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Supplementary materials for

Multi-channel photodissociation dynamics of ¹⁴N₂ in its b' ¹ Σ + u(v=20) state

Pan Jiang^{1,2}, Liya Lu^{1,2}, Min Liu^{1,2}, Hong Gao^{1,2*}

¹ Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry,

Chinese Academy of Sciences, Beijing 100190, China

² University of Chinese Academy of Sciences, Beijing 100049, China

* Email address: honggao2017@iccas.ac.cn (Hong Gao)



Figure S1 PHOFEX spectrum by detecting $N(^{2}D_{3/2})$ for the $b' \, ^{1}\Sigma + u(v=20)$ state of $^{14}N_{2}$. The intensities of the spectrum are not calibrated with the VUV laser intensity.



Figure S2 PHOFEX spectra by detecting $N(^{2}D_{5/2})$ (blue curve) and $N(^{2}D_{3/2})$ (red curve) for the b' $^{1}\Sigma$ + u(v=20) state of $^{14}N_{2}$ by using a thermalized molecular beam (see main text for details). The intensities of the spectra are not calibrated with the VUV laser intensity. The disappearance of the rotational transitions between 116930 cm⁻¹ and 117000 cm⁻¹ is mainly due to relatively weak VUV intensity in this range.



Figure S3 Relative branching ratios BR(${}^{2}D_{5/2}$) measured by detecting N(${}^{2}D_{5/2}$). The results are plotted versus J(J+1), and J is rotational quantum number of the upper level. The error bars represent the standard deviations (1 σ) of 3-6 independent measurements.



Figure S4 Relative branching ratios BR(${}^{2}D_{3/2}$) measured by detecting N(${}^{2}D_{3/2}$). The results are plotted versus J(J+1), and J is rotational quantum number of the upper level. The error bars represent the standard deviations (1 σ) of 3-6 independent measurements.



Figure S5 Measured predissociation linewidths of the $b' {}^{1}\Sigma + u(v=20)$ state of ${}^{14}N_2$ from Refs. 21 and 27.



Figure S6 PPRCs of channel $N(^{2}D_{3/2,5/2})+N(^{2}D_{3/2,5/2})$. Black squares are values from Figure 6 in main text. Red dots represent values by subtracting PPRCs of channels $N(^{4}S)+N(^{2}D_{3/2,5/2})$ and $N(^{4}S)+N(^{2}P_{1/2,3/2})$ from TPRCs by assuming that PPRCs of $N(^{4}S)+N(^{2}D_{3/2,5/2})$ and $N(^{4}S)+N(^{2}P_{1/2,3/2})$ are independent of *J*. The error bars are inherited from TPRCs only. The straight lines are linear fittings of the values for *J*=1-5, *J*=1-4, *J*=0-5 and *J*=0-5,14-21 respectively.

VUV(cm ⁻¹)	Rotational	$BR(^{2}D_{5/2})$		$BR(^{2}D_{3/2})$		BR(⁴ S)	
	transition	%	1σ	%	1σ	%	1σ
117207.2	R(0,1)	95.6	1.4	86.6	2.1	94.4	0.2
117205.7	R(2)	98.2	0.7	95.2	0.1	93.4	1.4
117202.3	R(3)	99.0	0.6	97.5	0.7	94.3	0.5
117200.9	P(1)	93.3	0.3	89.9	1.1	93.7	1.3
117197.0	R(4)	99.2	0.6	98.8	0.4	95.2	0.2
117195.1	P(2)	94.3	1.0	89.9	1.1	94.3	0.4
117189.9	R(5)	100.3	0.6	99.2	0.2	- 🗌	- 🗌
117187.4	P(3)	96.2	0.6	93.1	0.7	95.2	0.9
117181.0	R(6)	99.6	0.3	99.8	0.1	- 🗆	- 🗌
117177.9	P(4)	97.9	0.7	94.9	0.9	94.7	0.3
117170.2	R(7)	100.0	0.2	100.0	0.0	- 🗆	- 🗌
117166.5	P(5)	98.8	0.2	96.7	0.8	94.8	0.2
117157.5	R(8)	99.9	0.3	100.5	0.9	- 🗌	- 🗌
117153.3	P(6)	99.4	0.2	98.5	0.6	95.3	0.6
117143.0	R(9)	100.4	0.4	100.4	1.0	- 🗌	- 🗌
117138.2	P(7)	99.7	0.0	99.6	0.1	- 🗌	- 🗌
117126.6	R(10)	100.0	0.1	100.4	0.7	- 🗌	- 🗌
117121.3	P(8)	99.7	0.1	99.6	0.1	- 🗌	- 🗌
117108.4	R(11)	99.3	2.5	100.0	0.7	- 🗌	- 🗌
117102.5	P(9)	100.8	1.2	99.6	0.7	- 🗌	- 🗌
117088.3	R(12)	100.0	0.4	100.1	0.3	- 🗌	- 🗌
117081.9	P(10)	99.9	0.2	100.1	0.2	- 🗆	- 🗌
117066.4	R(13)	100.4	2.2	100.3	0.2	- 🗆	- 🗌
117059.4	P(11)	99.9	1.4	100.2	1.8	- 🗌	-

Table S1 Relative branching ratios BR(${}^{2}D_{5/2}$), BR(${}^{2}D_{3/2}$) and BR(${}^{4}S$) for the *b*' ${}^{1}\Sigma$ + u(v=20) state of ${}^{14}N_{2}$ measured by detecting N(${}^{2}D_{5/2}$), N(${}^{2}D_{3/2}$) and N(${}^{4}S$) respectively. The standard deviation (1 σ) is calculated from a total of 3-6 independent measurements.