrence Berkeley Laboratory (LBL). The beam line has now been completed and installed at the Stanford Synchrotron Radiation Laboratory (SSRL). Radiation is accepted from a 54 pole wiggler / undulator. A Rowland circle geometry, with a large radius of 55 m, is maintained with moveable entrance and exit slits. The complete photon energy range will be 40 - 1000 eV.

Figure 1 shows the layout of the beam line. The first optical component, a water-cooled plane mirror horizontally reflects a part of the intense wiggler beam by 5.6° away from an x-ray beam line. Next a toroidal mirror deflects the beam 5° vertically, while focussing vertically on the entrance slit and horizontally on the exit slit. The source is demagnified by 3 at the entrance slit and by 0.7 at the exit slit. A large grating chamber accommodates and provides water cooling for three gratings. At present a single fused Silica grating (600 l/mm) from Ferranti Astron Ltd., Middlesex, U.K., is installed (with no cooling). It is gold plated as are all other optical surfaces. The high quality of this grating (very small slope error and little surface roughness) has been confirmed by the observation of an unusually low contribution from scattered light. The polishing of four metal grating blanks has been completed by Perkin Elmer. The blanks are in the process of being ruled. Finally, a bent cylindrical mirror refocusses the beam onto the sample with a demagnification of 3.4. This refocussing mirror (now in place) was not installed during the measurements which will be described.

Since this monochromator is similar to the Dragon monochromator [1] at NSLS the differences should be pointed out. First, the source is a wiggler instead of a bending magnet, which under the conditions of SSRL provides a factor of 3 more flux than 15 mrad^2 of an NSLS bending magnet. Both slits of our monochromator are moveable, which allows the Rowland circle condition, and the highest resolution, to be satisfied over a

range of energies: 269 - 462 eV for the 600 l/mm grating. The capacity of our grating chamber for three gratings will extend the accessible photon energy range. Our present estimate is that water cooled gratings are not mandatory for operation at SSRL but rather for the lower emittance and higher brightness of the Advanced Light Source (ALS) in Berkeley, for which this beam line is a prototype.

The resolution of a Rowland circle-type monochromator scales with the grating radius for given slit openings. Because of the large radius of the grating, this monochromator has a very good theoretical resolution. For example, a calculated value at the nitrogen edge is 71 MeV full width zero height for a point source. The actual resolution was tested using nitrogen gas in an ion chamber. A thin Al window (1500 Å) and an interlock protected the ulta-high vacuum (UHV) of the monochromator from the pressure of the sample, about 10 mTorr. Figure 2 displays the ion yield from nitrogen at the 1s to π^* resonance taken with 10 μ slits. Five clearly resolved vibrational final states of the nitrogen stretching mode are seen.

To evaluate the resolution, the nitrogen spectrum was fit with Voigt functions, the convolution of a Gaussian and a Lorentzian peak form. The Lorentzian or lifetime width was fixed at 128 MeV FWHM following the electron impact experiments of King et al. [2] Alternatively, letting this parameter vary gave a lifetime in complete agreement with the earlier work. This procedure resulted in experimental resolutions of 80 MeV for 10 μ slits and 60 MeV for 5 μ slits. Thus a maximum resolving power of 6600 has been achieved. Because the experimental resolution to be determined is smaller than the broadening from the Auger process, the resolution is sensitive to the analysis method. Our nitrogen spectrum and the one presented by Chen and Sette at SRI 1988 [1] are of comparable quality with regard to resolution. Chen and Sette assign a larger natural width to condensed nitrogen, 148 - 160 MeV. More diffuse condensed nitrogen valence orbitals in solid nitrogen would lead to a slower Auger decay. Instead, not equivalent environments of neighboring nitrogen molecules perhaps give an nonhomogeneous broadening to the π^* level.

The nitrogen $1s \rightarrow \pi^*$ resonance was measured at many different slit positions, in order to be sure the slits were in fact at the Rowland circle, and for different slit openings. In Figure 3 is shown spectra with entrance and exit slit opening varying together from 5 μ to 50 μ. The monochromator resolution resulting from the analysis with Voigt functions is shown in figure 4. That the curve does not go to zero for completely closed slits implies a small, remaining amount of aberrations. Suggesting the same, the resolution at 10 μ slits improves from 80 to 60 MeV when the vertical aperture is reduced by a factor of three. The resolution at 50 μ slit openings is adequate for studies of chemisorbed molecules. The SGM monochromators have reached the regime where the main contribution to the observed widths are from physical processes, usually Auger decay.

The photon intensity from the beam line is clearly also important, determining collection times and what types of experiments are feasible. The flux was measured with an Aluminum photodiode from the James A.R. Samson, University of Nebraska. Figure 5 shows a scan of the monochromator output over the energy range of the 600 l/mm grating, 180 - 820 eV. This energy range covers the C, N, O and F edges. The first two harmonics of the wiggler / undulator at a field of 0.5 T generate strong intensity maxima at about 220 and 440 eV. In fact, the intensity maxima from the harmonics do not occur at precisely nhnf because the monochromator accepts radiation off the central axis of the wiggler / undulator. A strong excitation of the oxygen 1s near edge structure is observed starting at 535 eV because of the oxide layer on the Al surface. In addition, the increase at 300 eV can be attributed to carbon on the photodiode. The decrease in intensity at low photon energies is a geometrical effect with more of the beam missing the optical surface of the grating. On the other hand the decrease at high energies results from the lower efficiencies of the mirrors and grating. Two small sharp peaks near 350 eV are Ca 2p→3d transitions representing an impurity from a nearby metal evaporator.

The Al photoyield should also be kept in mind; it decreases slowly (except at the O K-edge) from 0.04 to 0.03 electrons/photon over this energy range. [3]

From the Al photodiode current, an absolute photon flux can be calculated accurate to within a factor of two. This analysis yields $4x10^{10}$ photons/sec at 440 eV and 40 mA in the SPEAR storage ring. This intensity was observed with 100 μ slits, which corresponds to 0.5 eV resolution. For 10 μ slit openings required for the outstanding resolution, the intensity will be lower by a factor of 100. Therefore, at the best resolving power, some experiments will be difficult, for example gas phase photoemission. The measured intensity was artificially low because for beamline commissioning the M0 mirror [4] was only modestly inserted into the radiation fan (an intensity of 4-9 % was subtracted from the x-ray branch line). However, the design intensities have not been achieved. There is only a poor focus at the entrance slit mainly due to the bad optical quality of the M0 mirror. This mirror was welded after polishing to remove a small leak in the vacuum guarding the water connections. With a new M0 mirror, which is now being installed in the mirror chamber, an intensity increase by ten is expected.

It should be stressed that for the SGM the quality requirements on all the optical elements are very high because of the long distances between the mirrors and grating and the slits. For the toroidal M1 mirror for example, slope errors of 2 arcsec or less would be required for a vertical focus of 100 μ at the entrance slit. The M1 mirror was manufactured by traditional methods utilizing test plates, and zone polishing. Because of the difficulty of obtaining high quality toroidal mirrors by these methods, in the future design for the ALS the plane and toroidal mirrors will be replaced by two spherical mirrors, as in the Dragon monochromator.

In the photoyield curve a second order oxygen peak is observed at 270 eV. From the peak height, the second order contribution near the C edge is estimated to be 28 %. This positive result is due to the square wave profile of the grating and its cleanliness.

A laser interferometer encodes the wavelength drive with the laser beam reflecting off a cube corner on the grating rotation arm. The smallest step is 4 x 10-4 Å or 5 MeV at 400 eV. Once the zero order position was set, the energies from the monochromator computer were accurate within one eV.

Vibrational Fine Structure in Molecular Absorption, Ethylene

Absorption spectra of some gas-phase molecules have been taken. The results of ethylene, C_2H_4, will be presented in order to discuss in general the vibrational fine structure of resonances where a core electron, here carbon 1s, is excited to molecular or Rydberg excited states. Comparable work on physisorbed ethylene has been done recently by K. Baberschke and coworkers. [5 In addition, Chen and coworkers have done experiments on ethylene as well. [6] Our measurements were performed using the same ion chamber used to test the monochromator resolution.

For different vibrational states to be excited, the final state molecular geometry must differ from the initial geometry. This rule follows from the Franck-Condon principle. Two factors can contribute to a change in bond distance. First, the creation of the core hole, essentially increasing the nuclear charge by one, will repulse the neighboring nuclei, and attract the electrons. Since the same vibrational fine structure is not observed for every resonance, another factor must be involved. The anti-bonding character of the excited orbitals is also important in determining which vibrational modes are excited. Conversely, these spectra provide information about the nature of these excited electronic states.

One issue is whether these excited orbitals should be described as molecular orbitals or as Rydberg states. Molecular orbitals are small in size and consequently have large oscillator strengths. Typically the excited molecular orbitals have anti-bonding character, for example the $2\pi^*$ orbital of ethylene. On the other hand, Rydberg orbitals are hydrogenic in form, large and have small oscillator strengths. They are non-bonding. Traditionally, the lowest energy resonance is labelled as molecular while the other resonances are assigned to Rydberg resonances. As will be shown a simple dichotomy is not possible. That the lower 'Rydberg' orbitals should have molecular character as well can be seen from the size of the 3s orbital. For this orbital, the radius of maximum electron density is 2.2 Å only slightly larger than the ethylene nuclear skeleton. [7]

The electronic states of ethylene have been examined with other techniques, which also resolve the vibrational fine structure. In the absorption spectra exciting valence electrons, vibrational peaks are assigned to four modes: ν_1 the C-H stretch, ν_2 the H-C-H bend, ν_3 the C-C stretch, and ν_4 the torsional mode. [8] A theoretical investigation of the valence absorption spectrum demonstrated a strong mixing between a molecular singlet $\pi\rightarrow\pi^*$ and a Rydberg $\pi\rightarrow 3d\pi$ state of the same symmetry. [9] The resulting mixed state has a large oscillator strength from the valence-type orbital and a large size from the Rydberg orbital. An analogous mixing of the core π^* and $3d\pi$ resonances is not expected because of the large energy separation between them, 4.6 eV. The valence photoelectron spectrum [10] shows the possible complexity of the vibrational motion. In the A^2B_3 band vibronic coupling makes a normal mode analysis invalid and more than 1000 lines are predicted. [10,11]

Figure 6 shows the core-level absorption spectrum of ethylene. Table I contains the assignments of the resonances to different excitations of the C 1s electron. This spectrum was accumulated with 20 μ slits. The π^* resonance will not be discussed here, but in the paper of Rabus, H., et. al. [5] The hn scale has been shifted such that the sharpest resonance, $3p\sigma$, occurs at the energy scale reported by Tronc et al., [12] while the term values in Table I are derived from a C 1s binding energy of 290.6 eV. [13] The assignments have been made comparing with the configuration interaction (CI) calculation of Barth et al. [14] In the 3s region there are two peaks separated by 0.36 eV, which agrees well with the ground state C-H stretch (ν_1) spacing 0.37 eV. [14] That the ν_1=1 transition has similar strength to the ν_1=0 transition implies that the 3s orbital has C-H anti-bonding character. Merer and Mulliken [7] show the 3s orbital having a node in the probability density lying between the C and H atoms. Two electronic 3p transitions are observed with σ and π symmetry, showing that the 3p is sensitive to the molecular symmetry. The oscillator strength of the $3p\sigma$ transition is much larger than is predicted by Barth et al., [14] implying more probability density near the molecular core. The $3p\sigma$ transition with an additional vibrational quantum can be explained by either a H-C-H bend (ν_2) or C-C stretch (ν_3) excitation. Approaching the ionization a number of other resonances are present whose assignment is uncertain.

In conclusion, the lower core-Rydberg resonances of ethylene have molecular orbital character. This mixed nature is especially evident in the strong $3s+\nu_1$ transition demonstrating the C-H anti-bonding character of the 3s orbital. Further theoretical effort would be very helpful to completely assign the spectrum and to describe the molecular potential surfaces.

One experiment planned for the future will study threshold photoionization. The zero volt analyzer has a resolution of about 30 MeV. The vibrational fine structure of core-level photoemission main lines and satellite lines will be examined.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical and Material Sciences Divisions of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 to Lawrence Berkeley Laboratory. In addition, the work was partially done at the Stanford Synchrotron Radiation Laboratory, and supported by the Department of Energy under Contract No DE-AC03-82ER13000, Office of Basic Energy Sciences, Division of Chemical Sciences.

References

1 Chen, C.T. and Sette, F., Third International Conference on Synchrotron Radiation Instrumentation: SRI-88, Tsukuba, Japan, July 1988, Review of Scientific Instruments Vol. 60 No. 7 (Part IIA), 1616 (1989).

2 King, G.C., Read, F.H. and Tronc, M., Chem. Phys. Lett. 52, 50 (1977).

3 Day, R.H., Lee, P., Saloman, E.B. and Nagel, D.J., J. Appl. Phys. 52, 6965 (1981).

4 DiGennaro, R., Gee, B., Guigli, J., Hogrefe, H., Howells, M. R., Nuclear Instruments and Methods in Physics Research A266, 498 (1988).

5 Rabus, H., Arvanitis, D., Comelli, G., Domke, M., Wenzel, L. and Baberschke, K.Ninth International Conference of Vacuum Ultraviolet Radiation Physics, Honolulu, Hawaii, July 17-21, 1989, submitted to Physica Scripta.

6 Chen, C.T., private communication.

7 Merer, A.J. and Mulliken, R.S., Chem. Rev. 69, 639 (1969).

8 McDiarmid, R., J. Phys. Chem. 84, 64 (1980).

9 Buenker, R.J. and Peyerimhoff, S.D., Chem. Phys. Lett. 36, 415 (1975).

10 Pollard, J.E., Trevor, D.J., Reutt, J.E., Lee, Y.T. and Shirley, D.A., J. Chem. Phys 81, 5302 (1984).

11 Köppel, H., Cederbaum, L.S. and Domke, W., J. Chem. Phys. 77, 2014 (1982).

12 Tronc, M., King, G.C. and Read, F.H., J. Phys. B 12, 137 (1979).

13 Davis, D.W. and Shirley, D.A., J. Electron Spectrosc. 3, 137 (1974).

Table I

hν	Term Value	Excitation	Calculation[a]
284.61	5.99	$1s \rightarrow \pi^*$	5.20
285.01	5.59	$\pi^* + \nu_1$	
287.19	3.41	3s	3.36
287.55	3.05	$3s + \nu_1$	
287.88	2.72	$3p\sigma$	2.47
288.07	2.53	$3p\sigma + \nu_2 \text{or} \nu_3$	
288.39	2.21	$3p\pi$	2.20
289.09	1.51	$3d\delta$	1.33
289.31	1.29	$3d\pi$	1.36
289.42	1.18	$4p\pi$	1.10
289.59	1.01		

[a]Ref. 13.

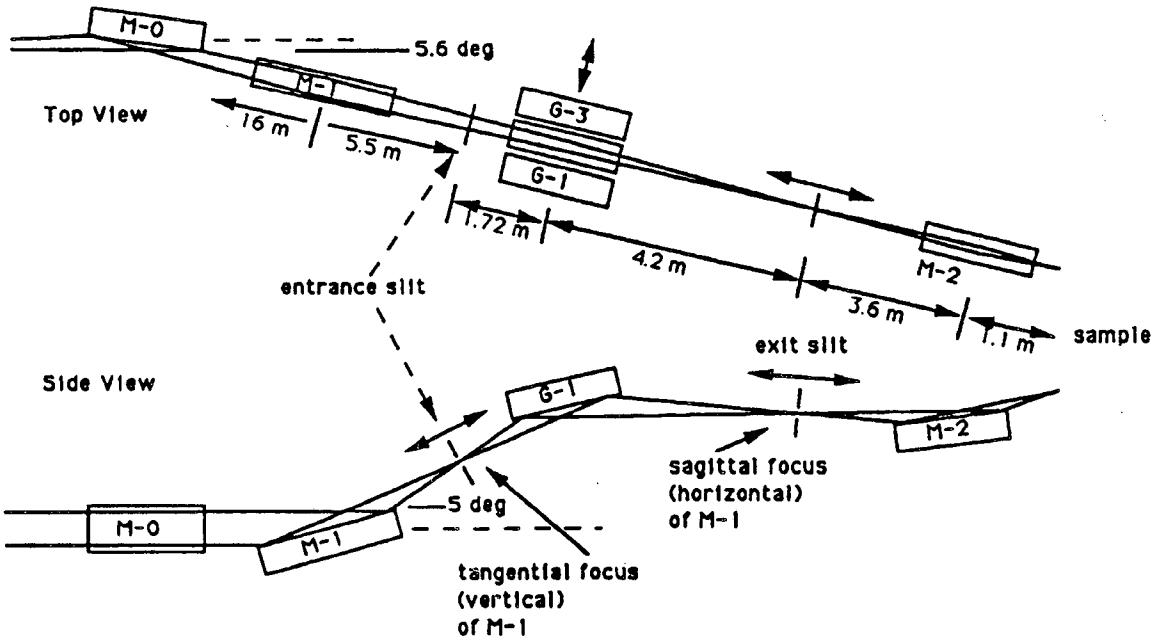


FIG. 1. A schematic diagram of the LBL SGM displaying plane (M-0), toroidal (M-1), and bent cylindrical (M-2) mirrors, gratings G-1, G-2, and G-3, and entrance and exit slits.

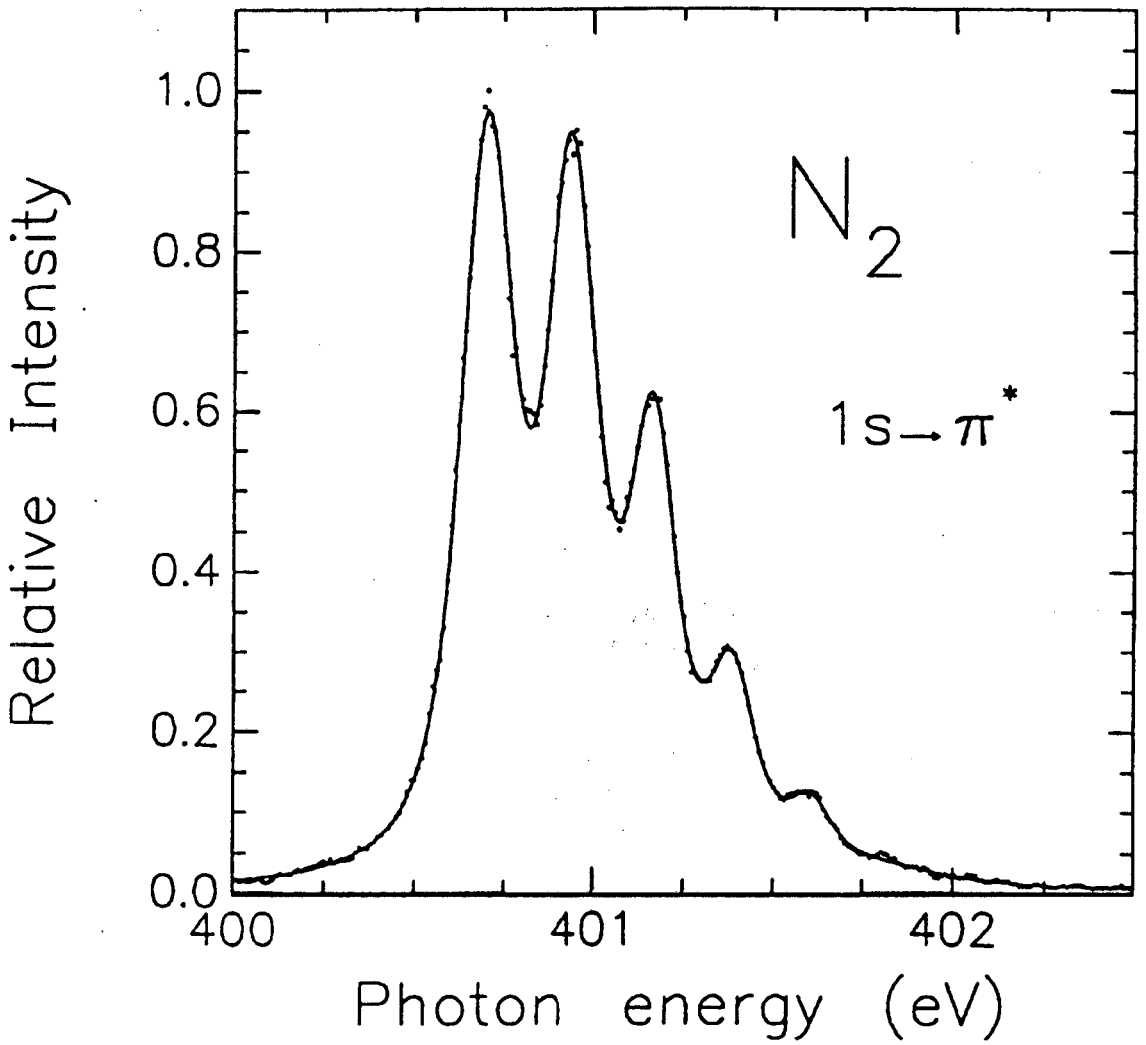


FIG. 2. The 1s→π* photoabsorption resonance of nitrogen gas accumulated with 10 m slit openings. The points represent the experimental data while the solid line shows a fit with five Voigt functions (Lorenztian width: 128 MeV, Gaussian width: 80 MeV).

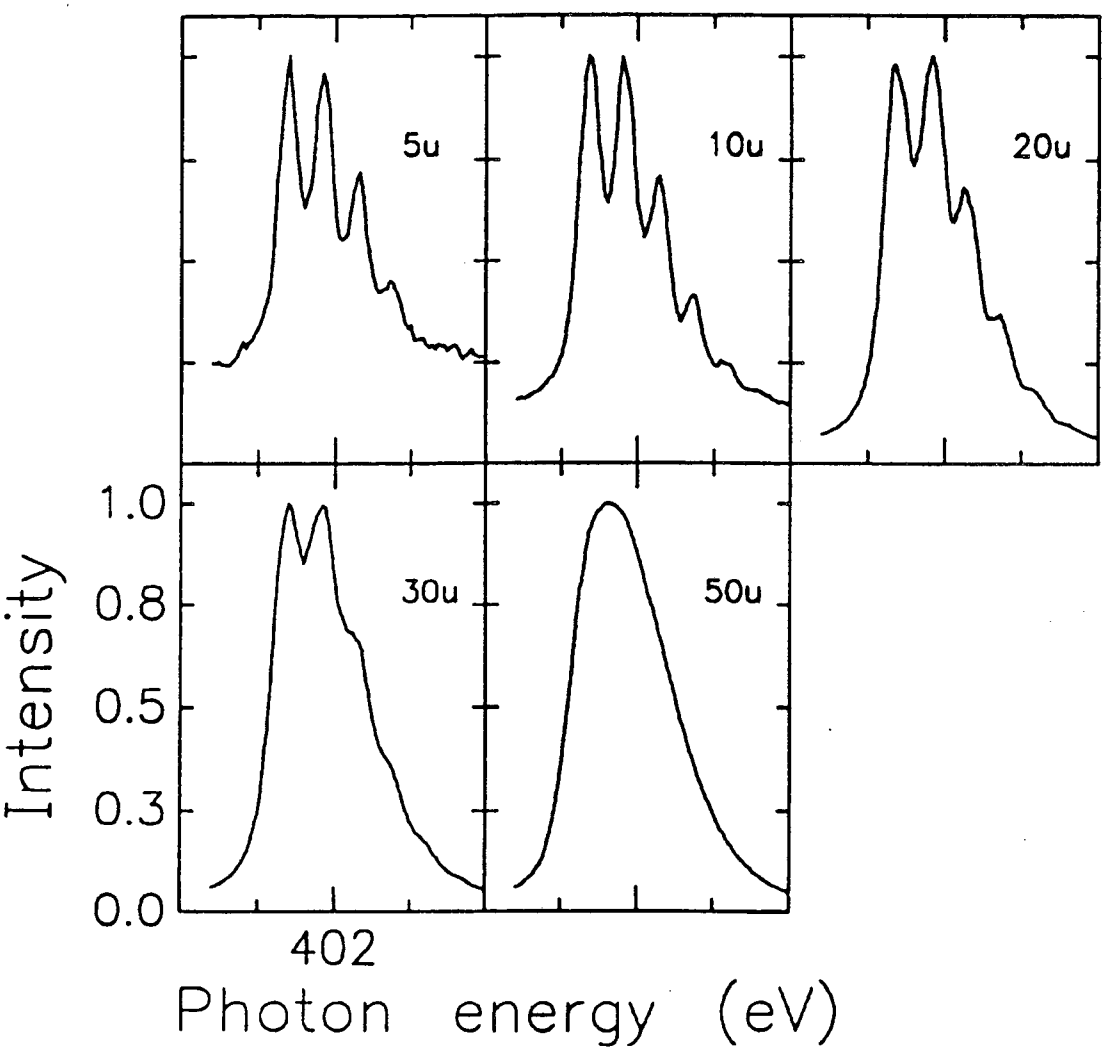


FIG. 3. Spectra of the nitrogen 1s→π* resonance taken with the widths of both the entrance and exit slits varying from 5 to 50 m.

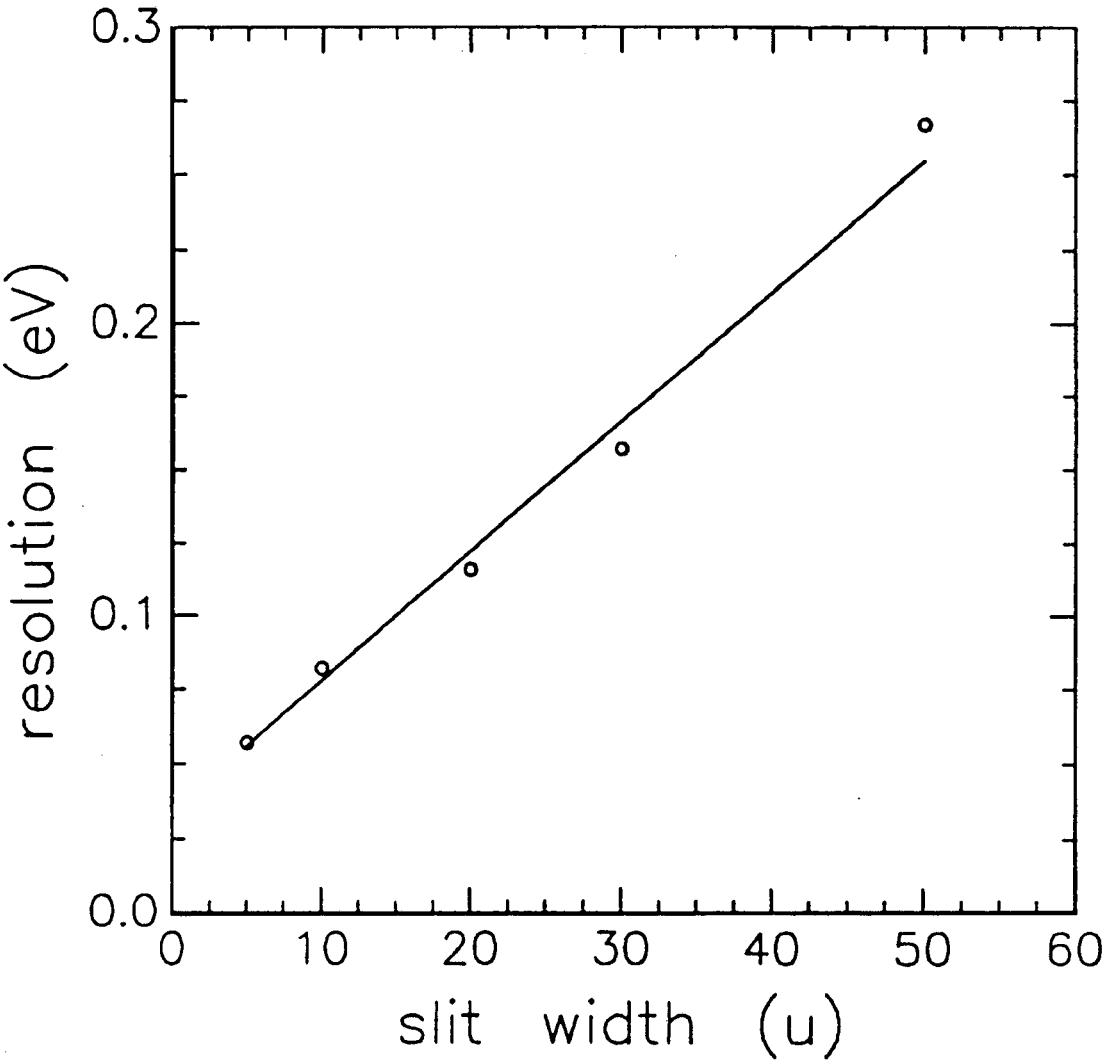


FIG. 4. The monochromator resolution versus slit opening inferred from fitting the sepectra in Fig. 3 with Voight-line shapes.

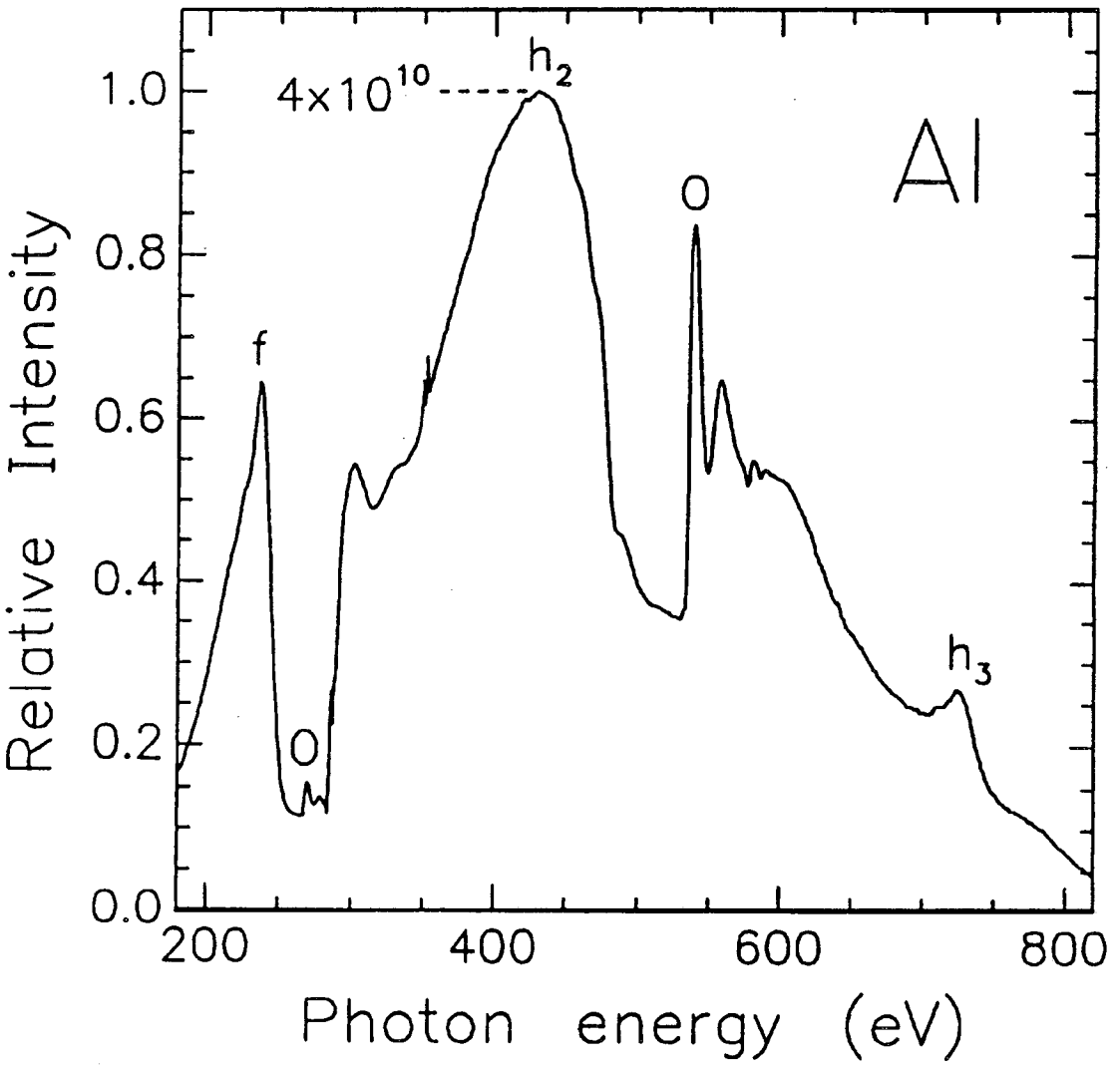


FIG. 5. The monochromator output of the 600 1/mm grating detected with an A1 photodiode. The SPEAR ring current was 40 mA, while the entrance and exit slits were opened to 100 m.

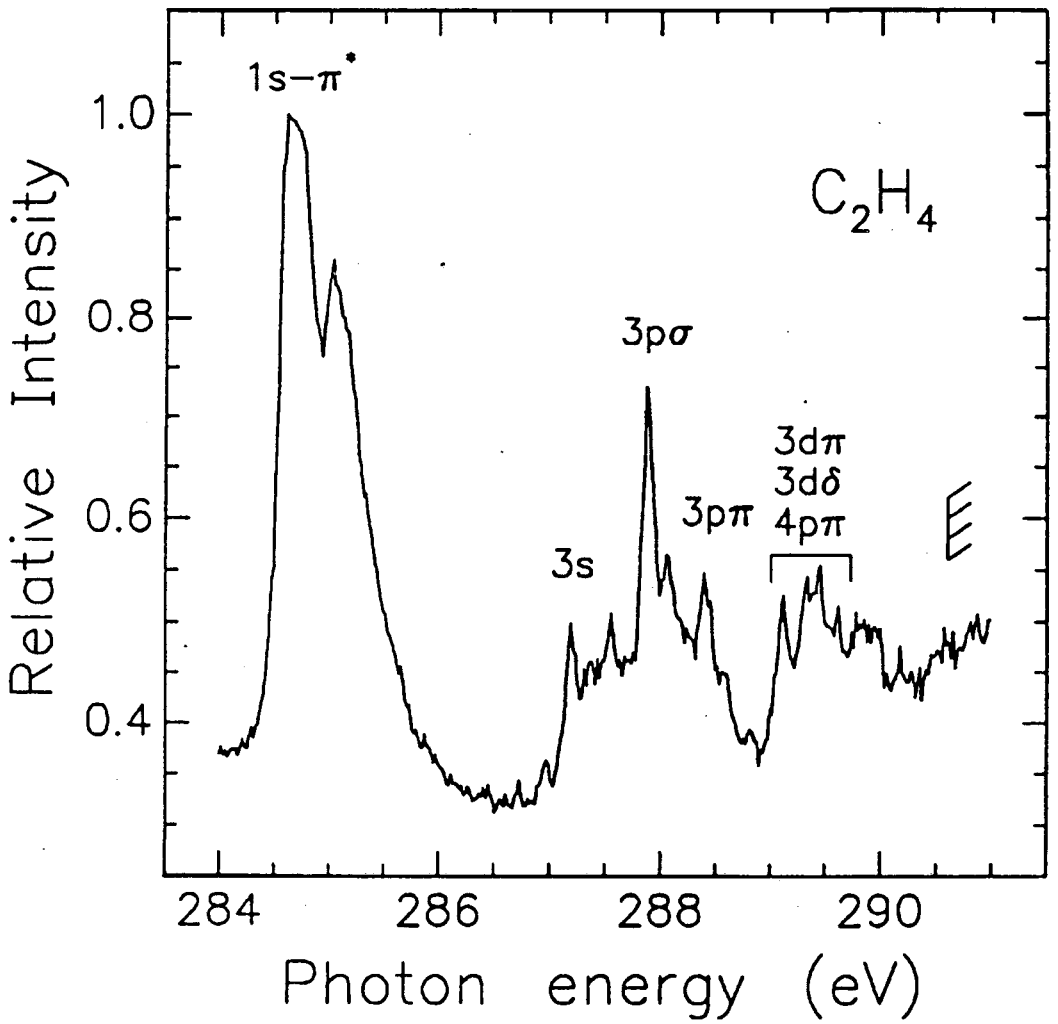


FIG 6. The photoabsorption spectrum of ethylene taken with 20 m slits.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720