Double-resonance spectroscopy of autoionizing states of N_2 near the ionization threshold

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Double-resonance spectroscopy of N_2 via the $a\ ^1\Pi_g$, $v'=5$ level has enabled the definitive assignment of a number of intense and heretofore unidentified bands observed in the single-photon spectrum in the region between the $X\ ^2\Sigma_g^+$ $v^+=0$ and 1 ionization thresholds. The results resolve several long-standing controversies concerning the assignment of Rydberg states of low principal quantum number that converge to the $A\ ^2\Pi_u$ and $B\ ^2\Sigma_u^+$ states of the ion and indicate that significant revisions of previous assignments are necessary. The spectra are discussed in the context of the entire manifold of states in this region, which includes high vibrational levels of the $b'\ ^1\Sigma_u^+$ valence state as well as Rydberg states that converge to the $X\ ^2\Sigma_g^+$, $A\ ^2\Pi_u$, and $B\ ^2\Sigma_u^+$ states of the ion.

I. INTRODUCTION

The single-photon absorption spectrum[1] of N_2 has been the subject of intense study for decades, yet many puzzles remain; one in particular involves a number of prominent unidentified bands in the energy region near the first ionization threshold. The failure to understand the threshold region is particularly striking in view of the considerable progress that has been made in understanding the spectrum at both longer and shorter wavelengths. The long-wavelength region of the dipole-allowed spectrum begins at about 1000 Å, and the complex appearance of the spectrum in this region is now understood to result from transitions to five electronic states—the $(X\ ^2\Sigma_g^+)3p\pi\ ^1\Pi_u$, $(X\ ^2\Sigma_g^+)3p\sigma\ ^1\Sigma_u^+$, and $(A\ ^2\Pi_u)3s\sigma\ ^1\Pi_u$ Rydberg states and the $b\ ^1\Pi_u$ and $b'\ ^1\Sigma_u^+$ valence states.[2–4] The higher members of the $(X\ ^2\Sigma_g^+)np\pi\ ^1\Pi_u$ and $(X\ ^2\Sigma_g^+)np\sigma\ ^1\Sigma_u^+$ Rydberg series that converge to $v^+=0$ are also well characterized.[5] In the region above the $v^+=1$ ionization threshold, the complicated absorption bands, which are broadened due to rapid decay by autoionization,[6] have been grouped into several Rydberg series and a number of vibrational progressions converging to the $A\ ^2\Pi_u$ and $B\ ^2\Sigma_u^+$ states of the ion.[5] Although these bands have not all been definitely correlated with electron configurations, the spectrum in this region shows considerable regularities. However, it is the region between, from just below to just above the $X\ ^2\Sigma_g^+$, $v^+=0$ ionization threshold, that has long been the subject of confusion and controversy. This region contains a number of intense features that must be due in part to Rydberg states of low principal quantum number that converge to the $A\ ^2\Pi_u$ and $B\ ^2\Sigma_u^+$ states of the ion; these features have been the object of considerable experimental[1,5–8] and theoretical[9–19] interest. Since it is important to the interpretation of the entire spectrum of molecular nitrogen that these Rydberg states of low principal quantum number be understood and be linked to their counterparts at higher principal quantum number, a number of efforts to assign the structure in this region are now ongoing.[20–22]

To provide a frame of reference for further discussion, Fig. 1 shows the single-photon ionization spectrum in the region near the $X\ ^2\Sigma_g^+$, $v^+=0$ ionization threshold, taken at a wavelength resolution of 2.5 cm^{-1} and a temperature of 78 K.[6] The $(X\ ^2\Sigma_g^+)np\sigma,\pi$ Rydberg complexes converging to $v^+=1$ are indicated; these transitions, which were first observed by Takamine and Tanaka[23] and later extended to high principal quantum number by Ogawa and Tanaka,[24] are extremely weak owing to the poor Franck-Condon overlap between $X\ ^1\Sigma_g^+$, $v''=0$ and $X\ ^2\Sigma_g^+$, $v^+=1$. Indeed, only the $8p$ complex is clearly identifiable in this spectrum; the higher np complexes are either overlapped by intense unidentified bands or are too weak to be conclusively assigned. The failure to assign the intense bands in this region results from an inability to resolve rotational structure in the single-photon spectrum and from poor correlations between the quantum defects of these bands and those of bands in other spectral regions.[2–6,24–32]

In the present paper, we report a new study in which double-resonance spectroscopy via numerous rotational levels of the $a\ ^1\Pi_g$, $v'=5$ level was used to probe the rotational structure of autoionizing bands between the $X\ ^2\Sigma_g^+$, $v^+=0$ and 1 ionization thresholds. This technique permits the observation of transitions from individual, selected rotational levels of the intermediate $a\ ^1\Pi_g$, $v'=5$ level, and it therefore greatly reduces spectral congestion in regions of overlapping or broadened bands. The spectrum was determined over the entire energy range from the first ionization threshold at $\sim 125\,667$ to $\sim 126\,850$ cm^{-1}; however, the present discussion is limited to the diffuse, unidentified bands shown in Fig. 1. Our results provide definitive assignments of many of these bands and indicate that significant revisions of previous assignments are necessary. The results are discussed in the context of the entire manifold of states in this region, which includes high vibrational levels of the $b'\ ^1\Sigma_u^+$ valence state as well as Rydberg states that converge to the $X\ ^2\Sigma_g^+$, $A\ ^2\Pi_u$, and $B\ ^2\Sigma_u^+$ states of the ion.

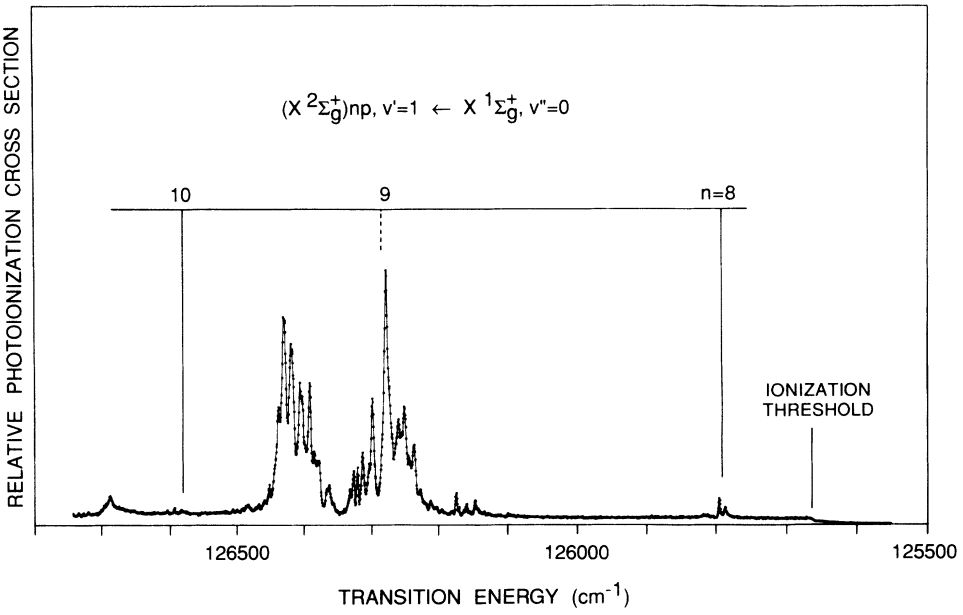

FIG. 1. Relative single-photon ionization cross section near the $X\,^2\Sigma_g^+$ $v^+=0$ ionization threshold taken at a wavelength resolution of 2.5 cm^{-1} and a temperature of 78 K (from Ref. 6).

II. EXPERIMENT

Two Nd:YAG-pumped dye laseres were used as the pump and probe lasers (YAG denotes yttrium aluminum garnet). The pump laser was used to excite specific two-photon $a\,^1\Pi_g$, $v'=5,J'\leftarrow X\,^1\Sigma_g^+$, $v''=0,J''$ transitions, and the probe laser was used to scan single-photon transitions from the selected $a\,^1\Pi_g$, $v'=5,J'$ level to the ionization continuum and to quasidiscrete autoionizing states. In the following discussions, levels of the $X\,^1\Sigma_g^+$ ground state are labeled by double primes, levels of the $a\,^1\Pi_g$ state are labeled by single primes, levels of the autoionizing states are labeled by an absence of superscripts, and levels of the ion are labeled by a superscript plus.

Pump laser light at ~260 nm with a pulse energy of ~300 μJ was produced by frequency doubling the output of a dye laser operated at ~520 mn in potassium dihydrogen phosphate (KDP). Probe laser light at ~205 nm with a pulse energy of ~15 μJ was produced by frequency tripling the output of a dye laser operated at ~615 nm. The frequency tripling was performed by first frequency doubling the fundamental beam in KDP. The fundamental and doubled beams then were separated, the polarization of the fundamental beam was rotated to match that of the doubled beam, and the beams were recombined and frequency mixed in β-BaB_2O_4. The pump and probe beams were focused colinearly into the interaction region by using a 15-cm focal-length lens. The probe pulse was delayed ~20 nsec from the pump pulse. The optogalvanic spectra of uranium and neon[33] were used to calibrate the wavelength of the probe laser. The transition energy is estimated to be accurate to ± 1 cm^{-1}, with the main source of uncertainty arising from nonlinearities in the wavelength drive of the probe laser.

The detection apparatus consists of a time-of-flight mass spectrometer and an electron energy analyzer,[34] only the mass spectrometer was used in the present experiment. The N_2 sample gas was introduced into the interaction region through an effusive jet. The background pressure in the chamber was 7×10^{-5} Torr, and the pressure in the ionization region was estimated to be 10–100 times higher. Ions were collected by using a pulsed drawout field of 12.5 V, delayed 50 nsec after the probe laser pulse, and were detected by a channeltron. A charge-sensitive analog-to-digital converter was used to average the ion signal over ten laser shots per point.

III. SPECTROSCOPIC BACKGROUND

Transitions from the $X\,^1\Sigma_g^+$ ground state may access states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry, while transitions from the $a\,^1\Pi_g$ state may access states of $^1\Sigma_u^+$, $^1\Pi_u$, and $^1\Delta_u$ symmetry. In principle, triplet states may also be excited; however, such transitions are expected to be weaker than the corresponding singlet transitions. Indeed, none of the bands observed here have been observed in studies of the photoionization of the $E\,^3\Sigma_g^+$ state,[35,36] and all of the states observed in the present work have been assigned as the more likely singlet states. A complete list of the single valence states and Rydberg series expected in the energy region considered in the present work is given in Table I.

Attempts to assign the observed Rydberg series and the diffuse bands observed near threshold to the electron configurations given in Table I have relied heavily on theoretical considerations and have shown considerable

TABLE I. Possible electronic transitions excited from the $X\,^1\Sigma_g^+$ and the $a\,^1\Pi_g$ states in the region between the $X\,^2\Sigma_g^+$, $v^+=0$ and 1 ionization thresholds.

Transition[a]	Excited-state description or preferred Rydberg-Series designation[b]
$b'\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	Valence state with configurations[c] $(1\pi_u)^4(3\sigma_g)^1(1\pi_g)^0(3\sigma_u)^1$ and $(1\pi_u)^3(3\sigma_g)^2(1\pi_g)^1(3\sigma_u)^0$
$(X\,^2\Sigma_g^+)np\sigma\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	Carroll-Yoshino series ($v^+=0$) Takamine-Tanaka series ($v^+=1$)
$(X\,^2\Sigma_g^+)np\pi\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	Worley-Jenkins series
$(A\,^2\Pi_u)ns\sigma\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	o_n series
$(A\,^2\Pi_u)nd\sigma\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	Ogawa-Tanaka series
$(A\,^2\Pi_u)nd\pi\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	(d)
$(A\,^2\Pi_u)nd\pi\,^1\Delta_u \leftarrow a\,^1\Pi_g$	*(Not observed)*
$(A\,^2\Pi_u)nd\delta\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	Worley's third series
$(B\,^2\Sigma_u^+)ns\sigma\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ or $a\,^1\Pi_g$	New Ogawa-Tanaka absorption series

[a]Relevant electron configurations for initial states are $X\,^1\Sigma_g^+$ $(1\pi_u)^4(3\sigma_g)^2$, $a\,^1\Pi_g$ $(1\pi_u)^4(3\sigma_g)^1(1\pi_g)^1$.
[b]Rydberg-series designations are those from $X\,^1\Sigma_g^+$ state.
[c]Electron configurations are from Ref. 44. The two configurations are weighted about equally.
[d]$(A\,^2\Pi_u)\,3d\pi\,^1\Sigma_u^+$, $v=0$ member observed by Roncin, Launay, and Yoshino.

disagreement over the years. Two recent assignments of series in the region considered here have been given by Kosman and Wallace[17] and by Lefebvre-Brion and Yoshino.[19]

Based on calculated quantum defects and dipole oscillator strengths, Kosman and Wallace[17] have assigned Worley's third series[24,29] to the $(A\,^2\Pi_u)nd\delta\,^1\Pi_u$ configuration; the less-intense Ogawa-Tanaka[24,29] series to the $(A\,^2\Pi_u)nd\sigma\,^1\Pi_u$ configuration; the $o_3\,^1\Pi_u$ Rydberg state[28] to the $n=3$ member of the $(A\,^2\Pi_u)ns\sigma\,^1\Pi_u$ configuration; and the new Ogawa-Tanaka absorption series to the $(B\,^2\Sigma^+)ns\sigma\,^1\Sigma_u^+$ configuration. Note that the $n=3$ member of the $(B\,^2\Sigma_u^+)ns\sigma\,^1\Sigma_u^+$ series, which is expected to appear in the region considered here, is the subject of considerable controversy. Although Carroll and Hagim[37] have assigned a band at 124 299 cm^{-1} as $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$, $v=0$, this assignment has been questioned by Huber and Jungen;[8] to date, there is no definitive assignment of this lowest member of the New Ogawa-Tanaka series.

A somewhat different interpretation of the spectrum in this region has been tentatively proposed by Lefebvre-Brion and Yoshino.[19] They offer the same assignment for Worley's third series as Kosman and Wallace[17] but assign the Ogawa-Tanaka series to the $(A\,^2\Pi_u)nd\delta\,^3\Pi_u$ configuration. They further assign the progressions denoted 1, 2, and 3 by Ogawa[25] to the $(A\,^2\Pi_u)nd\sigma\,^1\Pi_u$ configuration. In the energy region near the ionization threshold shown in Fig. 1, they propose that the band at $\sim$126 280 cm^{-1} is $(A\,^2\Pi_u)3d\delta\,^1\Pi_u$, $v=2$; the band at $\sim$126 400 cm^{-1} is $(A\,^2\Pi_u)3d\sigma\,^1\Pi_u$, $v=1$ (note that the assignment of these two bands reverses an earlier assignment of Giusti-Suzor and Lefebvre-Brion[16]); and the band at $\sim$126 690 cm^{-1} is $(A\,^2\Pi_u)3d\delta\,^3\Pi_u$, $v=3$ of the Ogawa-Tanaka series.

Considerable additional information on the bands in the region near the ionization threshold has come from the recent work of Huber and Jungen,[8] who determined the high-resolution, single-photon absorption spectrum of jet-cooled N_2. They reported in detail on the transitions to the $b'\,^1\Sigma_u^+$ valence state; the $(X\,^2\Sigma_g^+)np\sigma\,^1\Sigma_u^+$, $(X\,^2\Sigma_g^+)np\pi\,^1\Pi_u$, and $(X\,^2\Sigma_g^+)nf$ Rydberg states; and the $(A\,^2\Pi_u)3d\delta\,^1\Pi_u$, $v=0$ member of the Worley's third Rydberg series. The low sample temperature achieved in that work enabled detailed analyses of the $(X\,^2\Sigma_g^+)np$ and $(X\,^2\Sigma_g^+)nf$ series; however, even with only a few rotational levels thermally populated, significant broadening of many of the bands converging to the $A\,^2\Pi_u$ and $B\,^2\Sigma_u^+$ states of the ion made their analyses difficult or impossible. Because the present double-resonance technique enables excitation from a single selected rotational level, the observation of resolved rotational structure is possible even for such severely broadened bands.

IV. RESULTS AND DISCUSSION

Figure 2 shows a representative double-resonance ionization spectrum in the energy region of the diffuse bands shown in Fig. 1, excited via the $P(4)$ pump transition. A total of 12 two-photon pump transitions were employed: $P(2)$, $P(4)$, $P(5)$, $P(6)$, $P(7)$, $Q(1)$, $S(0)$, $S(1)$, $S(2)$, $S(10)$, $S(11)$, and $S(12)$.[31] The transition energies are referenced to the $X\,^1\Sigma_g^+$, $v''=0, J''=0$ ground state by using the known $a\,^1\Pi_g$, $v'=5, J' \leftarrow X\,^1\Sigma_g^+$, $v''=0, J''$ transition energies[38] and the ground-state rotational intervals.[39] The background signal is due to (2+2) photoionization of N_2 by the pump laser.

Because of the one-photon selection rule $+\leftrightarrow-$, the allowed rotational branches in transitions excited from an $a\,^1\Pi_g$, $v'=5, J'$ level depend both on the pump transition to the $a\,^1\Pi_g$ state and on the symmetry of the final state.[40] Pump transitions via O, Q, and S branches populate the Λ^+ component of the $a\,^1\Pi_g$ state, while those via P and R branches populate the Λ^- component. It is straightforward to determine that only P and R branches will be excited in $^1\Sigma_u^+ \leftarrow a\,^1\Pi_g^+$ probe transitions, while

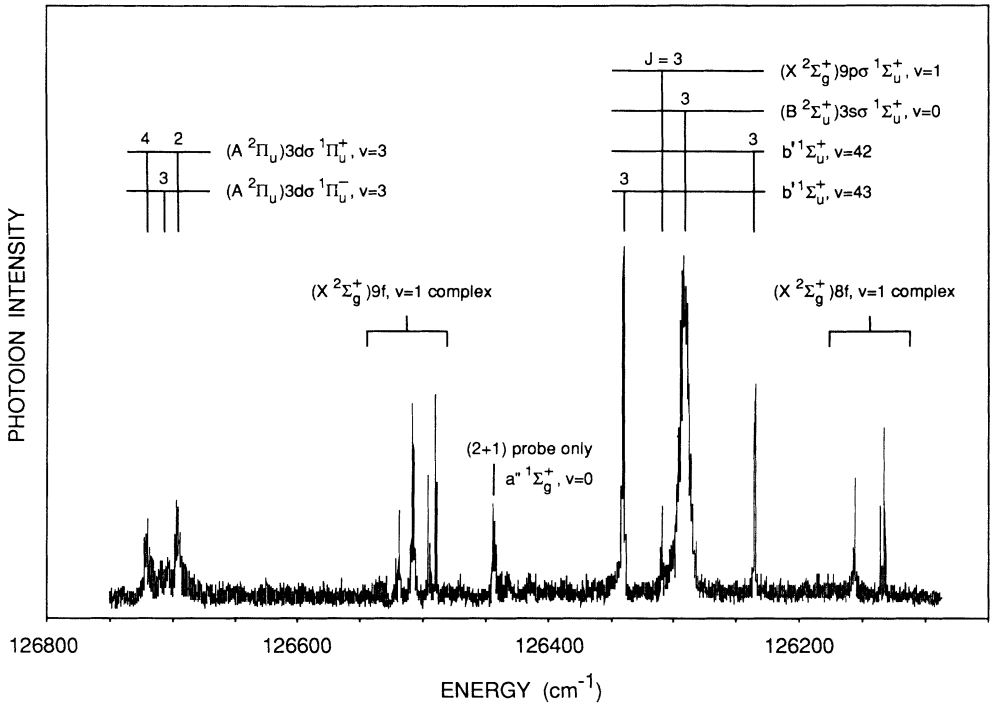

FIG. 2. The (2+1′) ionization spectrum via the $P(4)$ pump transition in a small region of the spectrum. The energy is referenced to $X\,^1\Sigma_g^+$ $v''=0, J''=0$.

only Q branches will be excited in $^1\Sigma_u^+ \leftarrow a\,^1\Pi_g^-$ probe transitions. Of course, all three P, Q, and R branches will be excited in $^1\Pi_u$ or $^1\Delta_u \leftarrow a\,^1\Pi_g$ probe transitions, since each rotational level of a Π or a Δ state has both plus and minus parity levels. Thus, a comparison of the observed branches from different levels of the $a\,^1\Pi_g$, $v'=5$ state helps to determine the symmetry of the final autoionizing states. In addition to the pattern of branches excited from the different levels of the $a\,^1\Pi_g$ state, the observation of low-lying rotational levels of the final autoionizing states also aids in the symmetry determination; $^1\Pi$ states will be missing $J=0$ levels, and $^1\Delta$ states will be missing $J=0$ and 1 levels.

Four main results are derived from the present work. First, the intense band at 126 280 cm^{-1} in the single-photon spectrum is a composite of transitions to four individual $^1\Sigma_u^+$ states. Second, the weak feature at 126 690 cm^{-1} in the single-photon spectrum is a transition to a $^1\Pi_u$ state. Third, the intense band at 126 400 cm^{-1} in the single-photon spectrum is absent in the present double-resonance spectrum. Fourth, two weak features in the single-photon spectrum are due to excitation of f complexes (Fig. 2); these complexes currently are being analyzed both by Huber and Jungen[20] and by us.[22]

Table II summarizes the term energies and rotational constants B_v for all of the states discussed in the present paper. In the following discussion, we first consider the assignment of the $^1\Pi_u$ state at 126 690 cm^{-1}; we then discuss the assignment of the four $^1\Sigma_u^+$ states at $\sim$126 280 cm^{-1}, and we finally present a tentative assignment for the band at $\sim$126 400 cm^{-1} observed only in the single-photon spectrum.

The $^1\Pi_u$ state at 126 690 cm^{-1} is readily seen to be the $n=3$, $v=3$ level of the Ogawa-Tanaka series based both on its term energy (the $n=3$, $v=0$ member is at 121 121 cm^{-1},[8] and the observed $n=3$, $v=0$–3 splitting of 5566 cm^{-1} is in good agreement with the $A\,^2\Pi_u$, $v^+=0$–3 splitting[41] of 5530.2 cm^{-1}) and on the observed rotational constants, which are in excellent agreement with those obtained by Huber and Jungen[8] for the $n=3$, $v=0$ level of this state. As already noted, members of the Ogawa-Tanaka series have been previously assigned $(A\,^2\Pi_u)nd\sigma\,^1\Pi_u$ by Kosman and Wallace[17] and $(A\,^2\Pi_u)nd\delta\,^3\Pi_u$ by Lefebvre-Brion and Yoshino.[19] Lefebvre-Brion and Yoshino[19] propose that the triplet transitions gain oscillator strength through mixing with members of the $(A\,^2\Pi_u)nd\delta\,^1\Pi_u$ (Worley's third) series; however, Huber and Jungen[8] argue convincingly that the observed relative intensities of members of the Ogawa-Tanaka and Worley's third series favor the $(A\,^2\Pi_u)nd\sigma\,^1\Pi_u$ assignment. Thus, we assign this band $(A\,^2\Pi_u)3d\sigma\,^1\Pi_u$, $v=3$.

Next, we consider the four $^1\Sigma_u^+$ states at 126 280 cm^{-1}; three of these states are straightforwardly assigned from the term energies and rotational constants given in Table II. The two states with rotational constants of 1.02 and 0.78 cm^{-1} are assigned $b'\,^1\Sigma_u^+$, $v=42$ and 43, respectively. The observed term energies of the $b'\,^1\Sigma_u^+$, $v=42$ and 43 levels of 126 223.0 and 126 331.1 cm^{-1} are in reasonable agreement with predicted term energies of 126 206 and 126 385 cm^{-1}, respectively, calculated from the vibrational constants of Stahel, Leoni, and Dressler.[4] The

TABLE II. Term energies and rotational constants for observed electronic states. All term energies and rotational constants are in units of cm^{-1}. Values of B_v were obtained by fitting the energies of rotational levels with $J<7$ to the function $E=B_vJ(J+1)$. In general, higher rotational levels were not used because rotational uncoupling at high J causes a departure from the $J(J+1)$ energy dependence. Errors in B_v are estimated to be ± 0.05 cm^{-1}. Uncertainties in the rotational term energies were sufficiently large to prevent accurate determinations of values of D_v.

J	$(X\,^2\Sigma_g^+)9p\sigma\,^1\Sigma_u^+$ $v=1$	$(A\,^2\Pi_u)3d\sigma\,^1\Pi_u, v=3$ $^1\Pi_u^+$	$^1\Pi_u^-$	$(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$, $v=0$	$b'\,^1\Sigma_u^+$, $v=42$	$b'\,^1\Sigma_u^+$, $v=43$
0	126 281.0			126 269.5	126 223.0	126 331.1
1	126 286.1	126 689.8	126 690.1	126 272.9	126 224.8	126 332.5
2		126 695.2	126 696.1	126 278.9	126 228.9	126 334.8
3	126 309.0	126 705.5	126 706.6	126 290.6	126 234.9	126 339.2
4	126 326.7	126 720.8	126 722.2	126 304.5	126 242.9	126 344.6
5	126 348.8	126 734.9	126 738.4	126 321.7	126 253.2	126352.8
6				126 339.8	126 266.4	126 364.3
11				126 526.4		
12	126 591.8		126 945.5			
13	126 654.2	126 980.5		126 612.6	126 386.1	126 494.5
14				126 668.3		
15	126 774.2					126 527.4
	$B_1=2.23$	$B_3=1.63$	$B_3=1.73$	$B_0=1.70$	$B_{42}=1.02$	$B_{43}=0.78$

discrepancies between observed and calculated term energies are similar in magnitude to those found by Huber and Jungen[8] for vibrational levels of the $b'\,\Sigma_u^+$ state in the range $v=32-40$. These discrepancies are not surprising because the vibrational levels of the $b'\,^1\Sigma_u^+$ state are known to be severely perturbed by the np complexes converging to $X\,^2\Sigma_g^+$, and it is expected that they will also be perturbed by states converging to $A\,^2\Pi_u$ or $B\,^2\Sigma_u^+$. Indeed, the ionization spectra shown in Fig. 3, excited via a number of $P(J)$ pump transitions, show that the $b'\,^1\Sigma_u^+$, $n=43$ level interacts strongly with at least one of the other $^1\Sigma_u^+$ states in this region, resulting in rather severe energy-level shifts and intensity alterations, as discussed below. Figure 1 shows that the $b'\,^1\Sigma_u^+$, $v=43$ level, which accounts for much of the structure in the region 126 300–126 330 cm^{-1}, is unusually intense in the single-photon spectrum as a result of these interactions.

The state with the rotational constant of 2.23 cm^{-1} is assigned $(X\,^2\Sigma_g^+)9p\sigma\,^1\Sigma_u^+$, $v=1$ on the basis of its term energy (the observed $n=9$, $v=0-1$ splitting of 2172.5 cm^{-1} is in excellent agreement with the $X\,^2\Sigma_g^+$, $v^+=0-1$ splitting[41] of 2174.8 cm^{-1}) and rotational constant, which is similar to that of the other $(X\,^2\Sigma_g^+)np\sigma\,^1\Sigma_u^+$, $v=1$ levels[8] and somewhat higher than that of the $X\,^2\Sigma_g^+$, $v^+=1$ state of the ion (1.903 cm^{-1}) (Ref. 41) due to the effect of l uncoupling.[8] The corresponding $(X\,^2\Sigma_g^+)9p\pi\,^1\Pi_u$, $v=1$ level is obscured by the broad, intense $^1\Sigma_u^+$ state discussed below.

The final $^1\Sigma_u^+$ state now remains to be assigned. It must be a Rydberg state converging to the $A\,^2\Pi_u$ or the $B\,^2\Sigma_u^+$ state of the ion; the summary of possible electronic states excited from $X\,^1\Sigma_g^+$ and/or $a\,^1\Pi_g$ given in Table I shows that the only possible electron configurations are $(A\,^2\Pi_u)nd\pi\,^1\Sigma_u^+$ and $(B\,^2\Sigma_u^+)ns\sigma\,\Sigma_u^+$. In order to choose between these and to assign the n and v values, it is necessary to use information derived from this and from other experiments; such information includes quantum defects, term energies, rotational constants, and Franck-Condon factors. For both possible electron configurations, the only value of the principal quantum number that provides a reasonable quantum defect is $n=3$.[42] The assignment of the vibrational quantum number is somewhat more difficult, but considerable information is provided from observed transition intensities. In particular, the single-photon ionization spectrum[6] shows that the band under consideration is very intense in the spectrum excited from $X\,^1\Sigma_g^+$ $v''=0$ but is absent in the spectrum excited from $X\,^1\Sigma_g^+$ $v''=1$. The Franck-Condon factors[43] for excitation from $X\,^1\Sigma_g^+$ $v''=0$ and 1 show that the only vibrational levels consistent with this observation are $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$, $v=1$ or 2 and $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma a_u^+$, $v=0$. Furthermore, the very small Franck-Condon factor (0.008) (Ref. 43) for the $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$, $v=1\leftarrow a\,^1\Pi_g$, $v'=5$ transition almost certainly eliminates $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$, $v=1$ as a possible final state. Thus, the two most likely electron configurations are $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$, $v=2$ (which yields $n^*=3.00$ and $\delta=0.00$) and $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$, $v=0$ (which yields $n^*=2.10$ and $\delta=0.90$). The resulting quantum defects are both reasonable. We have chosen to assign the band in question as $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$, $v=0$ for two reasons. First, the assignment of $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$, $v=0$ to the band at 126 269.5 cm^{-1} is consistent with the assignment by Helm and Cosby[35] of $(B\,^2\Sigma_u^+)3s\sigma\,^3\Sigma_u^+$, $v=1$ to a triplet band at 126 910 cm^{-1}. The experimental singlet-triplet splitting [obtained by assuming that the $(B\,^2\Sigma_u^+)3s\sigma$, $v=0-1$ splitting is identical to that of the ionic convergence limit] is then 1730 cm^{-1}, which is in reasonable agreement with the calculated value[18] of 2190 cm^{-1}. Note that the discrepancy between experiment and theory for the singlet-triplet splitting of the $(B\,^2\Sigma_u^+)3s\sigma$ state (460 cm^{-1}) is about the same as the

discrepancy for the singlet-triplet splitting of the $(X\,^2\Sigma_g^+)3s\sigma$ state (424 cm^{-1}). Second, Roncin, Launay, and Yoshino[7] have recently assigned the $(A\,^2\Pi_u)3d\pi$, $v=0$ level to a weak band at 123 309 cm^{-1}; the separation between this band and the band under consideration is 2960.5 cm^{-1}, which does not agree well with the $A\,^2\Pi_u$, $v^+=0-2$ splitting[41] of 3716.8 cm^{-1}.

Figure 3 shows ionization spectra excited via several $P(J)$ pump transitions in the energy region of the four $^1\Sigma_u^+$ states between 126 200 and 126 400 cm^{-1}. It is interesting to note the striking intensity variations as a function of J'. For $J'=1$, the transitions to the $(B\,^2\Sigma_u^+)3s\sigma$, $v=0$ and $b'\,^1\Sigma_u^+$, $v=42$ levels are both quite intense. However, for $J'=6$, the transitions to both of these levels are considerably weaker, with the intensity shifted primarily to the transition to the $b'\,^1\Sigma_u^+$, $v=43$ level; the $b'\,^1\Sigma_u^+$, $v=43$ level also appears to broaden in the spectra taken via higher J' values. Also note the appearance of a weak unidentified band to the red of the $b'\,^1\Sigma_u^+$, $v=42$ level in the spectra excited via $J'=5$ and 6. The linewidths of the $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$, $v=0$ transitions are ~ 4 cm^{-1}, yielding a decay rate, $k=2\pi c\Gamma$, of 7.5×10^{11} sec^{-1} for this state.

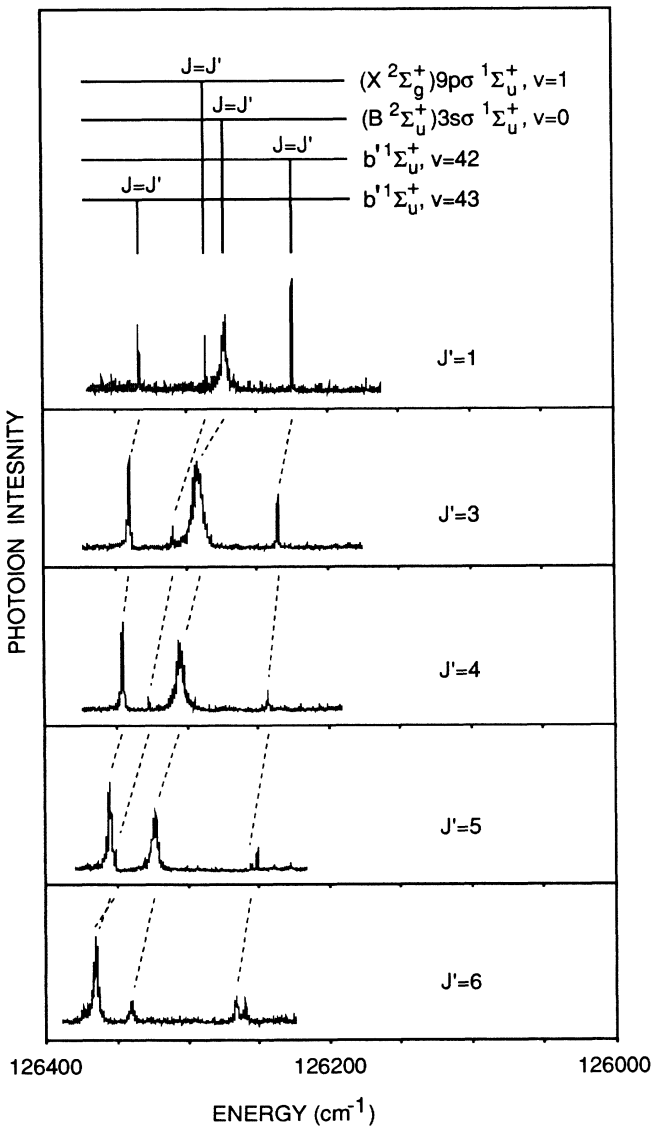

FIG. 3. The (2+1′) ionization spectra via several $P(J)$ pump transitions in a small region of the spectrum. The energy is referenced to $X\,^1\Sigma_g^+$ $v''=0, J''=0$.

Finally, the band observed at $\sim 126\,400$ cm^{-1} in Fig. 1 is not observed in either the present spectrum excited from $a\,^1\Pi_g$, $v'=5$ or the spectrum excited from $X\,^1\Sigma_g^+$, $v''=1$.[6] Without a rotational analysis of the band, it is not possible to make a definitive assignment; however, we suggest that this band is $(A\,^2\Pi_u)4s\sigma\,^1\Pi_u$, $v=2$ for the following reasons. First, using arguments based on Franck-Condon factors as discussed above and on the magnitudes of quantum defects, we believe that the band is either $(A\,^2\Pi_u)3d\lambda$, $v=2$ (where $\lambda=\sigma$, π, or δ) or $(A\,^2\Pi_u)4s\sigma\,^1\Pi_u$, $v=2$. We can readily eliminate three of these four possibilities. The $(A\,^2\Pi_u)3d\sigma\,^1\Pi_u$, $v=2$ level is eliminated as it already has been assigned to the band at 124 870 cm^{-1};[8] the $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$, $v=2$ level is eliminated for the reasons discussed above, namely that the $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$, $v=0$ level has been assigned to a band at 123 309.5 cm^{-1}, and the $A\,^2\Pi_u$, $v^+=0-2$ vibrational splitting is not consistent with the band under consideration;[7] and the $(A\,^2\Pi_u)3d\delta\,^1\Pi_u$, $v=2$ level is eliminated as it has already been tentatively assigned to a broad feature at $\sim 125\,830$ cm^{-1}.[20] The only remaining possibility is $(A\,^2\Pi_u)4s\sigma\,^1\Pi_u$, $v=2$, which results in values of $n^*=3.02$ and $\delta=0.98$. These values are in good agreement with the experimental values of $n^*=1.95$ and $\delta=1.05$ obtained for $(A\,^2\Pi_u)3s\sigma\,^1\Pi_u$, $v=2$ (i.e., the $v=2$ level of the o_3 state).[28] Higher members of the $(A\,^2\Pi_u)ns\sigma\,^1\Pi_u$ series have not yet been identified and are expected to be perturbed by s-d mixing with members of the $(A\,^2\Pi_u)nd\sigma\,^1\Pi_u$ series.

V. CONCLUSIONS

Double-resonance spectroscopy of N_2 via the $a\,^1\Pi_g$, $v'=5$ level has enabled definitive assignments of a number of intense and heretofore unidentified bands in the region between the $X\,^2\Sigma_g^+$, $v^+=0$ and 1 ionization thresholds. Coupling these results with some speculation on the nature of the band at $\sim 126\,400$ cm^{-1} (which is not observed in the present experiment), we believe that it is now possible to account for all of the lowest-lying single Rydberg states converging to the $A\,^2\Pi_u$ and $B\,^2\Sigma_u^+$ states of the ion that are observed in the single-photon spectrum. This includes the $(A\,^2\Pi_u)3,4s\sigma\,^1\Pi_u$; $(A\,^2\Pi_u)3d\sigma\,^1\Pi_u$; $(A\,^2\Pi_u)3d\pi\,^1\Sigma_u^+$; $(A\,^2\Pi_u)3d\delta\,^1\Pi_u$; and $(B\,^2\Sigma_u^+)3s\sigma\,^1\Sigma_u^+$ states. The transition to the $(A\,^2\Pi_u)3d\pi\,^1\Delta_u$ state, which is expected from the $a\,^1\Pi_g$ state but not from the $X\,^1\Sigma_g^+$ state, has not yet been observed. In order to more completely study these low-lying Rydberg states in N_2, future work in our laboratory will expand the energy range of the present studies, will include resonant intermediate states of different vibrational levels and possibly different symmetries, and will explore decay rates and decay mechanisms for the excited states that lie above the first ionization threshold.

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[1]For an overview of the absorption spectrum, see P. Gürtler, V. Saile, and E. E. Koch, Chem. Phys. Lett. **48**, 245 (1977).
[2]K. Dressler, Can. J. Phys. **47**, 547 (1969).
[3]H. Lefebvre-Brion, Can. J. Phys. **47**, 541 (1969).
[4]D. Stahel, M. Leoni, and K. Dressler, J. Chem. Phys. **79**, 2541 (1983).
[5]P. K. Carrol and K. Yoshino, J. Phys. B **5**, 1614 (1972); see also A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data **6**, 113 (1977), and references therein.
[6]P. M. Dehmer, P. J. Miller and W. A. Chupka, J. Chem. Phys. **80**, 1030 (1984).
[7]J. Y. Roncin, F. Launay, and K. Yoshino, J. Mol. Spectrosc. **134**, 390 (1989).
[8]K. P. Huber and Ch. Jungen, J. Chem. Phys. **92**, 850 (1990).
[9]C. Duzy and R. S. Berry, J. Chem. Phys. **64**, 2421 (1976).
[10]C. Duzy and R. S. Berry, J. Chem. Phys. **64**, 2431 (1976).
[11]J. L. Dehmer and D. Dill, J. Chem. Phys. **65**, 5327 (1976).
[12]T. N. Rescigno and P. W. Langhoff, Chem. Phys. Lett. **51**, 65 (1977).
[13]T. N. Rescigno, A. Gerwer, B. V. McKoy, and P. W. Langhoff, Chem. Phys. Lett. **66**, 116 (1979).
[14]T. N. Rescigno, C. F. Bender, B. V. McKoy, and P. W. Langhoff, J. Chem. Phys. **68**, 970 (1978).
[15]M. Raoult, H. LeRouzo, G. Raseev, and H. Lefebvre-Brion, J. Phys. **B16**, 4601 (1983).
[16]A. Giusti-Suzor and H. Lefebvre-Brion, Phys. Rev. A **30**, 3057 (1984).
[17]W. M. Kosman and S. Wallace, J. Chem. Phys. **82**, 1385 (1985).
[18]P. Cremaschi, A. Chattopadhyay, P. V. Madhavan, and J. L. Whitten, Chem. Phys. **109**, 117 (1986).
[19]H. Lefebvre-Brion and K. Yoshino (private communication).
[20]K. P. Huber (private communication).
[21]H. Lefebvre-Brion (private communication).
[22]E. F. McCormack, S. T. Pratt, J. L. Dehmer, and P. M. Dehmer (unpublished).
[23]T. Takamine and Y. Tanaka, Phys. Rev. **59**, 613 (1941). See also T. Takamine and Y. Tanaka, Sci. Papers. Inst. Phys. Chem. Res. (Tokyo) **39**, 427 (1942).
[24]M. Ogawa and Y. Tanaka, Can. J. Phys. **40**, 1593 (1962).
[25]M. Ogawa, Can. J. Phys. **42**, 1087 (1964).
[26]P. K. Carroll and C. P. Collins, Can. J. Phys. **47**, 563 (1969).
[27]P. K. Carroll, C. P. Collins, and K. Yoshino, J. Phys. B **3**, L127 (1970).
[28]K. Yoshino, Y. Tanaka, P. K. Carroll, and P. Mitchell, J. Mol. Spectrosc. **54**, 87 (1975).
[29]K. Yoshino, M. Ogawa, and Y. Tanaka, J. Mol. Spectrosc. **61**, 403 (1976).
[30]K. Yoshino, D. E. Freeman, and Y. Tanaka, J. Mol. Spectrosc. **76**, 153 (1979).
[31]S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, J. Chem. Phys. **81**, 3444 (1984).
[32]T. Ebata, A. Fujii, and M. Ito, J. Phys. Chem. **91**, 3125 (1987).
[33]B. A. Palmer, R. A. Keller, and R. Engleman, Jr., *An Atlas of Uranium Intensities in a Hollow Cathode Discharge,* Los Alamos Scientific Laboratory, Internal Report No. LA-8251-MS, 1980.
[34]S. T. Pratt, E. D. Poliakoff, P. M. Dehmer, and J. L. Dehmer, J. Chem. Phys. **78**, 65 (1983).
[35]H. Helm and P. C. Cosby, Phys. Rev. A **38**, 115 (1988).
[36]S. W. Sharpe and P. M. Johnson, J. Chem. Phys. **85**, 4943 (1986).
[37]P. K. Carroll and Kh. I. Hagim, Phys. Scr. **37**, 682 (1988).
[38]J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. **141**, 395 (1965).
[39]J. Bendtsen, J. Raman Spectrosc. **2**, 133 (1974).
[40]G. Herzberg, *Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
[41]T. A. Miller, T. Suzuki, and E. Hirota, J. Chem. Phys. **80**, 4671 (1984).
[42]Values of n^* and δ were calculated from the relations $E_n = E_\infty - 109\,735.166\ \mathrm{cm}^{-1}/(n^*)^2$ and $\delta = n - n^*$.
[43]Franck-Condon factors were calculated by using Morse potentials determined from the molecular constants given in K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV, Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[44]H. H. Michels, in *Advances in Chemical Physics,* edited by I. Prigogine and S. Rice (Wiley, New York, 1981), Vol. 45, p. 225.