

Photoion and photoelectron spectroscopy of CO and N₂

J. L. Gardner, and James A. R. Samson

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Photoion and photoelectron spectroscopy of CO and N₂

J. L. Gardner and James A. R. Samson

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508
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Dissociative photoionization processes in CO and N₂ have been studied via photoion and photoelectron spectroscopy. Kinetic energy spectra of both the ions and electrons formed in CO and N₂ have been recorded with a calibrated energy analyzer at incident wavelengths of 584, 462, and 304 Å. The 304 Å spectra are correlated in energy and intensity to deduce dissociation products. For CO, the $^2\Sigma^+$ state of CO⁺ formed by removing a $\sigma 2s$ electron dissociates to the products C⁺ ($2p\ ^2P^0$) and O ($3s\ ^3D^0$). The N₂ ion and electron spectra at 304 Å both contain evidence for dissociative transitions involving the D $^2\Pi_g$ state of N₂⁺. Energetic N⁺ ions produced upon removal of a $\sigma_g 2s$ electron are best explained by a dissociation limit of N⁺ ($2p\ ^3\ ^3P^0$) and N ($2p\ ^3\ ^4S^0$).

INTRODUCTION

Although photoelectron spectroscopy has been widely applied as a tool for studying photoionization processes, comparatively few studies have been made of photoion kinetic energy spectra. Doolittle *et al.*¹ and Schoen and Doolittle² have measured oxygen and nitrogen photoion spectra as a function of the incident wavelength, and a number of photoelectron-photoion coincidence studies of predissociation have been reported³⁻⁷ in which the kinetic energy distributions of the ions have been inferred from flight times. Much more data exist for ions produced by electron impact.⁸ Spectra excited by electron impact are expected to be more complex because other than dipole transitions are allowed and positive-negative ion pair production is possible for all electron energies above the threshold. Under photon impact, the positive-negative ion pair process (lacking the continuum of states available when an electron is ejected) can occur only over a narrow spectral range.

Photoionization mass spectrometer studies⁹⁻¹³ show that in gases, dissociative ionization processes occur almost as soon as they are energetically allowed. Most mass spectrometers used for these experiments discriminate against energetic ions and thus underestimate the importance of dissociative ionization producing energetic particles.

The energetics of dissociative ionization are well known from application of the Franck-Condon principle.^{1,8} Knowledge of the ionization potential and the corresponding kinetic energy of the ionized fragment is sufficient to determine the dissociation limit of the electronic state. The current experiment was undertaken in an attempt to identify the dissociation limits of ionizing transitions which occur in N₂ and CO, and which are predicted to be dissociative.¹⁴⁻¹⁶ Our experimental technique relied on correlation of the energy and intensity of the photoions and photoelectrons at a given wavelength; the photoion and photoelectron spectra were recorded independently with an energy analyzer of known transmission.

EXPERIMENTAL

A cylindrical mirror energy analyzer¹⁷ with a pre-retarding lens was used to record the spectra presented here. Spectra are recorded by sweeping the voltage on the lens while holding constant the deflection potential

across the cylinders. This operating mode produces constant resolution across the spectrum. The collecting efficiency of the analyzer for electrons was calibrated to better than 10% over the energy range 0-28 eV.¹⁸ The ionizing radiation was produced in dc discharges in helium and neon and selected with a Vodar type grazing incidence monochromator.

Photoelectron spectra were recorded at a pass energy of 3 eV (resolution of 45 meV) and the photoion spectra at a pass energy of 10 eV (resolution of 150 meV). The 45 meV resolution in the electron spectrum is sufficient to resolve vibrational structure in the simple diatomic molecules. Linewidths are much greater in the ion spectra because the mass of the ionized fragment is comparable to the mass of the parent molecule, which has a random thermal distribution of velocities with respect to the incident beam. Half-widths of 0.6 eV for ions of energy 2 eV are typical for diatomic molecules.^{19,20} The peak corresponding to nondissociated ionization has the halfwidth of the Maxwell-Boltzmann distribution (64 meV at 300K).

The collecting efficiency for ions was not measured. However, the electron data indicated that the transmission of the analyzer is determined by the brightness-energy relationship of the retarding lens and that the magnetic field within the analyzer was sufficiently small not to affect the transmission.¹⁸ Thus the transmission of the analyzer should be the same for the ions and the electrons. However, the efficiency of the Channeltron electron multiplier may have differed for the atomic and molecular ions.²¹ The cone potential of the multiplier was held at -2.6 keV. As a check, the photoion spectrum of oxygen at 584 Å (consisting of room temperature O₂⁺ ions and 0.8 eV O⁺ ions from predissociation of the $B^2\Sigma_g^-$ state) was recorded with varying cone potentials; no significant change was observed in the relative population of the peaks for cone potentials less than -2.4 keV.

The analyzer geometry is such that electrons of different angular distributions are not discriminated against.¹⁷ This is a direct consequence of the angular distribution form for dipole transitions. Thus energetic ions with different angular distributions should also suffer no discrimination, as the thermal motion of the parent molecule does not alter the form of the angular distribution.²²

CARBON MONOXIDE

Photoelectron spectra

Photoelectron spectra of CO were recorded at wavelengths of 584, 462, and 304 Å. Dissociative transitions were only observed in the 304 Å spectrum; only that spectrum is relevant to the current discussion and is thus reproduced here. We have previously reported a dispersed 304 Å photoelectron spectrum for CO.¹⁶ The spectrum was re-recorded with a more stable digital scanning system (enabling better statistics to be obtained), with reduced low energy background (through better trapping of unwanted electrons in the source), and with the transmission of the analyzer calibrated over the whole energy range. The resulting spectrum is shown in Fig. 1; only those portions of the spectrum for which transitions could be observed are included in the figure.

Carbon monoxide has the following electronic configuration for the valence electrons: $(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. Each of the electronic bands appearing in the photoelectron spectrum corresponds to removal of an electron from one of the valence orbitals. The vibrational distributions within the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of CO⁺ agree closely with those measured at 584 Å.²³ No vibrational structure is evident in transitions to the $2\Sigma^+$ state formed by removal of a 3σ electron. Thus, either the potential energy curve for this state has no minimum near the Franck-Condon region, or it is crossed by a repulsive curve and predissociates in a time less than a vibrational period.

Potts and Williams²⁴ have also recorded a 304 Å CO photoelectron spectrum, using an undispersed lamp with a polystyrene filter to reduce the intensity of the 584 Å radiation. In addition to the states listed above, they report five further weak bands which were not observed in our data.

The background under the $2\Sigma^+$ state was scaled from an argon spectrum at 584 Å, recorded at the same pressure (2×10^{-4} Torr). The relative population (branching ratios) for the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, and $2\Sigma^+$ ($\sigma 2s$) states were then determined to be 17.9, 48.7, 22.9, and 10.5%, respectively.

The $2\Sigma^+$ ($\sigma 2s$) peak in our spectrum occurs approxi-

mately 2.4 eV higher in energy than the value given by Potts and Williams (and 1.4 eV higher than that determined from ESCA spectra²⁵). The population of the $2\Sigma^+$ ($\sigma 2s$) state, relative to the X , A , and B states, is then three times greater than that given by Potts and Williams.

Similar discrepancies were found for the 304 Å nitrogen photoelectron spectrum, as discussed below. These discrepancies illustrate the problems of recording photoelectron intensities with energy analyzers of uncalibrated transmission (and whose results depend on the angular distribution of the emitted electrons^{26,27}), and with filtered light sources which have not been shown to be monochromatic.

Photoion spectra

Ion kinetic energy spectra were recorded at exciting wavelengths of 584, 462, and 304 Å. Energy increments were known from calibration of the digital scanning system. The absolute energy scale was obtained from the peak of the Maxwell-Boltzmann distribution for the CO⁺ ions. Since this distribution is non symmetric in energy, convolution with the approximately Gaussian response of the analyzer, FWHM 150 meV, shifts the peak maximum from 25.8 to 46.0 meV at 293 K. Thus the energy scale was calibrated by assigning the CO⁺ peak maximum an energy of 46 meV.

The 462 Å spectrum is plotted in Fig. 2(a). The high energy tail extends beyond that predicted by the convolution of the Maxwell-Boltzmann distribution with a Gaussian response. This was true also for the 584 Å spectrum, indicating that the response of the analyzer is not a true Gaussian; this fact is also known from line shapes in electron spectra. However, at 462 Å dissociative ionization processes involving excitation and ionization are possible and are seen in photoionization mass-spectrometer studies. The data of El-Sherbini and Van der Wiel¹³ indicate that approximately 3% of the transitions at 462 Å are dissociative and that atomic ions of low kinetic energy are produced. These processes will account for some of the high energy tail in the 462 Å spectrum.

The 304 Å ion spectrum is plotted in Fig. 2(b). In addition to the large CO⁺ peak, a further broad peak ap-

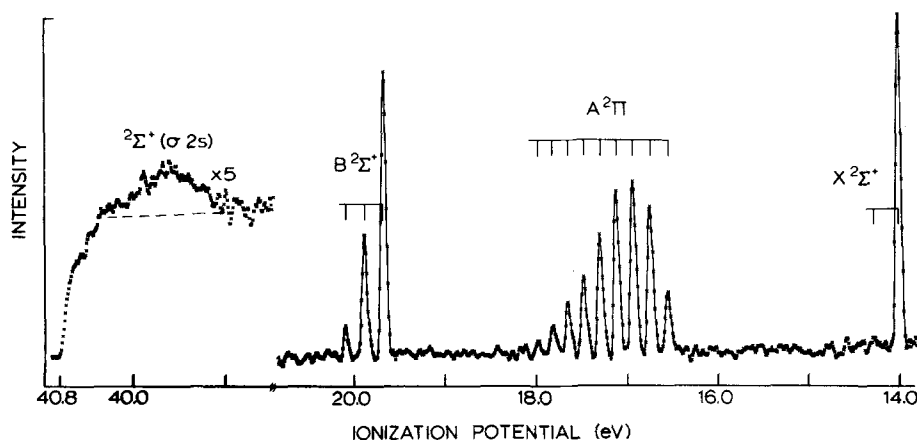


FIG. 1. Electron kinetic energy spectrum of CO at an exciting photon wavelength of 304 Å (40.8 eV), corrected for the analyzer transmission. The dashed line at low energy represents the scattered background. No peaks could be seen in the portion of the spectrum omitted from the figure.

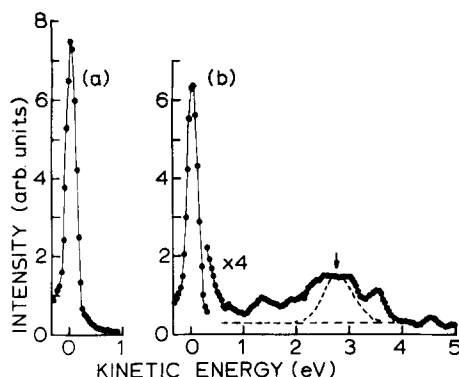


FIG. 2. Ion kinetic energy spectra of CO, corrected for the analyzer transmission, for incident photon wavelengths of (a) 462 Å and (b) 304 Å. The dashed peak in (b) was calculated as described in the text.

pears, centered about an energy of 2.77 eV. The smaller structure seen on this peak is an artifact of the least-squares smoothing that was applied to the raw spectrum. The spectrum plotted has been corrected for the analyzer transmission, assumed to be the same as for electrons. The actual count rate at the maximum of the energetic peak was 0.09 counts/sec.

Discussion

From the 304 Å ion spectrum, we estimate that approximately 22% of the ions formed are energetic. The error in this estimate is large because of the low count rates involved, the uncertainty in the transmission for ions, and the uncertainty in the relative detection efficiency for the various ions. From the 304 Å electron spectrum, we expect 11% of the ions to come from dissociative ionization of the $^2\Sigma^+$ state. The electron peak has a half-width of 1.2 eV. The corresponding half-widths for ions in the center of mass frame are 0.7 eV for C⁺ and 0.5 eV for O⁺. If these ions were produced with 2.77 eV of kinetic energy, the half-width expected in the ion spectrum in the laboratory frame would be 0.58 eV for C⁺ fragments and 0.67 eV for O⁺²⁰; convolution with the corresponding spread in electron energies yields an expected width of ≈ 0.9 eV. Ions are expected from dissociative transitions involving two electrons, but these are expected to have little kinetic energy,¹³ as in the 462 Å photoion spectrum.

The electron spectrum gives a vertical ionization potential for the $^2\Sigma^+$ state of 39.7 eV; thus the two possible dissociation limits are 33.23 and 34.85 eV for fragmentation into O⁺ and C⁺, respectively, referred to the CO ground state vibrationless level. Table I lists possible combinations of C⁺ with O and O⁺ with C in the energy range 32–36 eV.²⁸ Only combinations which can produce a doublet molecular state are considered.²⁹ The best agreement is with the dissociation limit C⁺($2p^2P^0$) + O($3s'^3D^0$).

Included in Fig. 2(b) is a calculated shape for the C⁺ fragments, assuming the suggested dissociation products. The theoretical distribution for a given kinetic energy released in the dissociation in the center of mass frame²⁰ was integrated over the Franck-Condon region, as

determined from the 304 Å electron spectrum. This convolution was then further convoluted with a 150 meV Gaussian response curve to give the calculated shape plotted in Fig. 2(b). The peak position is well fitted. The poor fit on the low energy side is partly caused by the low energy tail of the actual analyzer response. Further, the transitions reported by Potts and Williams²⁴ are also likely to be dissociative, and thus will contribute to the ion spectrum.

El-Sherbini and Van der Wiel¹³ report an increase in the C⁺ signal across the $^2\Sigma^+$ threshold, in agreement with the above prediction. Further, the $^2\Sigma^+$ state of CO⁺ is formed by the removal of a single electron from CO and a simple excitation of the dissociated products would be expected. The proposed dissociation limit corresponds to C⁺ in the ground state and O with an electron raised from a $2p$ orbital to a $3s$ orbital. This excited atom would produce radiation at 989 Å as it de-excites; no measurement of fluorescence of this wavelength in CO at exciting wavelengths short enough to remove a $3p$ electron have been reported.

NITROGEN

Photoelectron spectra

Photoelectron spectra of N₂ were recorded at incident wavelengths of 584, 462, and 304 Å; dissociative transitions were observed only in the 304 Å spectrum. Only that spectrum is reproduced here. The 304 Å spectrum, corrected for the analyzer transmission, is plotted in Fig. 3. Total accumulation time for the spectrum was 45 h, giving a statistical error in the count of about 5% in the high energy vibrational peaks, where the analyzer transmission was low, and also in the broad peak at low energy, where the transmission was high.¹⁸

The $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ states of N₂ are stable and do not produce energetic ions. The vibrational distributions over the $A^2\Pi_u$ and $B^2\Sigma_u^+$ states agree closely with those produced by continuum ionization at longer wavelengths.²³ However, the $v=1$ to $v=0$ intensity ratio of 13.1% for the $X^2\Sigma_g^+$ state is considerably higher than that seen at the longer wavelengths. The vibrational distri-

TABLE I. CO⁺ dissociation products and limits in the range 32–36 eV. Only products which can produce doublet molecular states are considered.

Products	Energy (eV)
O ⁺ ($2p^3^3D^0$) + C($3s^3P^0$)	35.514
C ⁺ ($2p^2P^0$) + O($3p^3P$)	33.348
C ⁺ ($2p^2D$) + O($2p^4^1D$)	33.616
C ⁺ ($2p^2P^0$) + O($4s^3S^0$)	34.290
C ⁺ ($2p^2S$) + O($2p^4^3P$)	34.323
C ⁺ ($2p^2P^0$) + O($3d^3D^0$)	34.446
C ⁺ ($2p^2P^0$) + O($4p^3P$)	34.718
C ⁺ ($2p^2P^0$) + O($3s'^3D^0$)	34.898
C ⁺ ($2p^2P^0$) + O($5s^3S^0$)	35.057
C ⁺ ($2p^2P^0$) + O($3s'^1D^0$)	35.008
C ⁺ ($2p^2P^0$) + O($4d^3D^0$)	35.118
C ⁺ ($2p^2P^0$) + O($5p^3P$)	35.237
C ⁺ ($2p^2P^0$) + O($6s^3S^0$)	35.398

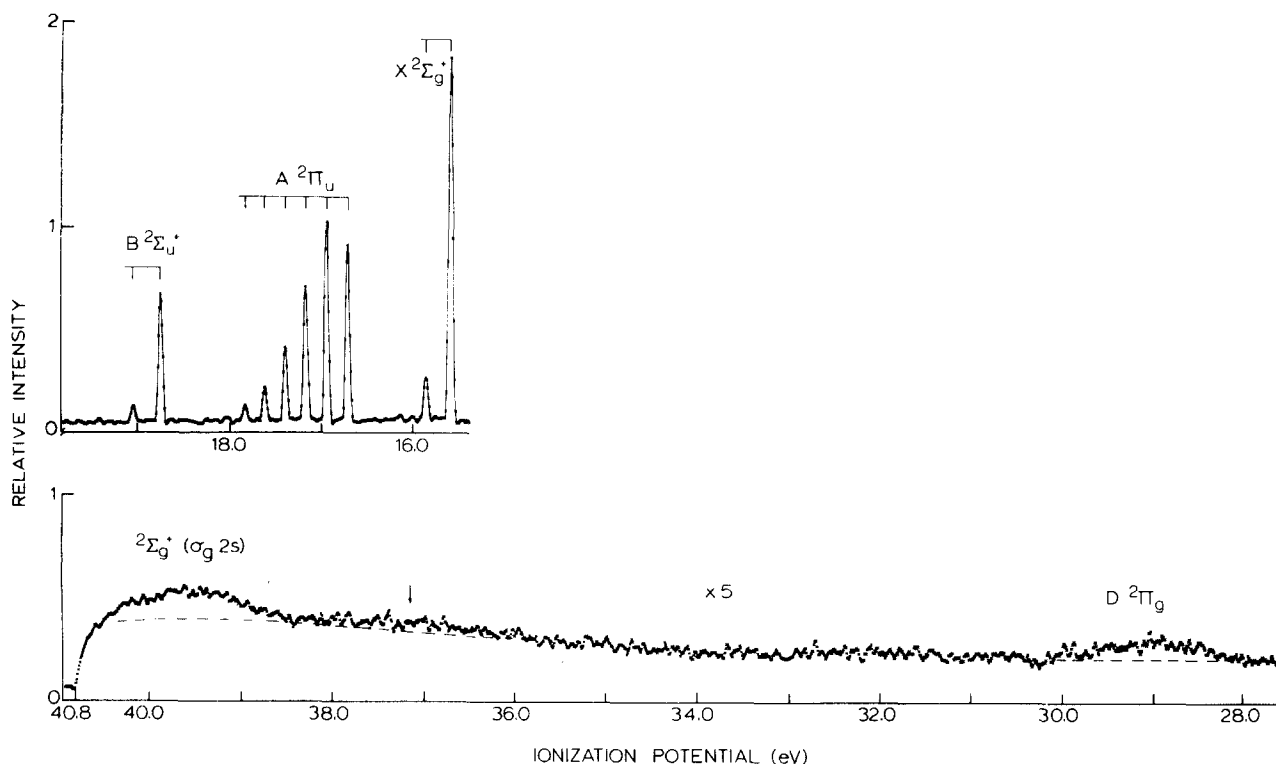


FIG. 3. 304 Å (40.8 eV) photoelectron spectrum of N₂. The data has been corrected for the transmission of the analyzer. No peaks could be seen in the portion of the spectrum omitted from the figure.

bution within the $X^2\Sigma_g^+$ state has also shown anomalous angular effects.³⁰

Three further broad peaks, with no evidence of vibrational structure, can be seen in the spectrum. These peaks result from transitions to states of N₂⁺ that dissociate to produce atomic ions. The strongest peak, with a vertical ionization potential of 39.8 eV, is associated with transitions to the $2\Sigma_g^+$ state formed by removal of a $\sigma_g 2s$ electron from N₂. Both the energy and intensity of this peak disagree significantly with the assignment of Potts and Williams,²⁴ which was derived from a photoelectron spectrum recorded with a filtered He discharge.

Potts and Williams suggest that the peak appearing at an ionization potential of 36.6 eV in their spectrum is due to transitions removing a $\sigma_g 2s$ electron; this peak probably corresponds to the weak peak at an energy near 37.1 eV in our spectrum.

Potts and Williams observe three further weak transitions; only one of these could be detected in our spectrum, that with an ionization potential of 29.0 eV. Potts and Williams suggest a number of transitions, involving configuration interaction, which could be responsible for this band. However this peak could be associated with transitions to the N₂⁺ $D^2\Pi_g$ state, which has been observed via optical spectroscopy.³¹ The configurations suggested by Gilmore³² for this level were not included by Potts and Williams. The intersection of the N₂ Franck-Condon region with an extrapolation of Gilmore's potential energy curve for the $D^2\Pi_g$ state lies near 29.0 eV,^{16,33} and thus in the following discussion, the band with an ionization potential of 29.0 eV is designated as corre-

sponding to transitions to the $D^2\Pi_g$ final state.

No transitions to the $C^2\Sigma_u^+$ state could be detected. This peak has been detected in spectra recorded with undispersed radiation, with an intensity about 8% of the $B^2\Sigma_u^+$ peak³⁴; these transitions were also observed by Potts and Williams.²⁴

The relative intensities of the peaks (expressed as a percentage of the total transitions seen) are $X^2\Sigma_g^+$, 27.1%; $A^2\Pi_u$, 41.0%; $B^2\Sigma_u^+$, 9.1%; Vert. I. P. 29.0 eV, 6.2%; Vert. I. P. 37.1 eV, 2.0% and $2\Sigma_g^+$ ($\sigma_g 2s$), 14.7%.

Photoion spectra

Photoion kinetic energy spectra of N₂ were recorded with a resolution of 150 meV at incident wavelengths of 584, 462, and 304 Å, corresponding to photon energies of 21.2, 26.9, and 40.8 eV, respectively. The energy scale for these spectra was calibrated by assigning the N₂⁺ peak maximum an energy of 0.046 eV, which represents the maximum of the Maxwell-Boltzmann distribution after convolution with a Gaussian analyzer response curve, FWHM 0.150 eV. The transmission of the analyzer for ions was assumed to be the same as for electrons and the spectra shown in Figs. 4 and 5 are corrected for this transmission.

The 584 and 462 Å ion kinetic energy spectra are plotted in Fig. 4. The tail of the 462 Å spectrum, Fig. 4(b), extends to higher energy than that of the 584 Å spectrum of Fig. 4(a). This difference may be due to dissociative transitions to the N₂⁺ $C^2\Sigma_u^+$ state,^{34,35} which are possible at 462 Å, but not at 584 Å. Transitions to the $C^2\Sigma_u^+$ state could not be detected in an electron kinetic

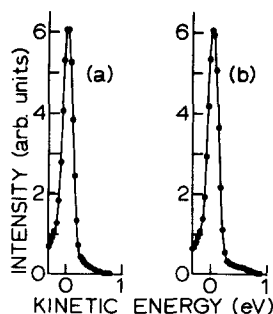


FIG. 4. Photoion kinetic energy spectra of N₂ at (a) 584 Å and (b) 462 Å. Both spectra are corrected for the analyzer transmission.

energy spectrum recorded at a wavelength of 462 Å.

The 304 Å photoion spectra of N₂ is plotted in Fig. 5. Before correcting for the analyzer transmission, the uniform background signal caused by noise in the detector (0.03 counts/sec) was subtracted. The small scale structure on the energetic peak is generated by the least squares smoothing of the data. The ratio of energetic (N⁺) ions to the N₂⁺ ions is 0.23, in excellent agreement with the data of Fryar and Browning.³⁶ Ions with energies up to 5 eV are detected, with a peak near 1.0 eV and an inflection near 2.5 eV. The origins of the energetic ions are postulated in the following section.

Discussion

The dominant energetic peak in the 304 Å ion energy spectrum is expected to coincide with dissociative transitions removing a $\sigma_g 2s$ electron from N₂; thus, the peak at 0.97 eV is assigned to these transitions. From the electron spectrum, the ionization potential at which this process is most probable is 39.8 eV; thus a dissociation limit near 37.86 eV is expected. Table II lists combinations of N and N⁺ levels with energies near 38 eV,²⁸ for which doublet molecular states are possible.²⁹ The closest limit to that expected is N (2p³4s⁰), with N⁺ (2p³3p⁰), i. e., N in its ground state and N⁺ with a 2s electron promoted to a 2p level. Such a simple excitation in the limit is in keeping with the excitation of a single electron excitation from a molecular orbital that is essentially a combination of the atomic 2s levels. A molecular ²Σ⁺ state with this limit is allowed by the Wigner-Wittmer correlation rules.²⁹

Assuming the above limit, the theoretical peak shape in the laboratory frame for ions from dissociative ionization²⁰ was integrated over the Franck-Condon region (read from the 304 Å spectrum) and convoluted with a 150 meV Gaussian analyzer response. The result is

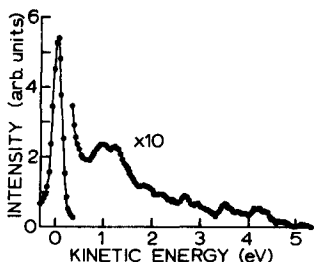


FIG. 5. Photoion kinetic energy spectrum of N₂ at 304 Å. Detector background counts have been subtracted and the data are corrected for the analyzer transmission.

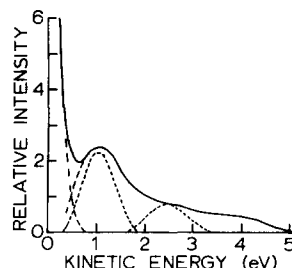


FIG. 6. Comparison of calculated distributions with the 304 Å data. The dashed lines at low energy represent subtraction of the N₂⁺ peak. The origin and normalization of the calculated peaks are discussed in the text.

plotted in Fig. 6 and compared with the experimental curve. The N₂⁺ ion distribution at 584 Å was subtracted from the 304 Å spectrum and the intensity of the calculated N⁺ distribution was normalized to the intensity of the N₂⁺ curve, as predicted from the 304 Å electron spectrum. Agreement between the calculated curve and the experimental data is seen to be good. The fragment from the predicted N⁺ (2p³3p⁰) limit should produce fluorescence at 916 Å as it de-excites; such fluorescence has been observed in electron impact studies^{37,38} with a measured onset of 40.8 eV. The electron impact data also show fluorescent radiation at 1085 Å with the same onset, from de-excitation of the N⁺ (2p³3d⁰) level; both processes occur mainly through optically forbidden mechanisms under electron impact.³⁸ Fluorescence from N₂ under photon impact has been observed in the wavelength band 1050–1240 Å, with a rise near the $\sigma_g 2s$ threshold.^{39,40} Radiation at wavelengths below 1050 Å could not be detected in that study. The closest limit to 37.8 eV involving the N⁺ (2p³3d⁰) level is a combination with N excited to the metastable 2p³2d⁰ level, at 38.119 eV; the distribution calculated with this limit retains much the same shape as that for the N⁺ (2p³3p⁰) and N (2p³4s⁰) limit, but the peak maximum shifts from 0.97 to 0.84 eV and the fit to the data is considerably worse.

From Fig. 11 of Ref. 40, the cross section for the process producing radiation in the 1050–1240 Å band, with an onset near 40 eV, is approximately 0.5 Mb, considerably less than the 1.7 Mb predicted from our electron spectrum. The process producing this radiation is probably a two-electron process whose Franck-

TABLE II. Dissociation products and limits for N, N⁺ combinations with energies near 38 eV. Only those combinations which can produce doublet molecular states are considered.

Products		Energy (eV)
N ⁺	N	
2p ² 3P	4s ² P	37.212
2p ² 3P	4p ⁴ S ⁰	37.662
2p ³ 3P ⁰	2p ³ 4S ⁰	37.841
2p ² 3P	5s ⁴ P	37.915
2p ² 3P	5s ² P	37.942
2p ² 3P	4d ⁴ F	37.963
2p ² 3P	4d ⁴ D	37.966
2p ² 3P	4d ² P	37.966
2p ² 3P	4d ² F	37.977
2p ³ 3D ⁰	2p ³ 2D ⁰	38.119
2p ² 1D	3p ² D ⁰	38.199
2p ² 1D	3p ² P ⁰	38.321

Condon region overlaps that of the $\sigma_g 2s$ electron removal, so that the processes producing radiation at 916 and 1085 Å cannot be distinguished in the electron spectrum or by different onsets.³⁷ If the two processes do overlap, the calculated peak near 1 eV (Fig. 6) should be reduced in height by 30% and this intensity transferred to the two-electron process. However, the peaks in the ion spectrum are not sufficiently well resolved to unambiguously assign the N ($2p^3 4S^0$) or N ($2p^3 2D^0$) level to accompany the N⁺ ($2p^3 3D_0$) level producing the 1085 Å fluorescence.

We have previously suggested that the dissociative transitions appearing in the 304 Å electron spectrum about a vertical ionization potential of 29.0 eV correspond to formation of the N₂⁺ $D^2 \Pi_g$ state.¹⁶ Such transitions have also been postulated to explain collision induced dissociation in N₂.³³ The dissociation limit for this state is N ($2p^3 4S^0$) + N⁺ ($2p^2 3P$) at 24.300 eV.³² Assuming this limit, the ion kinetic energy distribution was calculated for dissociative ionization to the $D^2 \Pi_g$ state, integrating over the Franck-Condon region as determined from the 304 Å electron spectrum. The distribution, peaking about 2.36 eV, is plotted in Fig. 6, normalized to the N₂⁺ distribution as predicted from the electron spectrum. The calculated peak provides a good explanation for the inflection in the data. Transitions to the $D^2 \Pi_g$ state would also explain the data of Schoen and Doolittle,² who reported ions with kinetic energies up to 3.1 eV at an exciting wavelengths of 358 Å (34.6 eV). Transitions to the $D^2 \Pi_g$ state are possible at this photon energy.

The transitions with an ionization potential near 29.0 eV may correspond to the configurations suggested by Potts and Williams,²⁴ and not the $D^2 \Pi_g$ configuration. If so, the discussion of the preceding paragraph shows that the dissociation limit of these transitions is N ($2p^3 4S^0$) + N⁺ ($2p^2 3P$) at 24.300 eV.

The energetic ions between 3 and 5 eV have the approximate intensity to originate with the weak dissociative peak appearing at a vertical ionization potential of 37.1 eV in the electron spectrum. The dissociation limit could be N⁺ ($2p^2 1D$) with either N ($2p^3 3D^0$) or N ($2p^3 3P^0$); the corresponding energies are 28.582 and 29.775 eV, respectively. All three of these levels are metastable.

Further weak two-electron dissociative transitions may be present in both of the 304 Å spectra.²⁴ Such weak broad peaks were not distinguishable from the background in the electron spectrum. However, most of the difference in the 304 Å ion spectrum between the sum of the theoretical peak shapes and the data is probably explained by the fact that the spectrometer response is not a true Gaussian; scattering is evident on the low side of a peak, and an extended tail appears on the high energy side.

ACKNOWLEDGMENT

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