## Supplementary materials for

Multi-channel photodissociation dynamics of ${ }^{14} \mathbf{N}_{\mathbf{2}}$ in its $\boldsymbol{b}^{\boldsymbol{1} \boldsymbol{\Sigma}+\mathbf{u}(\mathbf{v}=\mathbf{2 0}) \text { state }, ~}$

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Figure $\mathbf{S 1}$ PHOFEX spectrum by detecting $\mathrm{N}\left({ }^{2} \mathrm{D}_{3 / 2}\right)$ for the $b^{\prime}{ }^{1} \mathrm{\Sigma}+\mathrm{u}(\mathrm{v}=20)$ state of ${ }^{14} \mathrm{~N}_{2}$. The intensities of the spectrum are not calibrated with the VUV laser intensity.


Figure S2 PHOFEX spectra by detecting $\mathrm{N}\left({ }^{2} \mathrm{D}_{5 / 2}\right)$ (blue curve) and $\mathrm{N}\left({ }^{2} \mathrm{D}_{3 / 2}\right)$ (red curve) for the $b^{\prime}{ }^{1} \Sigma+u(v=20)$ state of ${ }^{14} \mathrm{~N}_{2}$ 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 $116930 \mathrm{~cm}^{-1}$ and $117000 \mathrm{~cm}^{-1}$ is mainly due to relatively weak VUV intensity in this range.


Figure S3 Relative branching ratios $\mathrm{BR}\left({ }^{2} \mathrm{D}_{5 / 2}\right)$ measured by detecting $\mathrm{N}\left({ }^{2} \mathrm{D}_{5 / 2}\right)$. 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 $(1 \sigma)$ of 3-6 independent measurements.


Figure S4 Relative branching ratios $\operatorname{BR}\left({ }^{2} \mathrm{D}_{3 / 2}\right)$ measured by detecting $\mathrm{N}\left({ }^{2} \mathrm{D}_{3 / 2}\right)$. 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 ( $1 \sigma$ ) of 3-6 independent measurements.


Figure S5 Measured predissociation linewidths of the $b^{\prime}{ }^{1} \Sigma+u(v=20)$ state of ${ }^{14} \mathrm{~N}_{2}$ from Refs. 21 and 27.


Figure S6 PPRCs of channel $N\left({ }^{2} \mathrm{D}_{32,5 / 2}\right)+\mathrm{N}\left({ }^{2} \mathrm{D}_{32,5 / 5}\right)$. Black squares are values from Figure 6 in main text. Red dots represent values by subtracting PPRCs of channels $N\left({ }^{4} \mathrm{~S}\right)+\mathrm{N}\left({ }^{2} \mathrm{D}_{3 / 2,5 / 2}\right)$ and $\mathrm{N}\left({ }^{4} \mathrm{~S}\right)+\mathrm{N}\left({ }^{2} \mathrm{P}_{1 / 2,3 / 2}\right)$ from TPRCs by assuming that PPRCs of $\mathrm{N}\left({ }^{4} \mathrm{~S}\right)+\mathrm{N}\left({ }^{2} \mathrm{D}_{3 / 2,5 / 2}\right)$ and $\mathrm{N}\left({ }^{4} \mathrm{~S}\right)+\mathrm{N}\left({ }^{( } \mathrm{P}_{1 / 2,3 / 2}\right)$ 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.

Table S1 Relative branching ratios $\operatorname{BR}\left({ }^{2} \mathrm{D}_{5 / 2}\right), \operatorname{BR}\left({ }^{2} \mathrm{D}_{3 / 2}\right)$ and $\mathrm{BR}\left({ }^{4} \mathrm{~S}\right)$ for the $b^{\prime}{ }^{1} \Sigma+\mathrm{u}(v=20)$ state of ${ }^{14} \mathrm{~N}_{2}$ measured by detecting $\mathrm{N}\left({ }^{2} \mathrm{D}_{5 / 2}\right), \mathrm{N}\left({ }^{2} \mathrm{D}_{3 / 2}\right)$ and $\mathrm{N}\left({ }^{4} \mathrm{~S}\right)$ respectively. The standard deviation $(1 \sigma)$ is calculated from a total of 3-6 independent measurements.

| VUV $\left(\mathrm{cm}^{-1}\right)$ | Rotational <br> transition | $\mathrm{BR}\left({ }^{2} \mathrm{D}_{5 / 2}\right)$ |  | $\mathrm{BR}\left({ }^{( } \mathrm{D}_{3 / 2}\right)$ |  | $\mathrm{BR}\left({ }^{4} \mathrm{~S}\right)$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 16 | $\%$ | $1 \sigma$ | $\%$ | $1 \sigma$ |  |
| 117207.2 | $\mathrm{R}(0,1)$ | 95.6 | 1.4 | 86.6 | 2.1 | 94.4 | 0.2 |
| 117205.7 | $\mathrm{R}(2)$ | 98.2 | 0.7 | 95.2 | 0.1 | 93.4 | 1.4 |
| 117202.3 | $\mathrm{R}(3)$ | 99.0 | 0.6 | 97.5 | 0.7 | 94.3 | 0.5 |
| 117200.9 | $\mathrm{P}(1)$ | 93.3 | 0.3 | 89.9 | 1.1 | 93.7 | 1.3 |
| 117197.0 | $\mathrm{R}(4)$ | 99.2 | 0.6 | 98.8 | 0.4 | 95.2 | 0.2 |
| 117195.1 | $\mathrm{P}(2)$ | 94.3 | 1.0 | 89.9 | 1.1 | 94.3 | 0.4 |
| 117189.9 | $\mathrm{R}(5)$ | 100.3 | 0.6 | 99.2 | 0.2 | $-\square$ | $-\square$ |
| 117187.4 | $\mathrm{P}(3)$ | 96.2 | 0.6 | 93.1 | 0.7 | 95.2 | 0.9 |
| 117181.0 | $\mathrm{R}(6)$ | 99.6 | 0.3 | 99.8 | 0.1 | $-\square$ | $-\square$ |
| 117177.9 | $\mathrm{P}(4)$ | 97.9 | 0.7 | 94.9 | 0.9 | 94.7 | 0.3 |
| 117170.2 | $\mathrm{R}(7)$ | 100.0 | 0.2 | 100.0 | 0.0 | $-\square$ | $-\square$ |
| 117166.5 | $\mathrm{P}(5)$ | 98.8 | 0.2 | 96.7 | 0.8 | 94.8 | 0.2 |
| 117157.5 | $\mathrm{R}(8)$ | 99.9 | 0.3 | 100.5 | 0.9 | $-\square$ | $-\square$ |
| 117153.3 | $\mathrm{P}(6)$ | 99.4 | 0.2 | 98.5 | 0.6 | 95.3 | 0.6 |
| 117143.0 | $\mathrm{R}(9)$ | 100.4 | 0.4 | 100.4 | 1.0 | $-\square$ | $-\square$ |
| 117138.2 | $\mathrm{P}(7)$ | 99.7 | 0.0 | 99.6 | 0.1 | $-\square$ | $-\square$ |
| 117126.6 | $\mathrm{R}(10)$ | 100.0 | 0.1 | 100.4 | 0.7 | $-\square$ | $-\square$ |
| 117121.3 | $\mathrm{P}(8)$ | 99.7 | 0.1 | 99.6 | 0.1 | $-\square$ | $-\square$ |
| 117108.4 | $\mathrm{R}(11)$ | 99.3 | 2.5 | 100.0 | 0.7 | $-\square$ | $-\square$ |
| 117102.5 | $\mathrm{P}(9)$ | 100.8 | 1.2 | 99.6 | 0.7 | $-\square$ | $-\square$ |
| 117088.3 | $\mathrm{R}(12)$ | 100.0 | 0.4 | 100.1 | 0.3 | $-\square$ | $-\square$ |
| 117081.9 | $\mathrm{P}(10)$ | 99.9 | 0.2 | 100.1 | 0.2 | $-\square$ | $-\square$ |
| 117066.4 | $\mathrm{R}(13)$ | 100.4 | 2.2 | 100.3 | 0.2 | $-\square$ | $-\square$ |
| 117059.4 | $\mathrm{P}(11)$ | 99.9 | 1.4 | 100.2 | 1.8 | $-\square$ | $-\square$ |

