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### Authors

Song, Y  
Gao, H  
Chang, YC  
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## QUANTUM-STATE DEPENDENCE OF PRODUCT BRANCHING RATIOS IN VACUUM ULTRAVIOLET PHOTODISSOCIATION OF N<sub>2</sub>

YU SONG<sup>1,4</sup>, HONG GAO<sup>1,4,5</sup>, YIH CHUNG CHANG<sup>1</sup>, D HAMMOUTÉNE<sup>2</sup>, H. NDOME<sup>3</sup>, M. HOCHLAF<sup>3</sup>, WILLIAM M. JACKSON<sup>1</sup>, AND  
 C. Y. NG<sup>1</sup>

<sup>1</sup> Department of Chemistry, University of California, Davis, CA 95616, USA; wmjackson@ucdavis.edu, cyng@ucdavis.edu

<sup>2</sup> Laboratoire de Thermodynamique et Modélisation Moléculaire, Faculté de Chimie, USTHB, BP32 El Alia, 16111 Bab Ezzouar, Alger, Algeria

<sup>3</sup> Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, F-77454 Marne-la-Vallée, France

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### ABSTRACT

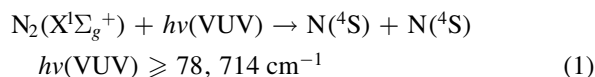
The branching ratios for the N(<sup>4</sup>S) + N(<sup>2</sup>D), N(<sup>4</sup>S) + N(<sup>2</sup>P), and N(<sup>2</sup>D) + N(<sup>2</sup>D) channels are measured for the photodissociation of N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>; v'' = 0, J'') in the vacuum ultraviolet (VUV) region of 100,808–122,159 cm<sup>-1</sup> using the VUV–VUV pump-probe approach combined with velocity-map-imaging-photoion detection. No evidence of forming the ground-state N(<sup>4</sup>S) + N(<sup>4</sup>S) products is found. No potential barrier is observed for the N(<sup>2</sup>D) + N(<sup>2</sup>D) channel, but the N(<sup>4</sup>S) + N(<sup>2</sup>P) channel has a small potential barrier of ≈740 cm<sup>-1</sup>. The branching ratios are found to depend on the symmetry of predissociative N<sub>2</sub> states instead of the total VUV excitation energy, indicating that N<sub>2</sub> photodissociation is nonstatistical. When the branching ratios for N(<sup>4</sup>S) + N(<sup>2</sup>D) and N(<sup>4</sup>S) + N(<sup>2</sup>P) products are plotted as a function of the VUV excitation energy for the valence N<sub>2</sub> <sup>1</sup>Π<sub>u</sub> and <sup>1</sup>Σ<sub>u</sub><sup>+</sup> states, oscillations in these ratios are observed demonstrating how these channels are competing with each other. These data can be used to select both the velocity and internal states of the atomic products by picking the quantum state that is excited. High-level ab initio potential energy curves of the excited N<sub>2</sub> states are calculated to provide insight into the mechanisms for the observed branching ratios. The calculations predict that the formation of both N(<sup>4</sup>S) + N(<sup>2</sup>D) and N(<sup>4</sup>S) + N(<sup>2</sup>P) channels involves potential energy barriers, in agreement with experimental observations. A discussion of the application of the present results to astronomy, planetary sciences, and comets is given.

*Key words:* ISM: kinematics and dynamics – ISM: molecules – methods: laboratory: molecular – molecular data – ultraviolet: ISM

### 1. INTRODUCTION

Nitrogen molecules are important in planetary and astronomical sciences because of the relatively large N<sub>2</sub>/H<sub>2</sub> universal abundance ratio of 1.6 × 10<sup>-4</sup>. The N<sub>2</sub> molecule dominates the atmospheres of Earth (Meier 1991; Feldman et al. 2001), Titan (Strobel & Shemansky 1982), and extrasolar planets (Moses et al. 2011). It also protects Earth from high-energy vacuum ultraviolet (VUV) radiation, and it plays a major role in the chemistry of the thermosphere (Torr & Torr 1979, 1982). The photochemistry of N<sub>2</sub> in a variety of environments, e.g., the interstellar medium, extrasolar planets, and circumstellar envelopes, is believed to be responsible for the synthesis of N-containing molecules that are precursors to larger molecules that are the building blocks of life (Knauth et al. 2004; Snow 2004; van Dishoeck 2006; Balucani 2012; Li et al. 2013, 2014).

Listed below are Reactions (1)–(4) with their energetic thresholds that can occur when N<sub>2</sub> molecules absorb high-energy VUV radiation in the energy [hν(VUV)] range of ≤122,159 cm<sup>-1</sup>:



The long radiative lifetimes and high internal energies of the excited N(<sup>2</sup>D) and N(<sup>2</sup>P) atomic photoproducts suggest that these atoms are highly reactive with other molecules, such as H<sub>2</sub>, in low-pressure space environments (Balucani 2012). By comparison, the reactivity of ground-state N(<sup>4</sup>S) atoms toward H<sub>2</sub> molecules is known to be very low (Herron 1999). Thus, understanding the mechanisms for the formation of excited N(<sup>2</sup>D) and N(<sup>2</sup>P) atoms from N<sub>2</sub> photodissociation plays a pivotal role in modeling the chemistry occurring in astronomical environments.

A fast-beam experiment (Helm & Cosby 1989; Walter et al. 1993, 1994) investigated the N<sub>2</sub> photochemistry in the energy range of 110,175–112,918 cm<sup>-1</sup>, which is significantly narrower than the present experimental range of 100,808–122,159 cm<sup>-1</sup>. This group also reported additional branching ratio information on Reactions (2) and (3) at an American Geophysical Union Meeting in 1996 (Cosby & Walter 1996). The same experimental technique has also been used by Buijsse & van der Zande (1997a, 1997b) to investigate the predissociation dynamics of N<sub>2</sub>(c<sub>4</sub><sup>1</sup>Π<sub>u</sub>, v' = 0) and N<sub>2</sub>(b<sup>1</sup>Σ<sub>u</sub><sup>+</sup>; v' = 16) states. The sensitivity of the fast-beam experiment is partly constrained by the high velocity of the N<sub>2</sub> beam required for coincident detection of N-atom products, but they were able to identify the formation of the spin-forbidden product channels (Reactions (2) and (3)). Nevertheless, these previous studies did not detect Reaction (4), and they mainly reported branching ratios for high J' levels owing to their experimental conditions. Besides the above photofragmentation

<sup>4</sup> These authors contributed equally to this work.

<sup>5</sup> Present address: Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland.

experiments, a high-resolution absorption spectroscopy method has long been used to study the photodissociation dynamics of  $N_2$  (Carroll & Collins 1969; Dressler 1969; Yoshino et al. 1975). Recently, very accurate theoretical calculations using the coupled-channel Schrödinger equation (CSE) method have been performed by Lewis et al. (2005, 2008b) in a relatively low energy region and revealed Rydberg–Rydberg, Rydberg–valence, and singlet-triplet interactions in the predissociation process of  $N_2$ .

Earlier, a tunable VUV laser combined with a time-slice velocity-map imaging photoion (VMI-PI) detection was used to both photodissociate  $N_2$  molecules in 109,369–109,611  $cm^{-1}$  and ionize nascent  $N(^2D)$  photoproduct atoms (Gao et al. 2011; Pan et al. 2011). This apparatus has been augmented with a second tunable VUV laser source, and with it, the VUV photoexcitation of  $N_2$  molecules and the VUV photoionization detection of product N atoms can be independently optimized (Song et al. 2012; Gao et al. 2013), increasing the experimental sensitivity. The motivations for this work are to provide the data needed for modelers of the various space environments described above and the benchmarks for state-of-the-art ab initio calculations of the potential energy curves (PECs), as well as for dynamics calculations on them.

The VUV absorption spectrum of  $N_2$  is complicated partly because of the large number of valence and Rydberg states with different multiplicities. Many of the previously studied excited states have been classified into the two main vibrational progressions corresponding to the predissociative  $N_2(b^1\Pi_u; v' = 0-23, J')$  and  $N_2(b'^1\Sigma_u^+; v' = 0-28, J')$  valence states (Carroll & Collins 1969; Dressler 1969). Interspersed between these valence states are predissociative Rydberg states with the same symmetries, such as  $N_2(c_n, o_n^1\Pi_u; v', J')$  and  $N_2(c'_n, ^1\Sigma_u^+; v', J')$ , which can also be reached by one-photon VUV excitations.

## 2. EXPERIMENTAL CONSIDERATION

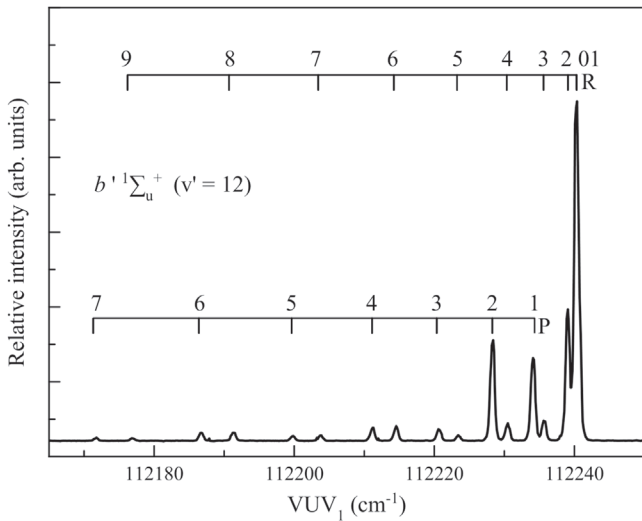
The VUV–VUV laser VMI-PI apparatus used for the present study has been previously reported in detail (Song et al. 2012; Gao et al. 2013; Lu et al. 2014), so only a brief description is given here. The apparatus consists of two independently tunable VUV lasers coupled to a VMI-PI detector. A pulsed supersonic molecular beam of  $N_2$  is generated through a pulsed valve (Even-Lavie Model: EL-5-2004, nozzle diameter = 0.2 mm) operating at 30 Hz and a total stagnation pressure of 30 psi. It is then skimmed and collimated by two skimmers before being crossed perpendicularly in the interaction region of the VMI-PI apparatus by two opposing unfocused VUV laser beams designated as  $VUV_1$  and  $VUV_2$ . The supersonically cooled  $N_2$  molecules in the interaction region are mostly in the  $N_2(X^1\Sigma_g^+; v'' = 0; J'' = 0)$  state, so that one-photon excitation by the  $VUV_1$  laser beam will only excite the molecule to ungerade predissociative rovibronic states. The  $VUV_2$  laser beam is tuned to selectively photoionize the  $N(^2D)$  or  $N(^4S)$  atomic photofragments. Using two-photon resonance-enhanced four-wave mixing schemes employing a pulsed Kr or Xe gas jet as the nonlinear medium generates the tunable VUV laser beams. This produces VUV outputs at the sum and difference-frequencies  $2\omega_1 \pm \omega_2$ , where  $\omega_1$  and  $\omega_2$  are the fundamental UV and VIS frequencies, respectively. The  $2\omega_1$  represents the two-photon UV resonant frequency fixed at a selected Kr or Xe electronic transition. The VIS  $\omega_2$  frequency is tunable to cover the VUV sum-

frequency ( $2\omega_1 + \omega_2$ ) output required for the experiment. The VUV laser output was measured to have an optical bandwidth of 0.4  $cm^{-1}$  (FWHM). The typical delay time between the arrival of the  $VUV_1$  photodissociation and the  $VUV_2$  photoionization lasers at the interaction region is 10–20 ns.

The  $N(^4S)$  atoms were detected by the  $VUV_2$  laser employing the VUV-VIS ( $1 + 1'$ ) ionization scheme. In this scheme, the  $VUV_2$  excitation of  $N^*[2s^22p^2(^3P)4d] \leftarrow N(^4S)$  is followed by photoionization of the excited state using the VIS  $\omega_2$  laser that is also present in the interaction region. The  $N(^2D)$  fragments are detected by tuning the  $VUV_2$  laser to excite  $N(^2D)$  to a resonant autoionization state at 110,296.0  $cm^{-1}$  (Kramida et al. 2014). The ions formed in the interaction region are accelerated by the ion imaging optics down a 72.5 cm flight tube, where they strike a dual microchannel plate (MCP) detector (active diameter = 7.5 cm) that converts them to electrons. A high-voltage pulse is applied to the front MCP at the expected arrival time of  $N^+$  ions to select them from other ions for detection. The optical image resulting from the electron impact on the phosphor screen is recorded using a CCD camera.

## 3. AB INITIO CALCULATIONS OF POTENTIAL ENERGY CURVES OF UNGERADE $N_2$ STATES

Single-photon VUV excitation from the  $N_2(X^1\Sigma_g^+)$  ground state can only populate the ungerade states. Many of these ungerade states can be coupled by spin–orbit or vibronic interactions. Hence, only the ungerade states of  $N_2$  are calculated and presented. Because of the potential diffuse nature of the excited states, their wavefunctions were calculated using a large basis set composed by the aug-cc-pVQZ quality, which is augmented by 3s and 2p diffuse Gaussian-type orbitals (GTOs; Dunning 1989; Kendall et al. 1992; Woon & Dunning 1995). In addition, the expected high density of the electronic states in this energy range should lead to the mixing of their electronic wavefunctions. Therefore, a multiconfigurational approach is adopted where the electronic computations were carried out using the Complete Active Space Self Consistent Field (CASSCF; Knowles & Werner 1985; Werner & Knowles 1985) approach followed by the internally contracted Multi Reference Configuration Interaction (MRCI; Knowles & Werner 1988; Werner & Knowles 1988) technique as implemented in MOLPRO (Werner et al. 2012). We followed the procedure established in Spelsberg & Meyer (2001), Ndome et al. (2008), and Hochlaf et al. (2010a, 2010b). Briefly, the CASSCF active space is constructed by the valence molecular orbitals (MOs) of  $N_2$  increased by one  $s_g$  and one  $p_g$  MOs. This allows better relaxation of the wavefunctions of the  $N_2$  electronic states whose configurations differ in their  $s$  and  $p$  orbital occupations as those of interest at present. In MRCI, all CASSCF configurations were taken into account as reference. Finally, the CASSCF wavefunctions were used to evaluate the spin–orbit matrix elements. These spin–orbit computations were performed in Cartesian coordinates, where the CASSCF wavefunctions were used as the multielectron basis for the two-step spin–orbit coupling calculation (Llusar et al. 1996; Zeng et al. 2011) through the Breit–Pauli Hamiltonian (Berning et al. 2000) as implemented in MOLPRO.



**Figure 1.** Photofragment excitation (PHOFEX) spectrum of  $N(^4S)$  atoms formed in the photodissociation of  $N_2(b'^1\Sigma_u^+; v' = 12, J')$  in the  $VUV_1$  region of  $112,165\text{--}112,250\text{ cm}^{-1}$ . The  $P(J')$  and  $R(J')$  rotational transition lines from the  $N_2(X^1\Sigma_g^+; v'' = 0, J'')$  state are denoted. The bandwidth of the  $VUV_1$  laser used is  $0.4\text{ cm}^{-1}$  (FWHM), which is narrower than the observed rotational bandwidth of  $0.5\text{--}1.0\text{ cm}^{-1}$  (FWHM), indicative of the Doppler effect due to the large recoil velocity of N atoms formed in the photodissociation process.

## 4. RESULTS AND DISCUSSION

### 4.1. Photofragment Excitation Spectrum

Figure 1(a) is an example of the photofragment excitation (PHOFEX) spectrum of  $N(^4S)$  atoms obtained by tuning the  $VUV_1$  energy [ $h\nu(VUV_1)$ ] in the range of  $112,165\text{--}112,250\text{ cm}^{-1}$  to excite the  $N_2(b'^1\Sigma_u^+; v' = 12) \leftarrow N_2(X^1\Sigma_g^+; v'' = 0)$  band, while setting the  $VUV_2$  laser output to ionize the  $N(^4S)$  atomic photofragments. The rotational line positions agree with known line positions for this band, with deviations in the range of  $0.5\text{--}1.0\text{ cm}^{-1}$  (Dressler 1969; Roncin et al. 1998). The measurements and reliable assignments of a PHOFEX spectrum are an important step in ensuring the correct identification of selected excited predissociative rovibronic states of  $N_2$ . The line widths of the individual rotational lines in Figure 1 are equal to  $0.82\text{ cm}^{-1}$  (FWHM), which should be mainly due to the Doppler effect caused by the large recoil velocity of N atoms formed in the

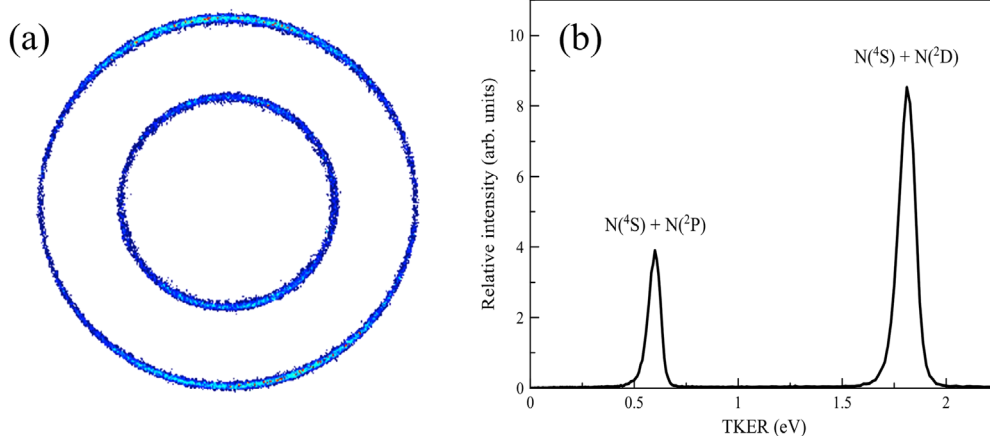
photodissociation process. The contribution of the power broadening effect to the observed experimental line width is expected to be unimportant because the VUV sum-frequency output is low ( $10\text{--}100\text{ }\mu\text{J/pulse}$ ) and unfocused.

### 4.2. State-selected Branching Ratios for State-correlated Photoproducts

Figure 2(a) shows the time-slice VMI-PI image of  $N(^4S)$  recorded by fixing the  $h\nu(VUV_1)$  at the  $R(2)$  rotational transition ( $112,239.0\text{ cm}^{-1}$ ) of the  $N_2(b'^1\Sigma_u^+; v' = 12)$  vibrational band and ionizing the  $N(^4S)$  atom 15 ns later with the  $h\nu(VUV_2)$ . There are two well-separated rings in the image, indicating the formation of two  $N(^4S)$  product channels in the photodissociation of  $N_2(b'^1\Sigma_u^+; v' = 12, J' = 3)$ . By measuring the radii of these circles and converting them to energies using the energy calibration of the VMI-PI apparatus, the center-of-mass kinetic energies ( $E_{\text{cm}}$ ) are determined for the two  $N_2$  photoproduct channels using Equation (5), which is derived based on the conservation of linear momentum and energy:

$$E_{\text{cm}} = E_{\text{TKER}} = h\nu(VUV_1) - D_0(N_2) - E(N \text{ atoms}). \quad (5)$$

Here  $E_{\text{cm}}$  is referred to as the total kinetic energy release ( $E_{\text{TKER}}$ ),  $D_0(N_2) = 78,714\text{ cm}^{-1}$  is the 0 K bond dissociation energy, and  $E(N \text{ atoms})$  is the internal electronic energies of the two photoproduct N atoms. The  $E(N \text{ atoms}) = 0, 19,224, 28,839, \text{ and } 38,448\text{ cm}^{-1}$  for the formation of  $N(^4S) + N(^4S)$ ,  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  channels, respectively (Kramida et al. 2014). The  $E_{\text{TKER}}$  spectrum converted from the VMI-PI image of Figure 2(a) is shown in Figure 2(b), where the two peaks resolved in the  $E_{\text{TKER}}$  spectrum are assigned to the formation of the  $N(^4S) + N(^2D)$  and  $N(^4S) + N(^2P)$  channels. The integrated areas of these two peaks yield a branching ratio  $N(^4S) + N(^2D):N(^4S) + N(^2P)$  of  $0.76 \pm 0.03:0.24 \pm 0.04$ . Similar procedures are used to determine the branching ratios for all of the upper energy levels of  $N_2$  that can be excited with the  $VUV_1$  laser in the energy range of  $100,808\text{--}122,159\text{ cm}^{-1}$ , and the results are collected in Tables 1–5. The error bars presented are simply the statistical uncertainties ( $1\sigma$ ) from three to four independent measurements and thus should only represent the lower limits of the real uncertainties. Those values without error bars are from single measurements except for unity and zero branching



**Figure 2.** (a) Time-slice VMI-PI image of  $N(^4S)$  produced by photodissociation of  $N_2$  with  $h\nu(VUV_1)$  set at the  $R(2)$  rotational line ( $112,239.0\text{ cm}^{-1}$ ) of  $N_2(b'^1\Sigma_u^+; v' = 12)$  band. (b) TKER spectrum converted from the VMI-PI image shown in (a). The assignment of the  $N(^4S) + N(^2D)$  and  $N(^4S) + N(^2P)$  channels is also marked in (b).

**Table 1**  
Product Branching Ratios for the  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  Channels from Excitation to the  $N_2(b^1\Pi_u; v' = 0-23, J')$  Valence States in  $N_2$  Photodissociation

Term	$v'$	$J''$	VUV <sub>1</sub> (cm <sup>-1</sup> )	N ( <sup>4</sup> S) + N( <sup>2</sup> D)	N ( <sup>4</sup> S) + N( <sup>2</sup> P)	N( <sup>2</sup> D) + N( <sup>2</sup> D)
$b^1\Pi_u$	$v' = 0$	P(2)	100807.7	1.000	0.000	0.000
		Q(2)	100813.5	1.000	0.000	0.000
		Q(1)	100815.6	1.000	0.000	0.000
		R(0)	100819.7	1.000	0.000	0.000
		R(1)	100821.5	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 1$	R(2)	100822.2	1.000	0.000	0.000
		P(2)	101442.3	1.000	0.000	0.000
		Q(2)	101448.0	1.000	0.000	0.000
		Q(1)	101450.3	1.000	0.000	0.000
		R(0)	101454.2	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 2$	R(1)	101456.0	1.000	0.000	0.000
		Q(2)	102148.2	1.000	0.000	0.000
		Q(1)	102150.7	1.000	0.000	0.000
		R(0)	102154.7	1.000	0.000	0.000
		R(1)	102156.2	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 3$	R(0)	102864.8	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 4$	P(2)	103539.6	1.000	0.000	0.000
		Q(2)	103545.4	1.000	0.000	0.000
		Q(1)	103547.6	1.000	0.000	0.000
		R(0)	103551.6	1.000	0.000	0.000
		R(1)	103553.4	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 5$	P(2)	104690.8	1.000	0.000	0.000
		Q(2)	104696.4	1.000	0.000	0.000
		Q(1)	104698.7	1.000	0.000	0.000
		R(0)	104702.7	1.000	0.000	0.000
		R(1)	104704.6	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 6$	R(2)	104705.1	1.000	0.000	0.000
		P(2)	105336.6	1.000	0.000	0.000
		Q(2)	105342.1	1.000	0.000	0.000
		Q(1)	105344.6	1.000	0.000	0.000
		R(0)	105348.6	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 7$	R(1)	105350.0	1.000	0.000	0.000
		P(2)	106100.2	1.000	0.000	0.000
		Q(2)	106105.6	1.000	0.000	0.000
		Q(1)	106108.3	1.000	0.000	0.000
		R(0)	106112.3	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 8$	R(1)	106113.6	1.000	0.000	0.000
		P(2)	106923.7	1.000	0.000	0.000
		Q(2)	106928.9	1.000	0.000	0.000
		Q(1)	106931.6	1.000	0.000	0.000
		R(0)	106935.6	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 9$	R(1)	106937.0	1.000	0.000	0.000
		P(2)	107642.3	1.000	0.000	0.000
		Q(2)	107647.8	1.000	0.000	0.000
		Q(1)	107650.3	1.000	0.000	0.000
		R(0)	107654.3	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 10$	R(1)	107655.8	1.000	0.000	0.000
		P(2)	108362.4	1.000	0.000	0.000
		Q(2)	108367.3	1.000	0.000	0.000
		Q(1)	108370.3	1.000	0.000	0.000
		R(0)	108374.4	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 11$	R(1)	108375.1	1.000	0.000	0.000
		Q(2)	109115.1	1.000	0.000	0.000
		Q(1)	109119.0	1.000	0.000	0.000
		R(3)	109120.0	1.000	0.000	0.000
		R	109122.8	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 12$	(0,1,2)				
		Q(2)	109826.1	$0.999 \pm 0.001$	$0.002 \pm 0.001$	0.000
		Q(1)	109829.4	$0.999^a$	$0.001^a$	0.000
$b^1\Pi_u$	$v' = 13$	R(0)	109833.5	$0.994 \pm 0.005$	$0.006 \pm 0.005$	0.000
		Q(1)	110527.3	1.000	0.000	0.000
$b^1\Pi_u$	$v' = 14$	R(0)	110530.8	1.000	0.000	0.000
		P(2)	111199.9	1.000	0.000	0.000

**Table 1**  
(Continued)

Term	$\nu'$	$J''$	VUV <sub>1</sub> (cm <sup>-1</sup> )	N ( <sup>4</sup> S) + N( <sup>2</sup> D)	N ( <sup>4</sup> S) + N( <sup>2</sup> P)	N( <sup>2</sup> D) + N( <sup>2</sup> D)
		Q(2)	111204.3	1.000	0.000	0.000
		Q(1)	111207.9	1.000	0.000	0.000
		R(2)	111210.9	1.000	0.000	0.000
		R(0,1)	111211.9	1.000	0.000	0.000
$b(^1\Pi_u)$	$\nu' = 15$	Q(2)	111866.6	0.980 ± 0.005	0.020 ± 0.005	0.000
		Q(1)	111870.4	0.978 ± 0.013	0.022 ± 0.005	0.000
		R(2)	111873.1	0.986 ± 0.002	0.014 ± 0.002	0.000
		R(0,1)	111874.4	0.982 ± 0.007	0.018 ± 0.007	0.000
$b(^1\Pi_u)$	$\nu' = 16$	Q(2)	112502.8	1.000	0.000	0.000
		Q(1)	112506.6	1.000	0.000	0.000
		R(2)	112509.2	1.000	0.000	0.000
		R(0,1)	112510.6	1.000	0.000	0.000
$b(^1\Pi_u)$	$\nu' = 17$	Q(2)	113121.4	0.118 ± 0.006	0.882 ± 0.006	0.000
		Q(1)	113125.4	0.136 ± 0.006	0.864 ± 0.006	0.000
		R(2)	113127.3	0.130 ± 0.007	0.870 ± 0.007	0.000
		R(0,1)	113129.3	0.119 ± 0.009	0.881 ± 0.009	0.000
$b(^1\Pi_u)$	$\nu' = 18$	Q(2)	113701.1	0.207 ± 0.020	0.793 ± 0.020	0.000
		Q(1)	113705.3	0.246 ± 0.012	0.754 ± 0.012	0.000
		R(2)	113707.1	0.250 ± 0.006	0.750 ± 0.006	0.000
		R(0,1)	113709.3	0.214 ± 0.009	0.786 ± 0.009	0.000
$b(^1\Pi_u)$	$\nu' = 19$	R(0,1)	114256.7	0.896 ± 0.023	0.104 ± 0.023	0.000
$b(^1\Pi_u)$	$\nu' = 22$	R(0)	115664.7	0.955 ± 0.003	0.045 ± 0.003	0.000
$b(^1\Pi_u)$	$\nu' = 23$	Q(1)	116026.6	1.000 ± 0.005	0.000 ± 0.005	0.000
		R(0)	116030.5	0.983 ± 0.005	0.017 ± 0.005	0.000

**Note.**

<sup>a</sup> Value determined by one ion image; the uncertainty is estimated to be 1%–3% based on the counting statistics.

ratios. Considering that the ion counts collected for each ion image for the branching ratio determination are more than 10,000 and the detection method used here is very clean, we have assigned the uncertainty of 1%–3% for those branching ratios from single measurements. The electronic states that are populated by single-photon VUV excitation are all singlet states except for the triplet  $N_2(C^3\Pi_u; \nu' = 16, J')$  states that have been previously observed in VUV absorption studies (Carroll & Mulliken 1965; Lewis et al. 2008a).

In the above example, where  $N_2$  is excited to the  $N_2(b^1\Sigma_u^+; \nu' = 12, J'=3)$  state at 112,239 cm<sup>-1</sup>, the spin-allowed  $N(^4S) + N(^4S)$  ground-state channel was not observed, i.e., the branching ratio for Reaction (1) is zero. The same result is found for all of the levels excited throughout the 100,808–122,159 cm<sup>-1</sup> range of the present study. This is in agreement with the earlier studies using the fast-beam method over a narrower energy range of 110,175–112,917 cm<sup>-1</sup> (Helm & Cosby 1989; Walter et al. 1993, 1994). This observation proves that internal conversion to the excited vibrational levels of the ground electronic state is not competitive with intersystem crossing at any of the energies in the present studies. Furthermore, it provides evidence that photoexcited  $N_2$  molecules cannot undergo spin-orbit allowed conversion to reach electronic states, which correlate to the  $N(^4S) + N(^4S)$  ground-state channel.

The branching ratios of Tables 1–5 cover the  $h\nu(\text{VUV}_1)$  range of 100,808–122,159 cm<sup>-1</sup>. Tables 1 and 2 list the branching ratios for the product channels,  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$ , via excitation to the valence  $N_2$  states, ( $b^1\Pi_u; \nu' = 0–23$ ), and the Rydberg  $N_2$  states, ( $c_3^1\Pi_u; \nu' = 0, 1, 3$ ), ( $o_3^1\Pi_u; \nu' = 0, 2–4$ ), ( $c_4^1\Pi_u; \nu' = 0–2$ ), ( $c_5^1\Pi_u; \nu' = 0$ ), ( $c_6^1\Pi_u; \nu' = 0$ ), and ( $o_4^1\Pi_u; \nu' = 0$ ),

respectively. The branching ratios for the product channels from the valence  $N_2$  states, ( $b^1\Sigma_u^+; \nu' = 1–28$ ), and the Rydberg  $N_2$  states, ( $c_4^1\Sigma_u^+; \nu' = 0–8$ ), ( $c_5^1\Sigma_u^+; \nu' = 0–2$ ), and ( $c_6^1\Sigma_u^+; \nu' = 0$ ), are given in Tables 3 and 4, respectively. Branching ratios produced via the valence  $N_2$  states, ( $C^3\Pi_u; \nu' = 16, J'$ ), and the Rydberg  $N_2(4f$  and  $5f)$  complex states, [ $X^+(0)4f; \nu' = 0–1, J'$ ], [ $X^+(1)4f; \nu' = 0–1, J'$ ], and [ $X^+(0)5f; \nu' = 0–1, J'$ ], are listed in Table 5. The branching ratios given in parentheses in the tables were reported previously by the fast ion beam study. Generally, the branching ratios obtained in the present measurements have smaller error limits than those reported previously. Taking into account experimental uncertainties, the branching ratios obtained here and those reported in the fast-beam experiment (Helm & Cosby 1989; Walter et al. 1993, 1994; Cosby & Walter 1996) are in reasonable agreement.

To better examine the trends of the branching ratios listed in Tables 1–4, they are plotted in Figures 3(a)–(d) for the  $N(^4S) + N(^2D)$  (blue curve),  $N(^4S) + N(^2P)$  (red curve), and  $N(^2D) + N(^2D)$  (green curve) channels as a function of  $h\nu(\text{VUV}_1)$ . The energetic thresholds for the formation of the  $N(^4S) + N(^2P)$  and  $N(^2D) + N(^2D)$  channels are also marked in these figures by downward-pointing red and green arrows, respectively. The energetic threshold of 97,938 cm<sup>-1</sup> for the  $N(^4S) + N(^2D)$  channel is well below the  $h\nu(\text{VUV}_1)$  range of the present study and is not marked in the figures. The valence  $N_2$  states ( $b^1\Pi_u; \nu' \leq 23$ ) that can be populated by single-photon VUV excitation are below the energetic threshold for the  $N(^2D) + N(^2D)$  channel, so they are not observed in Figure 3(a).

The comparison of photoproduct branching ratio curves of Figures 3(a)–(d) indicates that the branching ratios for Reactions (2)–(4) depend not only on  $h\nu(\text{VUV}_1)$  but also on

**Table 2**  
Product Branching Ratios for the  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  Channels from Excitation to the  $N_2(c_{3-6}$  and  $o_3^1\Pi_u; v', J')$ ,  
( $A^+(0)3d\sigma^1\Pi_u; v', J')$ , and ( $X^+(1)5p\pi^1\Pi_u; v', J')$  Rydberg States in  $N_2$  Photodissociation

Term	$v'$	$J'$	VUV <sub>1</sub> (cm <sup>-1</sup> )	$N(^4S) + N(^2D)$	$N(^4S) + N(^2P)$	$N(^2D) + N(^2D)$
$c_3(^1\Pi_u)$	$v' = 0$	P(2)	104129.4	1.000	0.000	0.000
		Q(2)	104135.5	1.000	0.000	0.000
		Q(1)	104137.4	1.000	0.000	0.000
		R(0)	104141.4	1.000	0.000	0.000
		R(1)	104143.3	1.000	0.000	0.000
		R(2)	104144.2	1.000	0.000	0.000
$o_3(^1\Pi_u)$	$v' = 0$	R(0)	105686.3	1.000	0.000	0.000
$c_3(^1\Pi_u)$	$v' = 1$	P(2)	106519.5	1.000	0.000	0.000
		Q(2)	106526.3	1.000	0.000	0.000
		Q(1)	106527.5	1.000	0.000	0.000
		R(0)	106531.5	1.000	0.000	0.000
		R(1)	106534.3	1.000	0.000	0.000
		R(2)	106536.6	1.000	0.000	0.000
$o_3(^1\Pi_u)$	$v' = 1$	Q(2)	107627.0	1.000	0.000	0.000
		R(0)	107632.6	1.000	0.000	0.000
$o_3(^1\Pi_u)$	$v' = 2$	Q(2)	109559.9	1.000	0.000	0.000
		Q(1)	109561.0	1.000	0.000	0.000
		R(0)	109564.9	1.000	0.000	0.000
		R(1)	109567.8	1.000	0.000	0.000
		R(2)	109570.1	1.000	0.000	0.000
$c_3(^1\Pi_u)$	$v' = 3$	Q(1)	110795.4	1.000	0.000	0.000
		R(0)	110799.8	1.000 (0.96) <sup>a</sup>	0.000 (0.04) <sup>a</sup>	0.000
$o_3(^1\Pi_u)$	$v' = 3$	P(2)	111438.9	1.000	0.000	0.000
		Q(4)	111441.5	1.000	0.000	0.000
		Q(3)	111444.1	1.000	0.000	0.000
		Q(2)	111445.6	1.000	0.000	0.000
		Q(1)	111446.8	1.000	0.000	0.000
		R(0)	111450.8	1.000	0.000	0.000
		R(1)	111453.7	1.000	0.000	0.000
		R(2)	111455.9	1.000	0.000	0.000
		R(3)	111457.5	1.000 (>0.99) <sup>a</sup>	0.000 (<0.01) <sup>a</sup>	0.000
		R(4)	111458.5	1.000	0.000	0.000
$o_3(^1\Pi_u)$	$v' = 4$	Q(2)	113305.7	1.000	0.000	0.000
		Q(1)	113306.8	1.000	0.000	0.000
		R(0)	113310.9	1.000	0.000	0.000
		R(1)	113313.6	1.000	0.000	0.000
		R(2)	113316.0	1.000	0.000	0.000
$c_3(^1\Pi_u)$	$v' = 5$	Q(2)	114830.3	0.979 ± 0.004	0.021 ± 0.004	0.000
		Q(1)	114831.4	0.978 ± 0.009	0.022 ± 0.009	0.000
$o_3(^1\Pi_u)$	$v' = 5$	Q(2)	115253.0	0.864 <sup>b</sup>	0.136 <sup>b</sup>	0.000
		Q(1)	115256.9	0.863 <sup>b</sup>	0.137 <sup>b</sup>	0.000
		R(0,2)	115260.8	0.866 ± 0.007	0.134 ± 0.007	0.000
$c_4(^1\Pi_u)$	$v' = 0$	Q(1)	115565.4	1.000	0.000	0.000
$c_4(^1\Pi_u)$	$v' = 0$	R(0)	115569.4	0.984 ± 0.021 (0.938 ± 0.004) <sup>c</sup>	0.017 ± 0.021 (0.062 ± 0.004) <sup>c</sup>	0.000
		R(1)	115573.1	0.917 ± 0.013 (0.873 ± 0.006) <sup>c</sup>	0.083 ± 0.013 (0.127 ± 0.006) <sup>c</sup>	0.000
		R(2)	115576.6	0.841 ± 0.010 (0.79 ± 0.02) <sup>c</sup>	0.160 ± 0.010 (0.21 ± 0.02) <sup>c</sup>	0.000
$c_4(^1\Pi_u)$	$v' = 1$	R(0)	117750.8	0.042 ± 0.013	0.000	0.958 ± 0.035
$c_5(^1\Pi_u)$	$v' = 0$	Q(1)	119739.1	0.862 ± 0.034	0.000	0.138 ± 0.034
		R(0)	119743.0	0.862 ± 0.026	0.000	0.138 ± 0.026
		R(1)	119746.4	0.847 ± 0.029	0.000	0.153 ± 0.029
		R(2)	119749.7	0.840 ± 0.028	0.000	0.160 ± 0.028
$c_4(^1\Pi_u)$	$v' = 2$	Q(1)	119890.0	0.000	0.000	1.000
		R(0)	119894.2	0.000	0.000	1.000
$A^+(0)3d\sigma^1\Pi_u$	$v' = 0$	Q(2)	121118.6	0.870 ± 0.008	0.000	0.130 ± 0.008
		Q(1)	121119.6	0.862 ± 0.000	0.000	0.138 ± 0.000
		R(0)	121123.7	0.847 ± 0.007	0.000	0.153 ± 0.007
		R(1)	121126.1	0.862 ± 0.007	0.000	0.138 ± 0.007
$c_6(^1\Pi_u)$	$v' = 0$	R(0)	121774.1	0.822 ± 0.007	0.000	0.178 ± 0.002
$X^+(1)5p\pi^1\Pi_u$	$v' = 1$	R(0)	121924.6	0.455 ± 0.052	0.000	0.545 ± 0.052
$A^+(0)3d\delta^1\Pi_u$	$v' = 0$	R(0)	122159.1	0.884 ± 0.005	0.000	0.116 ± 0.005

**Notes.**<sup>a</sup> Reported by Walter et al. (1993).<sup>b</sup> Value determined by one ion image; the uncertainty is estimated to be 1%–3% based on the counting statistics.<sup>c</sup> Reported by Cosby & Walter (1996).

**Table 3**  
Product Branching Ratios for the  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  Channels from Excitation to the  $N_2(b^1\Sigma_u^+; \nu' = 1-28, J')$  Valence States in  $N_2$  Photodissociation

Term	$\nu'$	$J'$	VUV <sub>1</sub> (cm <sup>-1</sup> )	$N(^4S)+N(^2D)$	$N(^4S)+N(^2P)$	$N(^2D)+N(^2D)$
$b'(^1\Sigma_u^+)$	$\nu' = 1$	R(0)	104420.4	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 2$	R(0)	105153.3	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 3$	P(2)	105859.7	1.000	0.000	0.000
		P(1)	105865.3	1.000	0.000	0.000
		R(0)	105871.6	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 4$	P(2)	106637.2	1.000	0.000	0.000
		P(1)	106642.7	1.000	0.000	0.000
		R(0)	106649.2	1.000	0.000	0.000
		R(1)	106650.3	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 5$	P(2)	107316.5	1.000	0.000	0.000
		P(1)	107322.2	1.000	0.000	0.000
		R(0)	107328.4	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 6$	P(3)	107982.1	1.000	0.000	0.000
		P(2)	107989.3	1.000	0.000	0.000
		P(1)	107994.7	1.000	0.000	0.000
		R(3)	107999.1	1.000	0.000	0.000
		R(0,2)	108001.2	1.000	0.000	0.000
		R(1)	108002.0	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 7$	P(2)	108943.1	1.000	0.000	0.000
		P(1)	108948.2	1.000	0.000	0.000
		R(0)	108954.9	1.000	0.000	0.000
		R(1)	108956.5	1.000	0.000	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 8$	P(2)	109534.2	0.997 <sup>a</sup>	0.003 <sup>a</sup>	0.000
		P(1)	109539.8	0.997 <sup>a</sup>	0.003 <sup>a</sup>	0.000
		R(2)	109545.6	0.993 <sup>a</sup>	0.007 <sup>a</sup>	0.000
		R(0)	109546.2	0.997 ± 0.002	0.003 ± 0.002	0.000
		R(1)	109546.4	0.988 <sup>a</sup>	0.012 <sup>a</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 9$	P(2)	110187.2	0.639 ± 0.007	0.361 ± 0.007	0.000
		P(1)	110192.7	0.618 ± 0.017	0.382 ± 0.017	0.000
		R(2)	110198.4	0.672 ± 0.019 (0.96) <sup>b</sup>	0.328 ± 0.019 (0.04) <sup>b</sup>	0.000
		R(0)	110199.0	0.694 ± 0.004	0.307 ± 0.004	0.000
		R(1)	110199.5	0.674 ± 0.007	0.326 ± 0.007	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 10$	P(2)	110932.8	0.987 ± 0.001	0.013 ± 0.001	0.000
		P(1)	110938.2	0.986 ± 0.004	0.015 ± 0.004	0.000
		R(2)	110944.8	0.988 ± 0.003 (1.00 ± 0.03) <sup>c</sup>	0.012 ± 0.003 (0.00 ± 0.03) <sup>c</sup>	0.000
		R(0)	110945.3	0.979 <sup>a</sup> (0.98) <sup>b</sup>	0.021 <sup>a</sup> (0.02) <sup>b</sup>	0.000
		R(1)	110945.9	0.987 ± 0.005(0.99) <sup>b</sup>	0.013 ± 0.005 (0.01) <sup>b</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 11$	P(3)	111563.6	0.986 <sup>a</sup>	0.014 <sup>a</sup>	0.000
		P(2)	111571.1	0.994 ± 0.002	0.006 ± 0.002	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 11$	P(1)	111576.9	0.992 ± 0.001 (0.97) <sup>b</sup>	0.008 ± 0.001 (0.03) <sup>b</sup>	0.000
		R(3)	111578.9	0.977 <sup>a</sup> (0.99 ± 0.05) <sup>c</sup>	0.023 <sup>a</sup> (0.01 ± 0.05) <sup>c</sup>	0.000
		R(2)	111582.1	0.987 <sup>a</sup> (1.00 ± 0.05) <sup>c</sup>	0.013 <sup>a</sup> (0.00 ± 0.05) <sup>c</sup>	0.000
		R(0,1)	111583.0	0.990 ± 0.006 (0.97 ± 0.05) <sup>c</sup>	0.010 ± 0.006 (0.03 ± 0.05) <sup>c</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 12$	P(6)	112186.7	0.687 <sup>a</sup> (0.78 ± 0.02) <sup>c</sup>	0.313 <sup>a</sup> (0.22 ± 0.02) <sup>c</sup>	0.000
		R(8)	112191.5	0.702 <sup>a</sup> (0.72) <sup>b</sup>	0.298 <sup>a</sup> (0.28) <sup>b</sup>	0.000
		P(5)	112199.8	0.734 <sup>a</sup> (0.73 ± 0.04) <sup>c</sup>	0.266 <sup>a</sup> (0.27 ± 0.04) <sup>c</sup>	0.000
		R(7)	112203.9	0.619 <sup>a</sup> (0.77) <sup>b</sup>	0.381 <sup>a</sup> (0.23) <sup>b</sup>	0.000
		P(4)	112211.3	0.764 ± 0.022 (0.79 ± 0.03) <sup>c</sup>	0.236 ± 0.022 (0.21 ± 0.03) <sup>c</sup>	0.000
		R(6)	112214.5	0.761 ± 0.079 (0.76) <sup>b</sup>	0.239 ± 0.079 (0.24) <sup>b</sup>	0.000
		P(3)	112220.7	0.773 ± 0.016 (0.78 ± 0.07) <sup>c</sup>	0.227 ± 0.016 (0.22 ± 0.07) <sup>c</sup>	0.000
		R(5)	112223.6	0.753 ± 0.072 (0.80) <sup>b</sup>	0.247 ± 0.072 (0.2) <sup>b</sup>	0.000
		P(2)	112228.6	0.771 ± 0.027	0.229 ± 0.027	0.000
		R(4)	112230.5	0.758 ± 0.023 (0.73) <sup>b</sup>	0.242 ± 0.023 (0.27) <sup>b</sup>	0.000
		P(1)	112234.1	0.759 ± 0.030	0.241 ± 0.030	0.000
		R(3)	112235.6	0.771 ± 0.023 (0.79) <sup>b</sup>	0.229 ± 0.023 (0.21) <sup>b</sup>	0.000
		R(2)	112239.0	0.761 ± 0.028 (0.86) <sup>b</sup>	0.239 ± 0.028 (0.14) <sup>b</sup>	0.000
		R(0,1)	112240.4	0.784 ± 0.014 (0.78 ± 0.07) <sup>c</sup>	0.210 ± 0.015 (0.22 ± 0.07) <sup>c</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 13$	P(2)	112898.4	0.216 ± 0.023 (0.248 ± 0.036) <sup>c</sup>	0.784 ± 0.023 (0.752 ± 0.036) <sup>c</sup>	0.000
		P(1)	112904.0	0.220 ± 0.016 (0.22) <sup>b</sup>	0.780 ± 0.016 (0.78) <sup>b</sup>	0.000
		R(0,2)	112910.3	0.182 ± 0.016	0.818 ± 0.016	0.000
		R(1)	112911.1	0.205 ± 0.002 (0.255 ± 0.03) <sup>c</sup>	0.795 ± 0.002 (0.745 ± 0.03) <sup>c</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 14$	P(2)	113530.6	0.054 ± 0.014	0.946 ± 0.014	0.000
		P(1)	113536.6	0.053 ± 0.014	0.947 ± 0.014	0.000



**Table 3**  
(Continued)

Term	$\nu'$	$J''$	VUV <sub>1</sub> (cm <sup>-1</sup> )	N( <sup>4</sup> S)+N( <sup>2</sup> D)	N( <sup>4</sup> S)+N( <sup>2</sup> P)	N( <sup>2</sup> D)+N( <sup>2</sup> D)
$b'(^1\Sigma_u^+)$	$\nu' = 15$	R(2)	113541.0	0.047 ± 0.016	0.953 ± 0.016	0.000
		R(0,1)	113542.6	0.057 ± 0.019	0.943 ± 0.019	0.000
		P(2)	114159.9	0.156 ± 0.008 (0.164 ± 0.07) <sup>c</sup>	0.844 ± 0.008 (0.836 ± 0.07) <sup>c</sup>	0.000
		P(1)	114165.7	0.145 ± 0.008 (0.116 ± 0.01) <sup>c</sup>	0.855 ± 0.008 (0.884 ± 0.01) <sup>c</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 16$	R(2)	114170.3	0.166 ± 0.010 (0.159 ± 0.049) <sup>c</sup>	0.834 ± 0.010 (0.841 ± 0.049) <sup>c</sup>	0.000
		R(0,1)	114171.9	0.163 ± 0.010	0.838 ± 0.010	0.000
		P(4)	114730.5	0.977 ± 0.003 (0.985 ± 0.004) <sup>c</sup>	0.023 ± 0.003 (0.015 ± 0.004) <sup>c</sup>	0.000
		P(3)	114738.4	0.982 ± 0.005 (0.982 ± 0.013) <sup>c</sup>	0.018 ± 0.005 (0.018 ± 0.013) <sup>c</sup>	0.000
		P(2)	114744.8	0.990 ± 0.001 (0.998 ± 0.001) <sup>c</sup>	0.010 ± 0.001 (0.002 ± 0.001) <sup>c</sup>	0.000
		R(5)	114748.6	0.980 ± 0.002 (0.968 ± 0.008) <sup>c</sup>	0.020 ± 0.002 (0.032 ± 0.008) <sup>c</sup>	0.000
		P(1)	114749.9	0.993 ± 0.001 (0.907 ± 0.036) <sup>c</sup>	0.007 ± 0.001 (0.093 ± 0.036) <sup>c</sup>	0.000
		R(4)	114753.5	0.968 ± 0.003 (0.976 ± 0.004) <sup>c</sup>	0.032 ± 0.003 (0.024 ± 0.004) <sup>c</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 17$	R(0)	114756.7	0.987 ± 0.001 (0.998 ± 0.001) <sup>c</sup>	0.013 ± 0.001 (0.002 ± 0.001) <sup>c</sup>	0.000
		R(0,2)	114758.2	0.984 ± 0.002	0.016 ± 0.002	0.000
		P(2)	115359.5	0.535 ± 0.013 (0.347 ± 0.112) <sup>c</sup>	0.465 ± 0.013 (0.653 ± 0.112) <sup>c</sup>	0.000
		P(1)	115365.2	0.540 ± 0.007 (0.465 ± 0.152) <sup>c</sup>	0.460 ± 0.007 (0.535 ± 0.152) <sup>c</sup>	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 18$	R(0)	115371.4	0.532 ± 0.007 (0.347 ± 0.112) <sup>c</sup>	0.468 ± 0.007 (0.653 ± 0.112) <sup>c</sup>	0.000
		P(2)	116197.2	0.241 ± 0.006	0.759 ± 0.006	0.000
		P(1)	116202.5	0.235 ± 0.003	0.765 ± 0.003	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 19$	R(0)	116209.1	0.207 ± 0.028	0.793 ± 0.028	0.000
		R(0,2)	116210.2	0.222 ± 0.011	0.778 ± 0.011	0.000
		P(2)	116672.7	0.054 ± 0.007	0.946 ± 0.007	0.000
		P(1)	116678.4	0.050 ± 0.005	0.950 ± 0.005	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 20$	R(2)	116683.6	0.064 ± 0.001	0.936 ± 0.001	0.000
		R(0,1)	116684.7	0.053 ± 0.004	0.947 ± 0.004	0.000
$b'(^1\Sigma_u^+)$	$\nu' = 21$	R(0,1)	117206.9	0.054 ± 0.006	0.925 ± 0.005	0.021 ± 0.007
$b'(^1\Sigma_u^+)$	$\nu' = 22$	R(0)	117684.2	0.400 ± 0.043	0.156 ± 0.030	0.444 ± 0.028
$b'(^1\Sigma_u^+)$	$\nu' = 22$	P(1)	118481.1	0.235 ± 0.053	0.000	0.765 ± 0.053
$b'(^1\Sigma_u^+)$	$\nu' = 23$	R(0,1)	118487.4	0.332 ± 0.091	0.333 ± 0.001	0.635 ± 0.078
$b'(^1\Sigma_u^+)$	$\nu' = 23$	R(0,1)	118970.0	0.257 ± 0.087	0.023 ± 0.001	0.710 ± 0.089
$b'(^1\Sigma_u^+)$	$\nu' = 24$	R(0,1)	119431.7	0.426 ± 0.076	0.051 ± 0.001	0.523 ± 0.077
$b'(^1\Sigma_u^+)$	$\nu' = 25$	R(0,1)	119837.0	0.460 ± 0.019	0.000	0.540 ± 0.019
$b'(^1\Sigma_u^+)$	$\nu' = 26$	R(0)	120586.2	0.342 ± 0.025	0.000	0.658 ± 0.025
$b'(^1\Sigma_u^+)$	$\nu' = 27$	R(0)	121037.2	0.327 ± 0.015	0.000	0.673 ± 0.015
$b'(^1\Sigma_u^+)$	$\nu' = 28$	R(0)	121453.5	0.000	0.000	1.000

**Notes.**<sup>a</sup> Value determined by one ion image; the uncertainty is estimated to be 1%–3% based on the counting statistics.<sup>b</sup> Reported by Walter et al. (1993).<sup>c</sup> Reported by Cosby & Walter (1996).

the predissociative rovibronic states of N<sub>2</sub>. Although Figures 3(a)–(d) cover the common  $h\nu$ (VUV<sub>1</sub>) range, the branching ratio curves associated with the respective four sets of predissociative N<sub>2</sub> states, i.e., valence and Rydberg N<sub>2</sub>(Π<sub>u</sub>;  $\nu'$ ,  $J'$ ) and N<sub>2</sub>(<sup>1</sup>Σ<sub>u</sub><sup>+</sup>;  $\nu'$ ,  $J'$ ) states, are distinctly different. The different predissociative N<sub>2</sub> states with similar internal energies are found to follow different dissociation pathways, indicating that they are not statistical. Therefore, the formation of a selected photoproduct can be controlled by exciting a particular quantum state.

For N<sub>2</sub> photodissociation via the valence and Rydberg N<sub>2</sub>(Π<sub>u</sub>;  $\nu'$ ,  $J'$ ) states at  $h\nu$ (VUV<sub>1</sub>) < 117,184 cm<sup>-1</sup>, Figures 3(a) and (b) show that the branching ratios for N(<sup>4</sup>S) + N(<sup>2</sup>D) are near unity, except in the energy region from 113,121 to 113,709 cm<sup>-1</sup>, where the competing N(<sup>4</sup>S) + N(<sup>2</sup>P) channel becomes the major pathway with branching ratios in the range of 0.75–0.88. These correspond to the Q(1,2), R(0,1), and R(2) transitions of the valence N<sub>2</sub>(<sup>1</sup>Π<sub>u</sub>;  $\nu' = 17$ –18) bands (see Figure 3(a) and Table 1). The spin-forbidden product channel

N(<sup>4</sup>S) + N(<sup>2</sup>P) was observed only weakly, with branching ratios ≤ 0.16 at the R(0), R(1), and R(2) transitions of the Rydberg N<sub>2</sub>(c<sub>4</sub><sup>1</sup>Π<sub>u</sub>,  $\nu' = 0$ ) band in the  $h\nu$ (VUV<sub>1</sub>) range of 115,569–115,577 cm<sup>-1</sup> (see Figure 3(b) and Table 2).

The lowest energy for the formation of the spin-allowed N(<sup>2</sup>D) + N(<sup>2</sup>D) channel is observed when N<sub>2</sub> molecules are excited to the R(0,1) line of the N<sub>2</sub>(<sup>1</sup>Σ<sub>u</sub><sup>+</sup>,  $\nu' = 20$ ) band at 117,206.9 cm<sup>-1</sup> (see Figure 3(c) and Table 3). This is only ~45 cm<sup>-1</sup> above the threshold energy for the spin-allowed channel N(<sup>2</sup>D) + N(<sup>2</sup>D), indicating that there is no potential barrier for this channel. The lowest Rydberg states that are observed to form this product channel are R(0) transitions of the bands N<sub>2</sub>(c<sub>4</sub><sup>1</sup>Π<sub>u</sub>,  $\nu' = 1$ ) and N<sub>2</sub>(c<sub>5</sub><sup>1</sup>Σ<sub>u</sub><sup>+</sup>,  $\nu' = 1$ ) at 117,750.8 and 118,074.2 cm<sup>-1</sup>, respectively, and they are 588.8 and 912.2 cm<sup>-1</sup> above the energetic threshold, respectively. The branching ratio curves of Figures 3(b)–(d) all show that the N(<sup>2</sup>D) + N(<sup>2</sup>D) channel becomes the major dissociation pathway above its energetic threshold. Nevertheless, the spin-forbidden N(<sup>4</sup>S) + N(<sup>2</sup>D) and N(<sup>4</sup>S) + N(<sup>2</sup>P) channels for

**Table 4**  
Product Branching Ratios for the  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  Channels from Excitation to the  $N_2(c_4', c_5', c_6', \text{ and } c_7'^1\Sigma_u^+; v', J')$  Rydberg States in  $N_2$  Photodissociation

Term	$v'$	$J''$	VUV <sub>1</sub> (cm <sup>-1</sup> )	$N(^4S) + N(^2D)$	$N(^4S) + N(^2P)$	$N(^2D) + N(^2D)$
$c_4'(^1\Sigma_u^+)$	$v' = 0$	P(2)	104314.3	1.000	0.000	0.000
		P(1)	104318.4	1.000	0.000	0.000
		R(0)	104326.4	1.000	0.000	0.000
		R(1)	104330.1	1.000	0.000	0.000
		R(2)	104333.7	1.000	0.000	0.000
$c_4'(^1\Sigma_u^+)$	$v' = 1$	P(2)	106360.0	1.000	0.000	0.000
		P(1)	106364.6	1.000	0.000	0.000
		R(0)	106372.0	1.000	0.000	0.000
		R(1)	106374.8	1.000	0.000	0.000
		R(2)	106377.1	1.000	0.000	0.000
$c_4'(^1\Sigma_u^+)$	$v' = 2$	P(2)	108535.9	1.000	0.000	0.000
		P(1)	108541.0	1.000	0.000	0.000
		R(0)	108547.8	1.000	0.000	0.000
		R(1)	108549.6	1.000	0.000	0.000
		R(2)	108550.0	1.000	0.000	0.000
$c_4'(^1\Sigma_u^+)$	$v' = 3$	P(2)	110652.7	0.937 <sup>a</sup> (0.85) <sup>b</sup>	0.063 <sup>a</sup> (0.15) <sup>b</sup>	0.000
		R(0)	110659.9	0.943 <sup>a</sup>	0.057 <sup>a</sup>	0.000
		R(1)	110662.4	0.936 <sup>a</sup>	0.064 <sup>a</sup>	0.000
$c_4'(^1\Sigma_u^+)$	$v' = 4$	P(2)	112759.7	0.385 ± 0.016	0.615 ± 0.016	0.000
		P(1)	112764.2	0.390 ± 0.012 (0.606 ± 0.148) <sup>c</sup>	0.610 ± 0.012 (0.394 ± 0.148) <sup>c</sup>	0.000
		R(0)	112771.7	0.426 ± 0.037	0.574 ± 0.037	0.000
		R(1)	112774.2	0.410 ± 0.018 (0.517 ± 0.057) <sup>c</sup>	0.590 ± 0.018 (0.483 ± 0.057) <sup>c</sup>	0.000
		R(2)	112776.1	0.413 ± 0.021 (0.439 ± 0.045) <sup>c</sup>	0.587 ± 0.021 (0.561 ± 0.045) <sup>c</sup>	0.000
$c_4'(^1\Sigma_u^+)$	$v' = 5$	P(1)	114824.0	0.774 ± 0.024	0.226 ± 0.024	0.000
		R(0)	114834.8	1.000	0.000	0.000
		R(1)	114837.9	1.000	0.000	0.000
		R(2)	114839.9	1.000	0.000	0.000
$c_5'(^1\Sigma_u^+)$	$v' = 0$	R(0)	115851.8	0.367 ± 0.015 (0.36 ± 0.041) <sup>c</sup>	0.633 ± 0.0015 (0.64 ± 0.041) <sup>c</sup>	0.000
		R(0,2)	115853.4	0.386 ± 0.021	0.615 ± 0.021	0.000
$c_4'(^1\Sigma_u^+)$	$v' = 6$	R(0)	116810.3	0.725 ± 0.028	0.275 ± 0.028	0.000
		R(1)	116813.5	0.712 <sup>a</sup>	0.288 <sup>a</sup>	0.000
		R(2)	116816.1	1.000	0.000	0.000
$c_5'(^1\Sigma_u^+)$	$v' = 1$	R(0)	118074.2	0.000	0.000	1.000
$c_4'(^1\Sigma_u^+)$	$v' = 7$	R(0)	118770.7	0.011 ± 0.002	0.010 ± 0.001	0.979 ± 0.002
		R(1)	118771.9	0.008 ± 0.002	0.000	0.992 ± 0.002
$c_6'(^1\Sigma_u^+)$	$v' = 0$	R(0)	119944.5	0.000	0.000	1.000
$c_5'(^1\Sigma_u^+)$	$v' = 2$	R(0,1)	120194.3	0.450 ± 0.024	0.000	0.550 ± 0.024
$c_4'(^1\Sigma_u^+)$	$v' = 8$	R(0,1)	120689.0	0.369 ± 0.030	0.181 ± 0.019	0.450 ± 0.011
		R(2)	120693.5	0.226 ± 0.039	0.000	0.774 ± 0.049
$c_7'(^1\Sigma_u^+)$	$v' = 0$	R(0)	121870.0	0.353 ± 0.040	0.000	0.642 ± 0.040

**Notes.**

<sup>a</sup> Value determined by one ion image; the uncertainty is estimated to be 1%–3% based on the counting statistics.

<sup>b</sup> Reported by Walter et al. (1993).

<sup>c</sup> Reported by Cosby & Walter (1996).

some predissociative  $^1\Pi$  and  $^1\Sigma_u^+$  states remain competitive with the spin-allowed  $N(^2D) + N(^2D)$  channel at an energy up to 4997 cm<sup>-1</sup> beyond its energetic threshold.

By populating the valence states with  $^1\Pi_u$  symmetry, the lowest energy observed for the formation of the  $N(^4S) + N(^2P)$  channel was at the Q(2) line (109,826.1 cm<sup>-1</sup>) of the  $N_2(b^1\Pi_u; v' = 12)$  band (see Table 1 and the magnified branching ratio curve of Figure 3(a)). For exciting the valence  $N_2$  states with  $^1\Sigma_u^+$  symmetry, the lowest energy observed for the  $N(^4S) + N(^2P)$  channel is at the R(2) transition (109,534.2 cm<sup>-1</sup>) of the  $N_2(b'^1\Sigma_u^+, v' = 8)$  band (see Table 3 and the magnified branching ratio curve of Figure 3(c)). Taking into account that the energetic threshold for the  $N(^4S) + N(^2P)$  channel is 107,553 cm<sup>-1</sup>, these experimental results suggest an upper

bound for the potential energy barrier of 1981 cm<sup>-1</sup> for the formation of  $N(^4S) + N(^2P)$  products. This observation of a potential energy barrier is consistent with the expectation that the formation of the spin-forbidden  $N(^4S) + N(^2P)$  products necessarily involves a singlet to triplet crossing (Ndome et al. 2008; Hochlaf et al. 2010b). By directly exciting the triplet  $N_2(C^3\Pi_u; v' = 16, J')$  states, the lowest energy observed for this channel is found to be  $\approx 108,290$  cm<sup>-1</sup>. This observation yields a lower upper bound value of  $\approx 740$  cm<sup>-1</sup> for the potential barrier of the  $N(^4S) + N(^2P)$  channel.

The present experiment shows that the branching ratios for the competing spin-forbidden channels,  $N(^4S) + N(^2D)$  and  $N(^4S) + N(^2P)$ , of the valence  $N_2(^1\Sigma_u^+)$  states exhibit oscillatory structures in the  $h\nu(\text{VUV}_1)$  region below the

**Table 5**  
Product Branching Ratios for the  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  Channels from Excitation to Valence  $N_2$  States, ( $C^3\Pi_u$ ;  $v' = 16, J$ ), and Rydberg  $N_2$  States, ( $X^+(0) 4f$ ,  $X^+(0) 4f$ , ( $X^+(1) 4f$ ) and ( $X^+(0) 5f$ ), in  $N_2$  Photodissociation

Term	$v'$	$J''$	VUV <sub>1</sub> (cm <sup>-1</sup> )	$N(^4S)+N(^2D)$	$N(^4S)+N(^2P)$	$N(^2D)+N(^2D)$
$C^3\Pi_u$	$v' = 16$	P(3)	108276.4	0.925 ± 0.005	0.075 ± 0.005	0.000
		P(2)	108283.6	0.887 ± 0.019	0.113 ± 0.019	0.000
		Q(2)	108288.2	0.954 ± 0.004	0.046 ± 0.004	0.000
		R(3)	108291.5	0.892 ± 0.015	0.108 ± 0.015	0.000
$X^+(0) 4f, L = +3$	$v' = 0$	R(0,1)	108295.5	0.959 ± 0.011	0.041 ± 0.011	0.000
		Q(2), R(2)	118707.8	0.012 ± 0.007	0.000	0.988 ± 0.007
		P(2)	118710.4	0.000	0.000	1.000
		R(1)	118715.1	0.011 ± 0.006	0.000	0.989 ± 0.006
$X^+(0) 4f, L = -3$	$v' = 0$	R(0)	118722.3	0.006 ± 0.008	0.000	0.994 ± 0.008
		P(1)	118726.5	0.070 <sup>a</sup>	0.000	0.930 <sup>a</sup>
		R(2)	118787.8	0.008 ± 0.002	0.000	0.992 ± 0.002
		P(2), Q(2), R(2)	120872.4	0.144 ± 0.019	0.000	0.856 ± 0.019
$X^+(0) 4f, L = -1$	$v' = 0$	R(1)	120878.8	0.302 ± 0.021	0.000	0.698 ± 0.021
		R(0)	120884.9	0.388 ± 0.193	0.000	0.612 ± 0.193
		Q(0)	120888.3	0.384 ± 0.008	0.000	0.616 ± 0.008
		R(0)	121242.4	0.909 ± 0.003	0.000	0.091 ± 0.003
$X^+(0) 5f, L = +3$	$v' = 0$	R(0)	121242.4	0.909 ± 0.003	0.000	0.091 ± 0.003
		Q(0)	121274.5	0.872 ± 0.027	0.000	0.128 ± 0.027

**Note.**

<sup>a</sup> Value determined by a single ion image; the uncertainty is estimated to be 1%–3% based on the counting statistics.

energetic threshold of the  $N(^2D) + N(^2D)$  channel. Three oscillatory peaks of the branching ratio curve for the  $N(^4S) + N(^2P)$  channel located at 110,192.7 cm<sup>-1</sup> [ $N_2(b'^1\Sigma_u^+; v' = 9)$ ], 113,541.0 cm<sup>-1</sup> [ $N_2(b'^1\Sigma_u^+; v' = 14)$ ], and 116,678.4 cm<sup>-1</sup> [ $N_2(b'^1\Sigma_u^+; v' = 19)$ ] are clearly observed in Figure 3(c). These peak positions coincide with the minima positions of the branching ratio curve for the  $N(^4S) + N(^2D)$  channel, indicating the competitive nature of the two product channels. To our knowledge, these oscillatory structures have not been observed previously. The comparison of the branching ratio curves of Figures 3(a) and (c) shows that the two peaks at 110,192.7 and 113,541.0 cm<sup>-1</sup> for  $N(^4S) + N(^2P)$  resolved in Figure 3(c) are also discernible in Figure 3(a), although the peak appearing near 110,192.7 cm<sup>-1</sup> in Figure 3(a) is very weak. The two peaks at 113,541.0 and 116,678.4 cm<sup>-1</sup> are also partially resolved in Figure 3(d) for the Rydberg  $N_2$  states with  $^1\Sigma_u^+$  symmetry, while no obvious oscillation of the branching curve is apparent in Figure 3(b) for the Rydberg  $N_2$  states with  $^1\Pi_u$  symmetry.

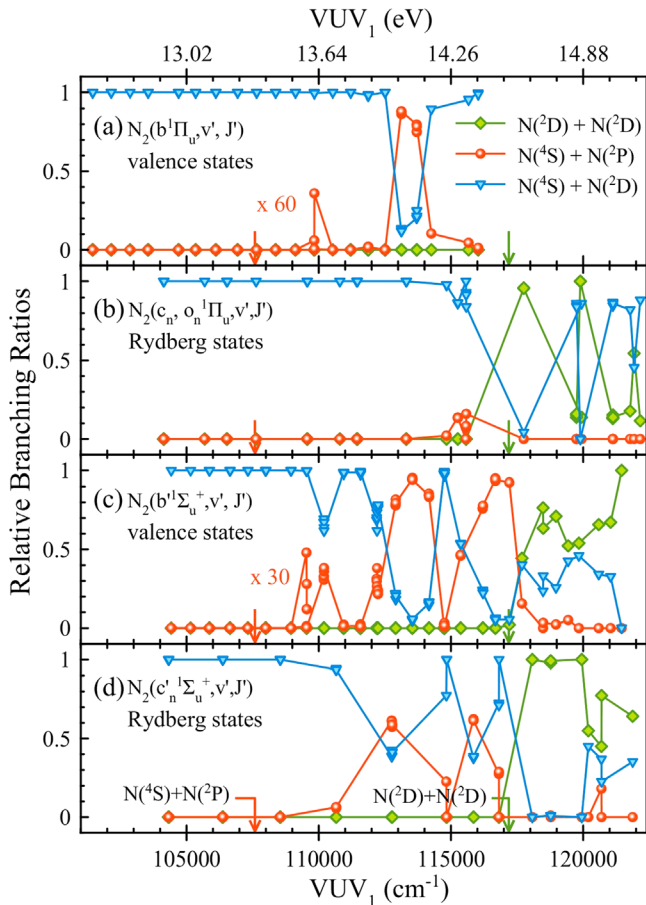
#### 4.3. Theoretical Potential Energy Curves of Relevance to VUV Photodissociation of $N_2$

In order to provide insight to the experimental observation, theoretical ab initio PECs for  $N_2$  states in the frequency range of 70,000–120,000 cm<sup>-1</sup> calculated as a function of the N–N distance [ $r(N-N)$ ] are shown in Figure 4. Since only ungerade states can be populated by VUV excitation from the gerade  $N_2(X^1\Sigma_g^+)$  ground state, only PECs of the ungerade states are depicted in the figure. The  $^1\Pi_u$  PECs are diabatic curves from Spelsberg & Meyer (2001). The most outstanding features of the PECs are the avoided crossings of  $C^3\Pi_u$  and  $C'^3\Pi_u$  at  $\approx 101,250$  cm<sup>-1</sup>,  $C^3\Pi_u$  and  $III^3\Pi_u$  at  $\approx 113,573$  cm<sup>-1</sup>, and  $b'^1\Sigma_u^+$  and  $c'^1\Sigma_u^+$  at  $\approx 110,000$ – $116,000$  cm<sup>-1</sup>, which are marked by dashed circles in Figure 4. Vibronic couplings induce these avoided crossings. The dissociation along the PECs of  $C^3\Pi_u$ ,  $C'^3\Pi_u$ , and  $III^3\Pi_u$  (shown in green) leads to the formation of the  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$  channels, respectively. The potential energy diagram of

Figure 4 shows that the PECs of states that correlate to the  $N(^4S) + N(^4S)$  ground-state channel are high-multiplicity states and cannot be populated readily from photoexcitation, indicating that the formation of the ground-state product channel is highly unfavorable, in accord with the present experimental findings.

The black vertical line marked as FC in Figure 4 shows the central Franck–Condon excitation region from  $N_2(X^1\Sigma_g^+; v'' = 0)$  at  $r(N-N) = 2.08$  Bohr. The accessible VUV excited  $N_2$  states with  $^1\Pi_u$  symmetry [( $b^1\Pi_u; v'$ ), ( $c_n^1\Pi_u; v'$ ), and ( $o_n^1\Pi_u; v'$ )] are shown in red, and those with  $^1\Sigma_u^+$  symmetry [( $b'^1\Sigma_u^+; v'$ ) and ( $c_n'^1\Sigma_u^+; v'$ )] are shown in blue. The initial formation of lower  $^1\Sigma_u^+$  and  $^1\Pi_u$  states by VUV excitation can populate the  $b^1\Pi_u$  and  $b'^1\Sigma_u^+$  states by vibronic couplings. Both these  $b^1\Pi_u$  and  $b'^1\Sigma_u^+$  states correlate to the  $N(^2D) + N(^2D)$  channel. The  $b^1\Pi_u$  can couple to the  $C^3\Pi_u$  and  $C'^3\Pi_u$  states by spin–orbit interactions at the  $C^3\Pi_u/C'^3\Pi_u$  avoided crossing, leading to the formation of  $N(^4S) + N(^2D)$  products via the  $C^3\Pi_u$  PEC. This is in agreement with the conclusion obtained by Lewis et al. (2005). The fact that the PECs for  $b^1\Pi_u$  and  $b'^1\Sigma_u^+$  states are nearly overlapping with the  $C^3\Pi_u$  state in the  $r(N-N)$  range of 2.5–4.0 Bohr can also promote spin–orbit interactions, resulting in the population of the  $C'^3\Pi_u$  state that correlates to the  $N(^4S) + N(^2P)$  channel.

The  $C^3\Pi_u$  PEC is predicted to have a potential barrier at the internuclear distance  $\approx 3.6$  Bohr. The top barrier of the  $C^3\Pi_u$  PEC, which defines the barrier height for the  $N(^4S) + N(^2D)$  channel, is predicted to be close to the  $N_2(b^1\Pi_u; v' = 0)$  state located at 100,808 cm<sup>-1</sup>. Since this state is the lowest predissociative state that can be populated by VUV excitation in the present experiment and the formation of  $N(^4S) + N(^2D)$  products is observed via this state, we conclude that the upper bound of the potential barrier for the  $N(^4S) + N(^2D)$  channel is 2870 cm<sup>-1</sup>. Based on the coupled-channel calculations by Lewis et al., the shallow potential well formed between the  $C^3\Pi_u/C'^3\Pi_u$  avoided crossing and the potential barrier at internuclear distance  $\approx 3.6$  Bohr can hold bound vibrational states, and they are predicted to be dissociative (Lewis et al.

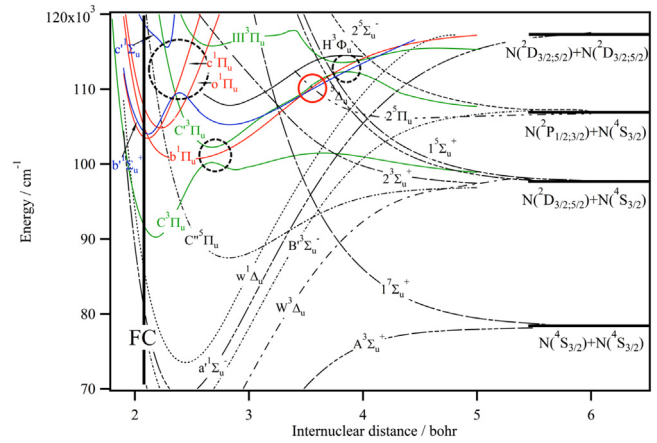


**Figure 3.** Branching ratios for the spin-forbidden  $N(^4S) + N(^2D)$  (blue) and  $N(^4S) + N(^2P)$  (red) channels and the spin-allowed  $N(^2D) + N(^2D)$  (green) channel observed in the photodissociation of  $N_2$  in the  $h\nu(VUV_1)$  range of 100,500–122,200  $cm^{-1}$ . This range covers excitation of (a) valence  $N_2$  states with  $^1\Pi_u$  symmetry, (b) Rydberg  $N_2$  states with  $^1\Pi_u$  symmetry, (c) valence  $N_2$  states with  $^1\Sigma_u^+$  symmetry, and (d) Rydberg  $N_2$  states with  $^1\Sigma_u^+$  symmetry. The downward-pointing red and green arrows mark the energetic thresholds of the  $N(^4S) + N(^2P)$  and  $N(^2D) + N(^2D)$  channels at 107,587.1 and 117,184.5  $cm^{-1}$ , respectively. A respective 60-fold and 30-fold magnification of the Y-axes of the (a) and (c) branching ratio curves is shown to illustrate the threshold for the  $N(^4S) + N(^2P)$  channel.

2005). This could lower the dissociation barrier for the  $N(^4S) + N(^2D)$  channel to about 1500  $cm^{-1}$ .

As shown in Figure 4, higher  $^1\Sigma_u^+$  states initially populated by VUV excitation in shorter  $r(N-N)$  range can couple with the  $C^3\Pi_u$  state by spin-orbit interactions as the  $C^3\Pi_u$  PEC passes through the  $b^1\Sigma_u^+/c^1\Sigma_u^+$  avoided crossing region (marked by dashed circles). At sufficiently high energies above the potential barrier of the  $b^1\Sigma_u^+$  state, excited  $N_2$  molecules initially prepared in  $^1\Sigma_u^+$  states can also couple with the  $^3\Pi_u$  states at the  $C^3\Pi_u/III^3\Pi_u$  avoided crossing, and then following the  $C^3\Pi_u$  PEC to produce  $N(^4S) + N(^2P)$  products. Based on the calculated PECs, the further excitation of  $N_2(X^1\Sigma_g^+)$  to high  $^1\Sigma_u^+$  states is expected to result in the formation of the  $N(^2D) + N(^2D)$  channel without a potential barrier. This prediction is also consistent with the experimental observation.

The theoretical calculations show that the  $C^3\Pi_u/III^3\Pi_u$  avoided crossing occurs at  $r(N-N) \approx 3.47$  Bohr, and the maximum of the  $C^3\Pi_u$  PEC is located at  $\approx 112,500$   $cm^{-1}$ , giving a value of  $\approx 4950$   $cm^{-1}$  for the potential barrier for the formation of  $N(^4S) + N(^2P)$  products. However, this value is



**Figure 4.** Ab initio PECs for the  $N_2$  molecule in the energy range of 70,000–120,000  $cm^{-1}$ . These PECs are computed at the CAS-SCF/MRCI/aug-cc-pVQZ(+3 s+2p) following procedures described in Ndome et al. (2008) and Hochlaf et al. (2010b). The vertical line marked FC represents the center Franck-Condon transition region. The PECs of the  $^1\Pi_u$ ,  $^1\Sigma_u^+$ , and  $^3\Pi_u$  states are shown in red, blue, and green, respectively. The  $^1\Pi_u$  PECs are diabatic curves from Spelsberg & Meyer (2001). The  $C^3\Pi_u/C^3\Pi_u$ ,  $C^3\Pi_u/III^3\Pi_u$ , and  $b^1\Sigma_u^+/c^1\Sigma_u^+$  avoided crossings are marked by dashed circles. The dissociation along the  $C^3\Pi_u$ ,  $C^3\Pi_u$ , and  $III^3\Pi_u$  states correlates with the dissociation channels  $N(^4S) + N(^2D)$ ,  $N(^4S) + N(^2P)$ , and  $N(^2D) + N(^2D)$ , respectively.

much higher than the estimate of  $\approx 740$   $cm^{-1}$  obtained in the present experiments by exciting the predissociative triplet  $N_2(C^3\Pi_u; v' = 16, J')$  states. Figure 4 shows that the  $2^5\Pi_u$  and  $C^3\Pi_u$  states intersect at  $\approx 110,000$   $cm^{-1}$  and  $r(N-N) \approx 3.5$  Bohr (marked by a red circle). Since the  $2^5\Pi_u$  state leads directly to  $N(^4S) + N(^2P)$  products, a further conversion from the triplet  $C^3\Pi_u$  to the quintet  $2^5\Pi_u$  state by spin-orbit coupling would lower the predicted potential barrier for this channel to  $\approx 2450$   $cm^{-1}$ . However, the latter value remains significantly higher than the experimental value of  $\approx 740$   $cm^{-1}$ . The large discrepancy observed between the theoretical and experimental potential barriers for the formation of the  $N(^4S) + N(^2P)$  channel is indicative of more complex pathways, which may involve multiple crossings or other quantum coupling mechanisms (Lewis et al. 2005).

The theoretical PECs have provided insight for the oscillations observed in the branching ratio curves in Figures 3(a) and (c). The photodissociation cross section of  $N_2$  depends on the Franck-Condon factor for photoexcitation, as well as the strength of electronic couplings of the excited states involved. The oscillations of the branching ratios as observed for the  $N_2(b^1\Pi_u; v' = 0-23)$  and  $N_2(b^1\Sigma_u^+; v' = 0-28)$  bands may be due to the variations of the integrals of vibrational wavefunctions. The theoretical PECs of Figure 4 show that the singlet  $b^1\Pi_u$  and  $b^1\Sigma_u^+$  states run parallel to the triplet  $C^3\Pi_u$  state so that the couplings between these states should depend on the vibrational overlap integrals between them over the  $r(N-N)$  range of 2.5–4.0 Bohr.

The peaks observed in the branching ratio curves for the  $N(^4S) + N(^2P)$  channel located at  $h\nu(VUV_1) \approx 113,541.0$   $cm^{-1}$  coincide with the location of the  $C^3\Pi_u/III^3\Pi_u$  avoided crossing, indicating that the formation of  $N(^4S) + N(^2P)$  products is strongly favored from dissociative valence  $N_2$  states situated at this energy gap. The lowest energy to the  $N(^4S) + N(^2P)$  channel located at 110,192.7  $cm^{-1}$  was also found to coincide with the energy position at which the  $C^3\Pi_u$  and  $2^5\Pi_u$  states

intersect. The highest-energy branching ratio peak observed at  $h\nu(\text{VUV}) \approx 116,678.4 \text{ cm}^{-1}$  for the  $\text{N}(^4\text{S}) + \text{N}(^2\text{P})$  channel could be ascribed to a higher efficiency for excitation to the  $(c^1\Sigma_u^+; v')$  state, which subsequently couples via spin-orbit interaction to the  $\text{C}^3\Pi_u$  state, leading to the formation of the  $\text{N}(^4\text{S}) + \text{N}(^2\text{P})$  channel. It appears from the experiment that for the production of the  $\text{N}(^4\text{S}) + \text{N}(^2\text{P})$  channel, excitation to the  $\text{N}_2(b^1\Sigma_u^+; v')$  states is more effective compared to the  $\text{N}_2(b^1\Pi; v')$  states. This observation could be rationalized that the  $\text{N}_2(b^1\Sigma_u^+; v')$  states can couple to the  $\text{C}^3\Pi_u$  state at short as well as long  $r(\text{N-N})$  ranges, whereas the  $\text{N}_2(b^1\Pi_u; v')$  states couple to the  $\text{C}^3\Pi_u$  state mostly in the long  $r(\text{N-N})$  range.

In the present study, we are mainly focusing on reporting the experimental branching ratios of  $\text{N}_2$  photodissociation over a very large photon energy range and theoretically explaining the overall trend of these ratios as the vibrational energy of the excited states changes. Our branching ratios are for low- $J'$  (mainly  $J' = 0-3$ ) states since a cold  $\text{N}_2$  molecular beam is generated by supersonic expansion. This is extremely useful in decoupling the spin-orbit interactions from rotational interactions when trying to explain the dissociation process theoretically. We have also measured the anisotropy parameters (or beta parameters) for the recoiling N atoms, which can be used in the theoretical model built by Buijssse and van der Zande (Buijssse et al. 1996; Buijssse & van der Zande 1997b) to provide more details of the dissociation dynamics. Detailed theoretical calculations and discussions of all the individual rotational states measured in the present experiment are beyond the scope of this paper and will be presented in separate publications.

#### 4.4. Implications for Astronomy and Planetary Sciences

Nitrogen molecules have always been known to be important in the atmospheres of the planets, their satellites, and the early history of our solar system (Torr & Torr 1979, 1982; Strobel & Shemansky 1982; Meier 1991; Feldman et al. 2001; Bakalian 2006), but their importance in extrasolar planets, the interstellar medium, circumstellar envelopes, and comets has only been recognized recently (Knauth et al. 2004; Snow 2004; van Dishoeck 2006; Moses et al. 2011; Balucani 2012; Li et al. 2013, 2014). Thus, the branching ratios that we have obtained here are important in all of these regions, and they depend on both the intensity and the energy distributions of the VUV radiation striking the region. There are two energy regions that have to be considered, namely, above and below the  $\text{IE}(\text{H}) = 109,678.8 \text{ cm}^{-1}$ . When the VUV radiation illuminates a region that contains many H atoms, only the radiation below the  $\text{IE}(\text{H})$  will be important because H atoms will absorb all the radiation with energies above  $109,678.8 \text{ cm}^{-1}$ . Considering the branching ratios in Figures 3(a)–(d), it is clear that only  $\text{N}(^4\text{S}) + \text{N}(^2\text{D})$  atoms are formed, and they have a maximum available recoil energy of 1.46 eV or 0.73 eV/atom. This translational recoil energy is not enough to drive the reactions of the  $\text{N}(^4\text{S})$  atoms with  $\text{H}_2$  and other molecules, but it will be enough for the  $\text{N}(^2\text{D})$  atoms to overcome any activation energy that is associated with chemical reactions between this atom and any other molecules that might be present (Herron 1999; Pascual et al. 2002). In those astronomical regions where light with energies above  $109,678.8 \text{ cm}^{-1}$  can penetrate, Reaction (4) becomes more important since two  $\text{N}(^2\text{D})$  are produced for every photon absorbed. These  $\text{N}(^2\text{D})$  have a lower recoil translational energy

since a significant amount of the available energy has gone into excitation of the second N atom. At these higher energies the  $\text{N}(^2\text{P})$  are also produced, but these atoms are considerably less reactive than  $\text{N}(^2\text{D})$  atoms (Herron 1999).

The lifetimes for the radiative decay of the excited  $\text{N}(^2\text{D}_J, J = 3/2 \text{ and } 5/2)$  spin-orbit states to the  $\text{N}(^4\text{S}_{3/2})$  ground state have values of 13.69 and 36.67 hr, respectively, because they are spin-forbidden processes (Godefroid & Fischer 1984). The  $\text{N}(^2\text{P}_J, J = 1/2 \text{ and } 3/2)$  atoms undergo faster radiative decay to both  $\text{N}(^2\text{D}_{3/2})$  and  $\text{N}(^2\text{D}_{5/2})$  states with lifetimes of 52.9 and 47.9 s, respectively (Godefroid & Fischer 1984). When the total number densities for molecular species in astronomical regions are greater than  $10^8 \text{ cm}^{-3}$ , the reactions of the  $\text{N}(^2\text{P}_J)$  state have to be considered because the collision time is shorter than the radiative lifetimes of these states. Since these excited atoms are considerably less reactive, they will probably only undergo energy transfer to the  $\text{N}(^2\text{D})$  and  $\text{N}(^4\text{S})$  states.

## 5. COMETARY IMPLICATIONS

The observation of  $\text{N}_2$  in comet 67/P Churyumov-Gerasimenko (67/P CG) by the ROSINA mass spectrometer on the *Rosetta* spacecraft when the comet was  $\approx 3 \text{ AU}$  from the Sun proves that this molecule is present in comets (Rubin et al. 2015). Satellite observations of numerous comets have shown that the dust and gas come out from the nucleus as jets similar to the jets formed in the laboratory from free expansion of a gas into a vacuum system. So like we have shown in this paper,  $\text{N}_2$  coming out of such jet will be exposed to solar radiation below 100 nm, and it is likely to dissociate to form  $\text{N}(^2\text{D})$  atoms that are highly energetic and long-lived. Once these atoms are formed, they are likely to collide and react with  $\text{H}_2\text{O}$  molecules depending on the astronomical region that is being discussed. The recommended rate constant for the reaction of  $\text{N}(^2\text{D})$  atoms with  $\text{H}_2\text{O}$  is about  $4 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  (Umamoto et al. 1999). The expected products for this reaction are  $\text{NH} + \text{OH}$ ,  $\text{H} + \text{HNO}$ , and  $\text{H}_2 + \text{NO}$  (Umamoto et al. 1999; Casavecchia et al. 2001). Collisions of both  $\text{N}(^2\text{D})$  and  $\text{N}(^2\text{P})$  atoms with  $\text{H}_2\text{O}$  molecules can lead to energy transfer between these metastable atoms and the  $\text{H}_2\text{O}$  that could then cascade down to the metastable  $6_{16}$  level of  $\text{H}_2\text{O}$  that may have been detected in several comets and the interstellar medium (Jackson et al. 1976; Altenhoff et al. 1983; Bird et al. 1997; Cosmovici et al. 1998, 2014; Cottin et al. 1999). Whether or not collisions of long-lived  $\text{N}(^2\text{D})$  and  $\text{N}(^2\text{P})$  atoms are important in explaining the later observations, it is clear that they are important in understanding the overall process in astronomical bodies.

## 6. CONCLUSIONS

The branching ratios are measured for the  $\text{N}(^4\text{S}) + \text{N}(^2\text{D})$ ,  $\text{N}(^4\text{S}) + \text{N}(^2\text{P})$ , and  $\text{N}(^2\text{D}) + \text{N}(^2\text{D})$  product channels from VUV photodissociation of  $\text{N}_2$  over a wide energy range from 100,808 to 122,159  $\text{cm}^{-1}$ . Comparisons between the current experimental measurements and those measured by Cosby and coworkers (Helm & Cosby 1989; Walter et al. 1993, 1994; Cosby & Walter 1996) are made for states with common rovibrational quantum numbers, and they are found to be in general agreement with each other. This energy range covers four sets of singlet predissociative  $\text{N}_2$  rovibronic states, namely, the  $(^1\Pi_u; v', J')$  and  $(^1\Sigma_u^+; v', J')$  valence and Rydberg states, as well as the  $\text{N}_2(\text{C}^3\Pi_u; v' = 16, J')$  states. The fact that the

branching ratio curves obtained for the four sets of singlet  $N_2$  states in this common energy range are distinctly different indicates that the branching ratios are dependent on the  $N_2$  predissociative state and the photodissociation of  $N_2$  is nonstatistical.

No experimental evidence for the production of the spin-allowed  $N(^4S) + N(^4S)$  ground-state channel is seen, in agreement with previous experimental measurements (Helm & Cosby 1989; Walter et al. 1993, 1994). The spin-allowed  $N(^2D) + N(^2D)$  channel occurs with no potential barrier and eventually becomes the dominant process at  $4173 \text{ cm}^{-1}$  above its energetic threshold.

In the energy region between the energetic thresholds for the  $N(^4S) + N(^2P)$  and  $N(^2D) + N(^2D)$  channels both the spin-forbidden  $N(^4S) + N(^2D)$  and  $N(^4S) + N(^2P)$  channels occur. The branching ratios for these channels exhibit oscillatory structures, when plotted as a function of  $h\nu(\text{VUV}_1)$  for the excitation of the ( $^1\Pi_u; v', J'$ ) and ( $^1\Sigma_u^+; v', J'$ ) valence and Rydberg states. This indicates that the dominant production of the  $N(^4S) + N(^2D)$  or  $N(^4S) + N(^2P)$  or  $N(^2D) + N(^2D)$  channels can be controlled by photoexcitation to selected  $N_2$  rovibronic states.

High-level ab initio PECs for the  $N_2$  states calculated in the energy range between  $70,000$  and  $120,000 \text{ cm}^{-1}$  predict that the formation of both spin-forbidden channels  $N(^4S) + N(^2D)$  and  $N(^4S) + N(^2P)$  involves potential barriers. The theoretical PECs suggest that by taking into account the spin-orbit interaction of the  $C^3\Pi_u$  and  $2^5\Pi_u$  states, the theoretical potential barrier can be lower for the  $N(^4S) + N(^2P)$  channel, putting it in closer agreement with the experimental measurements. The determination of the potential barrier for the  $N(^4S) + N(^2D)$  channel is limited by the lowest state [ $N_2(b^1\Pi_u; v' = 0)$ ] that can be prepared by VUV photoexcitation. Nevertheless, the upper bound of  $2870 \text{ cm}^{-1}$  for the potential barrier of the  $N(^4S) + N(^2D)$  channel obtained here is close to the theoretical prediction based on the PEC curves shown in Figure 4. The oscillatory peaks observed in the branching ratio curves for the  $N(^4S) + N(^2P)$  channel have also been rationalized based on the calculated PECs.

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