Single- and double-photoionization cross sections of atomic nitrogen from threshold to 31 Å

James A. R. Samson and G. C. Angel*
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111
(Received 27 March 1990)

The relative photoionization cross section of atomic nitrogen for the production of singly and doubly charged ions has been measured from 44.3 to 275 Å and from 520 to 852 Å. The results have been made absolute by normalization to one-half of the molecular nitrogen cross section at short wavelengths. The smoothed atomic nitrogen cross sections σ can be accurately represented, at short wavelengths, by the equation $\sigma(\text{Mb})=3.67\times10^{4}E^{-2.3}$ as a function of the photon energy E (eV), thereby allowing the cross sections to be extrapolated to the nitrogen K edge at 31 Å.

I. INTRODUCTION

Although there have been numerous calculations of the photoionization cross section of atomic nitrogen[1-9] few experimental studies have been made.[10,11] This is mainly because of the difficulty in producing a sufficient number of free atoms from the dissociation of N_2. The first measurement of the photoionization cross section of atomic nitrogen was reported in 1955 by Ehler and Weissler.[10] They used a direct absorption approach by measuring the intensity of radiation transmitted through a dc electrical discharge in nitrogen and compared this intensity to that transmitted with no discharge. Many assumptions regarding the condition of the discharge had to be made. To enhance the degree of dissociation of N_2 an axial magnetic field of about 2 kG was used. Absolute absorption cross sections were reported between 400 and 700 Å. Their results showed relatively good agreement with the only theory then available, namely, that of Bates and Seaton.[1] The only other measurement of the nitrogen cross section was reported by Comes and Elzer[11] over the range 450–852 Å. Measurements were again made with discharged N_2, alternatively switched on and off. In this case the discharge was produced by a high-voltage condensed spark and the products allowed to flow into the ion chamber of a magnetic mass spectrometer to isolate the N^+ signal. In addition to making cross-sectional measurements, they were able to show that the Rydberg series $2s^22p^4\rightarrow2s2p^4ns\,(^5S)$ autoionized. This series had originally been identified by Carroll *et al.*[12] using conventional photographic absorption techniques. More recently, Dehmer, Berkowitz, and Chupka[13] studied the photoionization of atomic nitrogen in detail throughout this series using a continuum light source covering the range 610–860 Å.

The purpose of the present experiment was to obtain an independent measurement of the absolute photoionization cross section for single and double ionization of atomic nitrogen and to extend the data to shorter wavelengths.

II. EXPERIMENT

The experiment was performed at the Synchrotron Radiation Center at the University of Wisconsin. Both a normal incidence (4 m) and a grazing-incidence monochromator (Grasshopper, Mark II) were used to cover the spectral range between 44.3 and 852 Å. Details of the experimental arrangement have been discussed in previous publications.[14,15] Briefly, a microwave discharge was used to dissociate pure N_2 and the products allowed to flow into the ion chamber of a magnetic sector mass spectrometer, where they were intercepted by the incident radiation. The mass spectrometer was designed specifically for photoionization studies.[16] The resulting ion signals were detected with a Johnston-type electron multiplier and recorded using counting techniques. Simultaneously, the incident radiation was monitored by use of a calibrated photodiode. At the low gas pressures used in the ion chamber ($\sim 10^{-5}$ Torr) the ratio of ions produced per incident photon is proportional to the photoionization cross section for producing that particular ion. However, to study the direct photoionization production of N^+ from N account had to be taken of any dissociative photoionization of N_2 that might occur. An analysis of the photoionization process yields the following equation[14] for $\sigma^+(\text{N})$, the single-photoionization cross section of atomic nitrogen, namely,

$$\sigma^+(\text{N})=CG[(N^+/I)_{\text{on}}-\alpha(N^+/I)_{\text{off}}]\,, \tag{1}$$

where G is the photon detector efficiency, C is the constant of proportionality and contains terms such as the number density of the gas and the ion collection efficiency, N^+ and I are the actual atomic nitrogen-ion count rates and photon signals recorded, respectively, and their ratios are measured with the microwave discharge turned on then off. The constant α represents the fraction of molecular nitrogen remaining undissociated by the microwave discharge and is equal to the ratio of the $N_2{}^+$-ion signal measured with the microwave discharge switched on and then off. No excited species are expected.[10] The fraction α was found to be about 0.99 indicating only 1% dissociation of molecular nitrogen. However, because the present mass spectrometer discriminated strongly against ions with kinetic energies in excess of room temperature the presence of energetic N^+ ions produced by dissociative photoionization [second term in Eq. (1)] was greatly reduced. The photodiode detector efficiency G was calibrated in relative units

against the rare gases as described previously.[15] The value of C stayed constant during a run. Thus, accurate measurements of the relative photoionization cross sections could be made. Equation (1) also applies to the determination of the relative cross sections for producing double ionization provided N^{2+} is substituted for N^{+}.

Thus, during a given run the sum of the relative cross sections for single and double ionization gives the total relative photoionization cross section for atomic nitrogen. These values can be placed on an absolute basis by normalizing the data to one-half of the total photoionization cross section of N_2 at wavelengths shorter than about 250 Å. When the total atomic photoionization cross section is known the constant C in Eq. (1) can be determined and hence the absolute values for $\sigma^{+}(\mathrm{N})$ and $\sigma^{2+}(\mathrm{N})$ can be found. This procedure assumes that the ion detection efficiency remains constant with respect to the different charged species. It is known that the detection efficiency of a particle multiplier is a function of the ion velocity.[17] However, Peart and Harrison[18] have shown that for ion velocities greater than about 2×10^5 m/s the detection efficiency changes very slowly with ion velocity and is essentially independent of the ionic charge. Ion velocities used in this work ranged from 2.5×10^5 to 3.5×10^5 m/s. Thus we have assumed a constant ion detection efficiency.

Relative cross-section measurements were made over the wavelength range from 44.3 to 850 Å. By necessity, this range was covered in two separate experiments using a normal-incidence and grazing-incidence monochromator. However, in the overlapping region between 300 and 500 Å no reliable data could be obtained because of the presence of higher-order spectra and/or weak light intensity.

III. RESULTS AND DISCUSSION

The total relative cross-sectional data taken at short wavelengths were normalized to a best fit to the experimental data represented by one-half of the molecular photoabsorption data[19–21] and the cross section of NH_3 minus 3 times the cross section of atomic hydrogen.[22,23] The results are shown in Fig. 1 and include a comparison with the tabulated data of Henke *et al.*[24] and the theoretical results of Le Dourneuf, Lan, and Hibbert.[9] The solid line represents the average of our experimental atomic photoionization data and can be represented, between 80 and 280 eV, by the hydrogenic equation

$$\sigma(\mathrm{N})=3.67\times10^{4}E^{-2.3}\,, \tag{2}$$

where the units of σ are in Mb and the photon energy is in eV. The extrapolation of the solid line, towards lower energy, lies a few percent above the upper dashed curve. The upper and lower dashed curves represent the dipole length and velocity approximations, respectively, of Le Dourneuf, Lan, and Hibbert's R-matrix calculation.[9] The normalized experimental cross sections were then used to determine the constant in Eq. (1), thus allowing the relative N^{2+} cross sections to be made absolute. The smoothed cross sections for single, double, and total photoionization are given in Table I for the wavelength range 31–281 Å. Equation (2) was used to extrapolate the results from 44 Å down to the nitrogen K edge (31 Å).

In order to place the long-wavelength experimental data on an absolute basis we continued the extrapolation of the solid line in Fig. 1 so that it would join smoothly onto the relative cross sections at 520 Å (see Fig. 2). The relative data were then adjusted so that the total oscillator strength had a value of 7, as required by the Thomas-

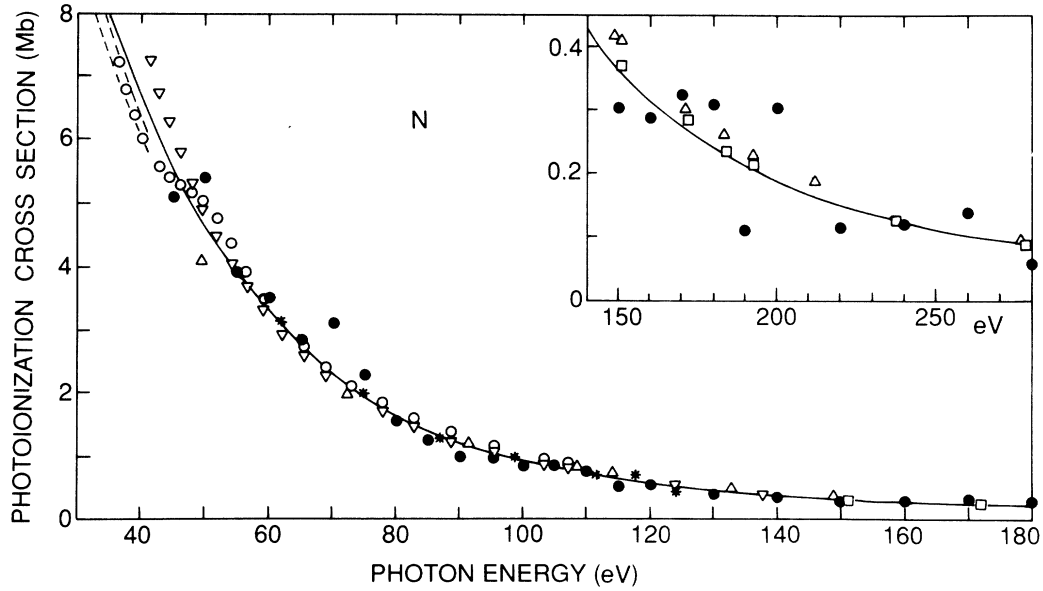

FIG. 1. Total photoionization cross section of atomic nitrogen as a function of photon energy. ●, present data (solid line represents best fit to data); ○, ∗, □, one-half N_2 total photoionization cross sections, Refs. 19, 20, and 21, respectively; ▽, photoionization cross section of NH_3 less three times the cross section of atomic hydrogen, Refs. 22 and 23; △, tabulated data of Henke *et al.* (Ref. 24).

TABLE I. Absolute photoionization cross sections for single, double, and total photoionization from 31 to 281 Å.

$h\nu$ (eV)	λ (Å)	N^+ (Mb)	N^{2+} (10^{-2} Mb)	σ_{tot} (Mb)	$h\nu$ (eV)	λ (Å)	N^+ (Mb)	N^{2+} (10^{-2} Mb)	σ_{tot} (Mb)
44.136	280.9	5.65	0.0	5.65	110	112.7	0.642	9.8	0.740
46	269.5	5.26	3.8	5.30	115	107.8	0.578	9.0	0.668
48	258.3	4.86	7.9	4.94	120	103.3	0.522	8.4	0.606
50	248.0	4.48	11.7	4.60	130	95.4	0.432	7.2	0.504
52	238.4	4.15	14.7	4.30	140	88.6	0.363	6.2	0.425
54	229.6	3.83	17.1	4.00	150	82.7	0.311	5.2	0.363
56	221.4	3.61	18.8	3.80	160	77.5	0.270	4.3	0.313
58	213.8	3.35	20.1	3.55	170	72.9	0.237	3.5	0.272
60	206.6	3.12	20.6	3.33	180	68.9	0.210	2.8	0.238
65	190.7	2.60	20.0	2.80	190	65.3	0.188	2.3	0.211
70	177.1	2.15	18.6	2.34	200	62.0	0.168	1.9	0.187
75	165.3	1.79	17.3	1.96	220	56.4	0.137	1.3	0.150
80	155.0	1.38	15.9	1.57	240	51.7	0.113	1.0	0.123
85	145.9	1.19	14.7	1.34	260	47.7	0.094	0.8	0.102
90	137.8	1.04	13.5	1.17	280	44.3	0.078	0.77	0.086
95	130.5	0.92	12.5	1.04	300	41.3			0.074
100	124.0	0.81	11.5	0.92	350	35.4			0.052
105	118.1	0.72	10.6	0.82	400	31.0			0.038

Reiche-Kuhn sum rule,[25] or as close to 7 as consistent with the smooth interpolation of the two sets of data. The oscillator strengths for the various spectral regions are given in Table II. The adjusted cross sections contribute a value of 2.72 yielding a total oscillator strength of 7.06 less than 1% deviation from the required value. The resulting cross sections from threshold to 250 Å are tabulated in Table III.

The error in the relative cross sections from 520 to 850 Å is about ±3%. To estimate the error in the absolute cross sections between 250 and 850 Å we note that the ±50% uncertainty in the discrete oscillator strength[26]

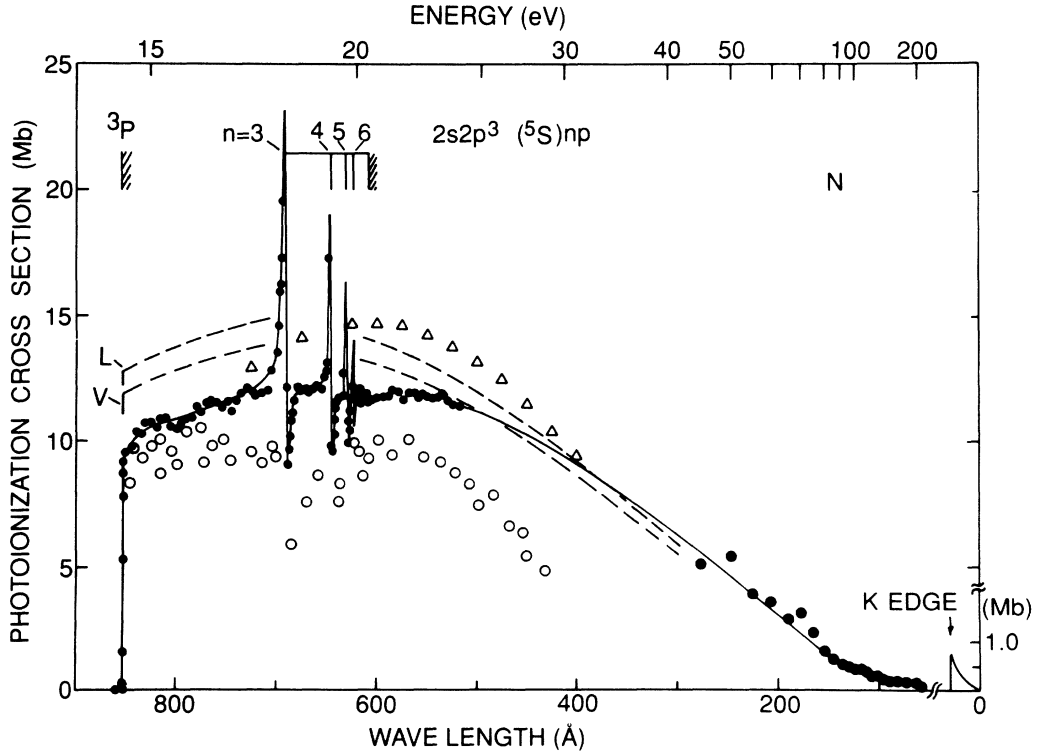

FIG. 2. Total photoionization cross section of atomic nitrogen as a function of wavelength. Solid data points and line, present data; △, Ref. 10; ○, Ref. 11; -----, theory, *L* dipole length and *V*, velocity approximations, Ref. 9.

TABLE II. Oscillator strengths f for the various spectral regions.

$\Delta\lambda$ (Å)	f value	References
0–31	1.82	Henke *et al.* (Ref. 24)
31–250	1.56	Present data
Σf (discrete)	0.96±50%	Wiese, Smith, and Glennon (Ref. 26)
Subtotal	4.34±0.48	
250–850	2.72	Present data adjusted
Total f value	7.06	

yields a value of 4.34±0.48 for the continuum f value from 0 to 250 Å plus Σf (discrete), as shown in Table I. Subtracting this value from 7 gives a value of $2.72^{+15.4\%}_{-20\%}$ for the continuum f value between 250 and 850 Å. That is, the average cross section in this region could vary between +15.4% to −20% of the values shown in Fig. 2. The uncertainty in the discrete oscillator strengths is the major source of error affecting the long-wavelength data. At short wavelengths, below 250 Å, the error is estimated to be ±5%.

Our present experimental data plus that of Ehler and Weissler, Comes and Elzer, and the theoretical results of Le Dourneur, Lan, Hibbert are also shown in Fig. 2. If we further adjust the relative data by +15.4% (the upper error limit) between 520 and 850 Å there would be very good agreement with the dipole velocity V curve on the long-wavelength side of the resonances and with the length L curve on the short-wavelength side. Note the curve joining the 250-Å region to the data at 520 Å is constrained to pivot about the 250-Å region. This adjustment would require the published discrete oscillator strengths to decrease about 50%. It should be noted that the R-matrix calculation predicts the shape and position of the $2s2p^3(^5S)np$ resonances in very good agreement with the present results.

The other experimental data have several points that lie within the absolute error limits of our adjusted cross sections. However, the relative shape of these curves falls outside of the ±3% error in our relative cross sections.

Figures 3 and 4 show the present results compared with the theoretical estimates presently available. The experimental data are shown as the closed circles. The resonances leading up to the ^5S threshold have been omitted for clarity.

The earliest calculation was that of Bates and Seaton[1] (BS) using the Hartree-Fock approximation. As can be seen from Fig. 3 their results lie about 13% below the experimental data, following almost exactly the shape of the experimental curve. Henry[3] [$H_1(L,V)$] extended the Hartree-Fock calculations to include the dipole length L

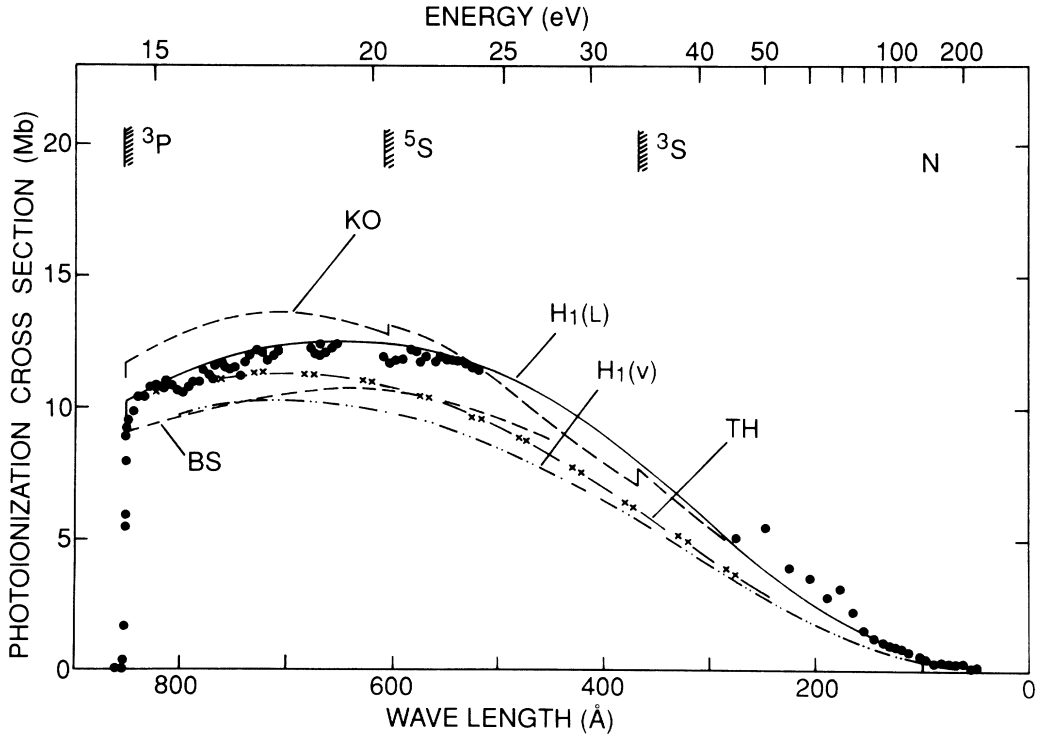

FIG. 3. Total photoionization cross section of atomic nitrogen as a function of wavelength. ●, present data; -----, BS, Ref. 1; — — —, KO, Ref. 7; ——, $H_1(L)$, Ref. 3; —··—, $H_2(V)$, Ref. 3; —×××—, TH, Ref. 5.

TABLE III. Absolute total photoionization cross sections of atomic nitrogen between 850 and 250 Å. Units are in Mb (1 Mb $=10^{-18}$ cm^2).

λ (Å)	$h\nu$ (eV)	σ_{tot} (Mb)	λ (Å)	$h\nu$ (eV)	σ_{tot} (Mb)
850	14.6	9.5	500	24.8	11.2
840	14.8	10.2	480	25.8	10.8
820	15.1	10.6	460	27.0	10.5
800	15.5	10.8	440	28.2	10.0
780	15.9	11.1	420	29.5	9.6
760	16.3	11.4	400	31.0	9.1
740	16.8	11.6	380	32.6	8.6
720	17.2	12.1	360	34.4	8.1
700	17.7	13.5	340	36.5	7.5
	Structure		320	38.7	6.9
610	20.3	11.6	300	41.3	6.3
600	20.7	11.7	290	42.8	5.9
580	21.7	11.8	280	44.3	5.6
560	22.1	11.8	270	45.9	5.3
540	23.0	11.7	260	47.7	5.0
520	23.8	11.5	250	49.6	4.7

and velocity V approximations. Their dipole length curve also follows the shape of the experimental curve, but lies slightly above it. His results also agree with the short-wavelength data below 160 Å. A recalculation by Henry[4] (H_2 in Fig. 4) included the effects of coupling between final-state channels. The dipole length results $H_2(L)$ give precise agreement in shape and magnitude between theory and experiment from threshold to 600 Å. However, towards shorter wavelengths the theory produces a step increase in the cross section at the ^5S threshold, which is not observed in the experimental data. The less rigorous approximations shown include those of Thomas and Helliwell[5] (TH), who used a central potential model, Kahler[6] (KA) and Koppel[7] (KO) using the scaled Thomas-Fermi method, and the independent-particle model used by Ganas[8] (G). Most of the calculations, with the exception of those by Kahler and Ganas, fall within the +15.4% and −20% experimental error limits.

We believe the present results provide a realistic picture of the photoionization cross sections of atomic nitrogen within the error limits quoted. Work is being initiated to measure the absolute cross section of atomic nitrogen at 584 Å. This would allow renormalization of the long-wavelength data and should decrease the absolute error limits.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (NSF) under Grant Nos. ATM-8617670 and PHY-8803911, and by the National Aeronautics and Space Administration under Grant No. NAGW-1751. It is with pleasure that we acknowledge the help of the personnel at the Stoughton Synchrotron Radiation Center, which is supported by NSF Grant No. DRM-8601349.

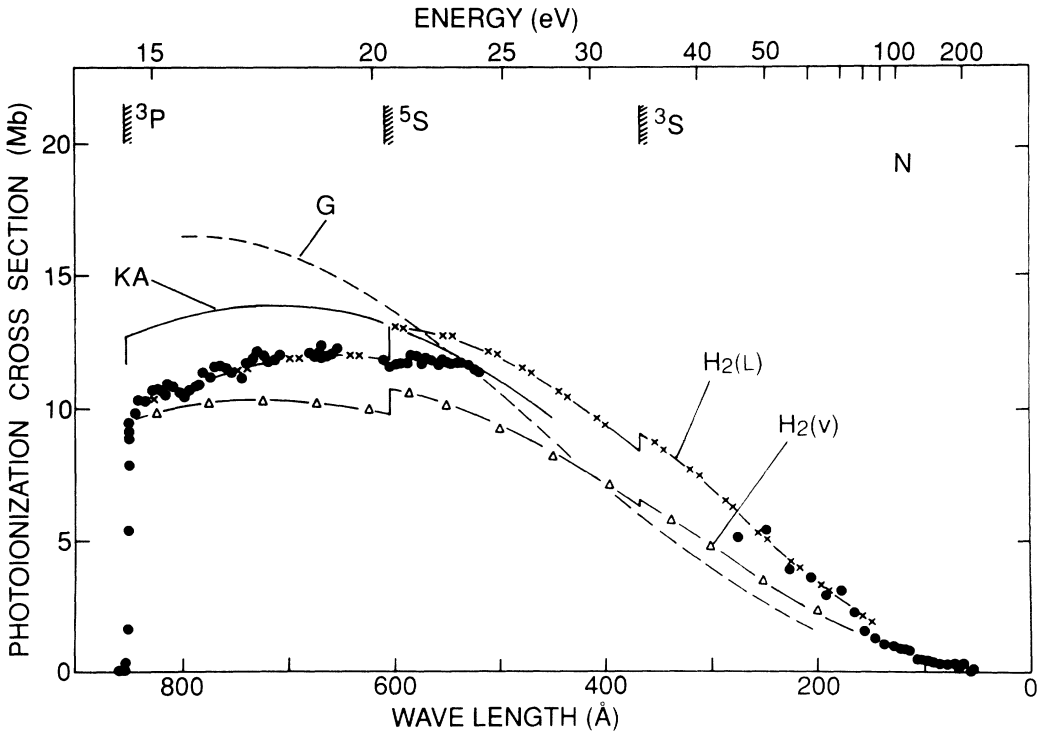

FIG. 4. Total photoionization cross section of atomic nitrogen as a function of wavelength. ●, present data; ——, KA, Ref. 6; -----, G, Ref. 8; —××, $H_2(L)$, Ref. 4; —△—, $H_2(V)$, Ref. 4.

*Present address: Eaton Corporation, Beverly, MA 01915.
[1]D. R. Bates and M. J. Seaton, Mon. Not. R. Astron. Soc. **109**, 698 (1949).
[2]A. Dalgarno and D. Parkinson, J. Atmos. Terr. Phys. **18**, 335 (1960).
[3]R. J. W. Henry, J. Chem. Phys. **44**, 4357 (1966).
[4]R. J. W. Henry, J. Chem. Phys. **48**, 3635 (1968).
[5]G. M. Thomas and T. M. Helliwell, J. Quant. Spectrosc. Radiat. Transfer **10**, 423 (1970).
[6]H. Kahler, J. Quant. Spectrosc. Radiat. Transfer **11**, 1521 (1971).
[7]J. U. Koppel, J. Chem. Phys. **55**, 123 (1971).
[8]P. S. Ganas, Phys. Ref. A **7**, 928 (1973).
[9]M. Le Dourneuf, Yo Ky Lan, and A. Hibbert, J. Phys. B **9**, L359 (1976).
[10]A. W. Ehler and G. L. Weissler, J. Opt. Soc. Am. **45**, 1035 (1955).
[11]F. J. Comes and A. Elzer, Phys. Lett. **25A**, 334 (1967); Z. Naturforsch. **23A**, 133 (1968).
[12]P. K. Carroll, R. E. Huffman, J. C. Larrabee, and Y. Tanaka, Astrophys. J. **146**, 553 (1966).
[13]P. M. Dehmer, J. Berkowitz, and W. A. Chupka, J. Chem. Phys. **60**, 2676 (1974).
[14]J. A. R. Samson and P. N. Pareek, Phys. Rev. A **31**, 1470 (1985).
[15]G. C. Angel and J. A. R. Samson, Phys. Rev. A **38**, 5578 (1988).
[16]W. Poshenrieder and P. Warneck, J. Appl. Phys. **37**, 2812 (1966).
[17]C. N. Burrous, A. J. Lieber, and V. T. Zavientseff, Rev. Sci. Instrum. **38**, 1477 (1967).
[18]B. Peart and M. F. A. Harrison, J. Phys. E **14**, 1374 (1981).
[19]J. A. R. Samson, T. Masuoka, P. N. Pareek, and G. C. Angel, J. Chem. Phys. **86**, 6128 (1987).
[20]L. De Reilhac and N. Damany, J. Quant. Spectrosc. Radiat. Transfer **18**, 121 (1977).
[21]D. R. Denne, J. Phys. D **3**, 1392 (1970).
[22]J. A. R. Samson, G. N. Haddad, and D. A. L. Kilcoyne, J. Chem. Phys. **87**, 6416 (1987).
[23]J. A. R. Samson, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates and I. Estermann (Academic, New York, 1966) Vol. 2, p. 237.
[24]B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, At. Data Nucl. Data Tables **27**, 1 (1982).
[25]J. Berkowitz, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy* (Academic, New York, 1979), p. 63.
[26]W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities,* Natl. Inst. Stand. Tech. (U.S.) Circ. No. 4 (U.S. GPO, Washington, D. C., 1966), Vol. I.