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Nonadiabatic quantum dynamics explores non-monotonic photodissociation branching of N₂ into the N(⁴S) + N(²D) and N(⁴S) + N(²P) product channels†

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Vacuum ultraviolet (VUV) photodissociation of N₂ molecules is a source of reactive N atoms in the interstellar medium. In the energy range of VUV optical excitation of N₂, the N–N triple bond cleavage leads to three types of atoms: ground-state N(⁴S) and excited-state N(²P) and N(²D). The latter is the highest reactive and it is believed to be the primary participant in reactions with hydrocarbons in Titan's atmosphere. Experimental studies have observed a non-monotonic energy dependence and non-statistical character of the photodissociation of N₂. This implies different dissociation pathways and final atomic products for different wavelength regions in the sunlight spectrum. We here apply *ab initio* quantum chemical and nonadiabatic quantum dynamical techniques to follow the path of an electronic state from the excitation of a particular singlet ¹Σ_g⁺ and ¹Π_u vibronic level of N₂ to its dissociation into different atomic products. We simulate dynamics for two isotopomers of the nitrogen molecule, ¹⁴N₂ and ¹⁴N¹⁵N for which experimental data on the branching are available. Our computations capture the non-monotonic energy dependence of the photodissociation branching ratios in the energy range 108 000–116 000 cm⁻¹. Tracing the quantum dynamics in a bunch of electronic states enables us to identify the key components that determine the efficacy of singlet to triplet population transfer and therefore predissociation lifetimes and branching ratios for different energy regions.

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Introduction

Space missions and radio astronomy can analyze the composition of upper levels of Earth's atmosphere, the atmospheres of other bodies in space and the interstellar medium. Up to nowadays, more than 200 individual molecular species from diatomic H₂ and N₂ to polyatomic Buckminsterfullerene and Rugbyballene were identified in space.^{1,2} These recent discoveries have formed the basis for astrochemistry, the study of molecular structure and processes in the interstellar medium.^{3–5}

The molecules that have been identified in space are composed of 19 different elements, but carbon, hydrogen,

nitrogen, and oxygen predominate. Despite the diversity of space chemistry, the main components of interstellar medium are H₂ and CO and only in the atmospheres of Earth, Pluto, Titan, and Triton have significant amounts of N₂ been detected. Its high chemical stability makes N₂ the most abundant nitrogen-containing molecule in the interstellar medium. However, the astrochemistry of nitrogen is diverse and rich: there are 92 different nitrogen-containing species¹ from diatomic CN (cyano radical)^{6–8} and NO (nitric oxide)^{9,10} to triatomic CaNC (calcium isocyanide)¹¹ and polyatomic CH₂NH (methanimine)^{12,13} and (NH₂)₂CO (urea).¹⁴ This has resulted in a great interest in the chemistry of N₂ in Earth's and Titan's atmospheres, where N₂ molecules are the major constituent.^{15–19} A combination of lab experiments in plasma and computer simulations shows possible reactions of the activated forms of N₂ with CH₄ and C₂H₄ in Titan's atmosphere.^{20–22} To understand the mechanism of these reactions and their complexity, one should have a closer look at the electronic structure of N₂.

The nitrogen molecule in its ground electronic state is a textbook example of high chemical stability: under standard conditions on Earth, its triple covalent bond is believed to be among the strongest known in nature. At the same time,

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nitrogen-containing molecules – purines, pyrimidines, pyrroles and indoles – play the essential role in life, and it is important to find out how the inert N_2 molecule can be converted in nature into more chemically active forms. Early studies proposed a possible active nitrogen:^{23,24} N_2 in its vibrationally excited ground state $X^1\Sigma_g^+$ and in the metastable electronically excited $A^3\Sigma_u^+$ state or excited-state N atoms. The optically excited states of N_2 are high in energy: from 100 000 to 120 000 cm^{-1} (from 12.4 to 14.9 eV) relative to its ground state. Only in upper levels of Earth's atmosphere, which are not shielded by the ozone layer, the sunlight covers this energy range and nitrogen molecules can be excited and then dissociate into nitrogen atoms in their ground and excited states. The chemical reactivity of the resulting nitrogen atoms is not equal. The ground-state $N(^4S)$ is known to be rather inert while the excited atoms are chemically active and even further, among $N(^2P)$ and $N(^2D)$ the latter is known to be much more reactive.^{25–27} Today, excited $N(^2D)$ atoms are believed to play the principal role in reactions with H_2 and hydrocarbons and forming HCN, C_2N_2 and other compounds in low-pressure space environments.^{28–32}

The first step in generation of chemically active nitrogen atoms is the optical excitation of the molecule in the VUV spectral region. The absorption spectrum of N_2 from 100 000 to 120 000 cm^{-1} was extensively studied both experimentally^{33,34} and theoretically.³⁵ Following classification based on selection rules, two types of one-photon optically accessible singlet states are possible for excitation from the electronic ground state: $^1\Sigma_u^+$ and $^1\Pi_u$. These states are reached by a parallel or a perpendicular orientation of the molecule relative to the light field. They are in principle coupled by L-uncoupling interaction which is negligible for low rotational levels, so these states of different symmetry practically do not interact with one another. However, states of the same symmetry and multiplicity can be coupled by a rather strong nonadiabatic terms and so the electronic states of either $^1\Sigma_u^+$ or $^1\Pi_u$ symmetry can be mixed among themselves. In the extensively studied lower energy region these states are bound.

In the energy range of interest here, the way to dissociation is through spin-orbit induced transfer from the singlets to the states of higher multiplicity which are dissociative. The photodissociation of N_2 has been experimentally studied by, first, electron impact³⁶ and further with fast-beams^{37–39} and wavelength selected VUV excitation.^{40,41} The latter was with special reference to isotopic selectivity. The most recent detailed work uses supersonic molecular beams coupled with velocity-mapped imaging method.^{42–45} In the energy range up to 120 000 cm^{-1} , there are three dissociation limits which lead to excited-state N atoms in the following states at the given thresholds:

$$N(^4S) + N(^2D), E > 12.143 \text{ eV} (97\,938 \text{ cm}^{-1})$$

$$N(^4S) + N(^2P), E > 13.335 \text{ eV} (107\,553 \text{ cm}^{-1})$$

$$N(^2D) + N(^2D), E > 14.526 \text{ eV} (117\,162 \text{ cm}^{-1})$$

The experiments consistently exhibit strong energy dependence in the photodissociation branching fractions: different predissociative N_2 states with similar internal energies are found to follow different dissociation pathways, thereby suggesting that the unimolecular dissociation is not statistical.

Experimental studies provide the accurate information on the final dissociation products but do not explain the origin of their energy dependence. Here theoretical approaches can be essential. High-level *ab initio* quantum chemistry methods allow a close examination of a group of electronic states of comparable energies so that one can simulate a realistic dependence of the potential energy of different electronic states on changes in the molecular bond distance. Quantum chemical calculations have accompanied experiments in interpretation of the electronic structure of N_2 in many directions: vibronic states energies and composition,^{46,47} nature of electronic transitions^{48,49} and band complexes.^{50,51} The potential energy curves were studied in detail^{52–59} as well as the spin-orbit⁵⁶ and nonadiabatic couplings.⁶⁰ Nowadays the quantum dynamical approaches^{61–64} have reached a level where they can offer a computational tool which allowed us to follow the time-evolution of an electronic wave packet travelling in the forest of electronic states, beyond the states directly accessed from the ground electronic state.⁶⁵

The approach has been applied to explore the mechanism of dissociative ionization of N_2 ^{66–68} and ultrafast electronic excitation and dissociation.^{69–72} We recently computed a realistic energy dependence in the dissociation branching arising from excitation of different single vibrational levels of $^1\Sigma_u^+$ electronic states of N_2 .^{65,73} These computations started from the molecule in the ground electronic state and excited it by a polarized laser pulse of a very long duration and of the required mean energy. In the present work we make a step further and present the results of the branching into the channels $N(^4S) + N(^2D)$ (Channel 1) and $N(^4S) + N(^2P)$ (Channel 2) accessed through the excited $^1\Pi_u$ states of N_2 . We highlight the differences in the results for these two distinct doorway excited states. First, following excitation of $^1\Sigma_u^+$ states there is an early opening of Channel 2 at 110 000 which is absent for the $^1\Pi_u$ singlets. Also, from 112 000 to 115 000 cm^{-1} there are oscillating changes in branching for $^1\Pi_u$ while for $^1\Sigma_u^+$ the change is smooth. For both types of the singlets, a drop is present at 115 000 cm^{-1} , but then for excited $^1\Sigma_u^+$ there is a preferable branching fraction into Channel 2 while for $^1\Pi_u$ the preference is for dissociation into Channel 1.

The manuscript is organized as follows: first, we review the selection rules relevant to the one-photon excitation and dissociation of N_2 and the computational scheme that we use for the simulations. Second, we compare the dissociation branching starting from excited $^1\Sigma_u^+$ or $^1\Pi_u$ states and we discuss the predissociation lifetime and isotope effect on the dynamics and branching. We conclude with a prospective outlook on excited state dissociative dynamics in the N_2 molecule in connection with reaction dynamics in the upper atmosphere and in the interstellar medium.

Computational details

Selection rules relevant for the one-photon excitation of N_2

The $^{14}N_2$ molecule belongs to $D_{\infty h}$ point group. This means the presence of inversion through a center of symmetry and infinite

number of horizontal mirror planes intersecting the principal symmetry Z axis along the N–N bond. Therefore, all the electronic states can be classified either “gerade” or “ungerade” relative to the inversion operation. In the present paper, we discuss one photon VUV excitation of N_2 from its ground state $X^1\Sigma_g^+$. The dipole allowed transitions are those with the change of parity and so only $^1\Sigma_u^+$ and $^1\Pi_u$ can be optically accessed. The symmetry of the final state depends on the orientation of the molecule relative to the laser: if the molecule aligns along X/Y axis, $^1\Pi_u$ states will be reached and if it aligns along Z axis $^1\Sigma_u^+$ states. These singlet states are coupled to other “ungerade” states of higher multiplicity *via* spin–orbit coupling.

There are three Cartesian components of the spin–orbit coupling integrals that differ along X , Y and Z axes in the molecular frame: LSX , LSY , LSZ . According to their orbital momentum Λ , all the states can be labelled as Σ , Π , Δ *etc.* Triplet and quintet electronic states are degenerate states with different S_z projection ($m_s = -1, 0, 1$ for triplets and $m_s = -2, -1, 0, 1, 2$ for quintets). The selection rules of the spin–orbit coupling play a key role in the interconnections of manifolds of states of different multiplicities. Two states with $\Delta\Lambda = 0$ are coupled by the Z component of the spin–orbit coupling, that we denote as LSZ and these two interacting states must have the same magnetic quantum number, $\Delta m_s = 0$. Two states with $\Delta\Lambda = \pm 1$ are coupled by the LSX/LSY component of the coupling and must differ as $\Delta m_s = \pm 1$. The implication is that while both singlet $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states can interact with the triplets, the triplet states that they couple to are different. $^1\Sigma_u^+$ singlet states are coupled by LSX/LSY component of the spin–orbit interaction to the $^3\Pi_u$ states and only $m_s = \pm 1$ of the triplet states can be populated. $^1\Pi_u$ are coupled by LSZ spin–orbit interaction to the $^3\Pi_u$ states and for this type of coupling the selection rule is $\Delta m_s = 0$ and so $m_s = 0$ of the triplet states can be populated. Similar considerations apply to coupling to the quintets: LSZ spin–orbit interaction between $^3\Pi_u$ and $^5\Pi_u$ and LSX/LSY spin–orbit coupling between $^3\Pi_u$ and $^5\Sigma_u^+$, $^5\Sigma_u^-$ and $^5\Delta_u$. Thus, considering different options for the magnetic quantum number, all the electronic states included into the Hamiltonian can be divided into two groups shown in Fig. 1 and therefore, a singlet state of $^1\Sigma_u^+$ or $^1\Pi_u$ symmetry exits to the dissociative channels in a different manner. A more detailed scheme shown in Fig. S1 of ESI.†

The states of the same symmetry and multiplicity are coupled by nonadiabatic interaction, and they can exchange population among themselves in the avoided crossings regions. We have included the nonadiabatic coupling among $^1\Sigma_u^+$, $^1\Pi_u$, $^3\Pi_u$ states. More details on selection rules can be found in ref. 74.

Quantum chemical calculations

We consider the states in energy range $90\,000$ – $120\,000$ cm^{-1} where the dissociation channels 1 and 2 are open, see Fig. 2. Thus, the electronic basis we use consist of the ground $X^1\Sigma_g^+$ state and the following excited electronic states: three $^1\Sigma_u^+$, three $^1\Pi_u$, one $^1\Sigma_u^-$, one $^1\Delta_u$, one $^3\Sigma_u^+$, one $^3\Sigma_u^-$, four $^3\Pi_u$, one $^3\Delta_u$, one $^5\Sigma_u^+$, one $^5\Sigma_u^-$, two $^5\Pi_u$ and one $^5\Delta_u$. 21 electronic states in all, and accounting for their magnetic degeneracy a total of 55

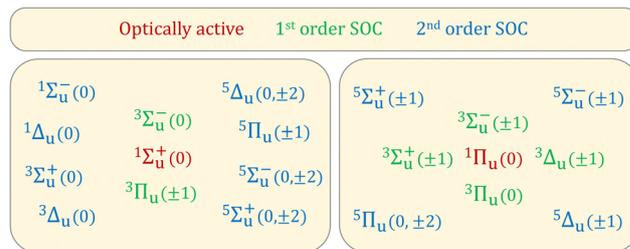


Fig. 1 Schematic representation of spin–orbit coupling between the electronic states depending on their magnetic quantum number m_s (indicated in parenthesis). There are two types of dipole-excited states shown in red: $^1\Sigma_u^+$ and $^1\Pi_u$ singlet states. They are directly coupled to the specific triplet states shown in green (1st order spin–orbit coupling). The last ones are further linked to the electronic states depicted in blue (2nd order spin–orbit coupling).

quantum electronic states. We represent the Hamiltonian in the adiabatic form and so the electronic states are labeled according to their energy. The reader should note that this classification is different from diabatic labeling commonly used in spectroscopy, however, diagonalizing the Hamiltonian in any given basis provides the same energy of the vibronic states. The following discussion will be given in the adiabatic representation which is the direct output of quantum chemical calculations.

The terms of the electronic Hamiltonian (electronic potential energy curves, nonadiabatic and spin–orbit couplings) of N_2 in the VUV energy range are calculated for each value of internuclear distance using a state-averaged complete active space self-consistent field (CASSCF) approach followed by multi-reference configuration interaction (MRCI)^{75,76}

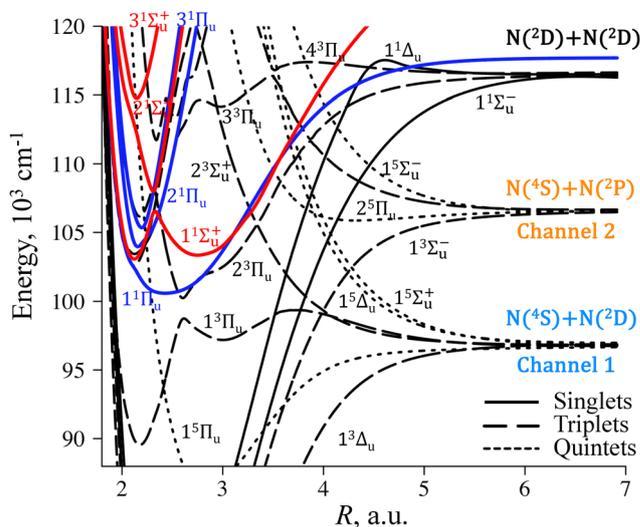


Fig. 2 Potential energy curves of “ungerade” electronic states of the nitrogen molecule in energy range $90\,000$ – $120\,000$ cm^{-1} . The colored singlets are the states that can be VUV optically accessible by one photon from the “gerade” ground electronic state. $^1\Sigma_u^+$ singlet states are shown in red and $^1\Pi_u$ are in blue. Other singlet states are shown with solid black lines, the triplet states with dashed lines and quintets with dotted lines. The lowest dissociative channels are in blue and orange.

calculations. This methodology was successfully applied to describe the electronic structure of N_2 and its cation multiple times.^{49,50,56,57,68,77} An active space of 17 orbitals ($4\sigma_u$, $3\sigma_g$, $4\pi_u$, $4\pi_g$, and $2\delta_g$) for 10 valence electrons is employed in all computations. The two lowest $1\sigma_u$ and $1\sigma_g$ orbitals are not included in the active space but are fully optimized in the CASSCF procedure. Restriction of only single occupancy for the higher Rydberg orbitals was used. We chose a doubly augmented cc-pVQZ basis set with additional bond-centered s and p diffuse functions for a proper description of Rydberg and valence singlet and triplet states according to the previously established methodology.³⁵ All the quantum chemistry calculations are performed with the MOLPRO program package.^{78,79} The computed potential energy curves are shifted by 850 cm^{-1} to be in accordance with previously published data.³⁵

The potential energy curves, nonadiabatic coupling and dipole moments of $^1\Pi_u$ states were taken in analytical form from ref. 35 and adiabaticized as explained in ref. 65. The derived adiabatic data along with presently computed spin-orbit coupling elements are given in Fig. S1–S8 of the ESI.†

Nonadiabatic quantum dynamics

We use the time-dependent Schrödinger equation of motion to compute quantum dynamics on a grid of internuclear distance for the 54 excited and 1 ground electronic states of definite multiplicity and magnetic quantum number. The equation of motion is defined for the amplitudes $C_{ng} = \Psi(R_g)$ at a given electronic state n and grid point g for the internuclear distance $R = R_g$, see ref. 80. Diagonal and off-diagonal kinetic energy terms were evaluated using a five-point finite difference approximation.⁸¹ At large internuclear distances, $R > 6.2\text{ a.u.}$, a complex absorbing potential, $V_{\text{CAP}}(R) = 0.01(R - 6.2)^3$, is applied for all the dissociative states. The nonadiabatic couplings $\tau_{nk}(R)$ between electronic states n and k are scaled by the finite difference momentum terms. The propagation of the equation of motion is solved *via* the Runge–Kutta method with the time step $\Delta t = 10^{-4}\text{ fs}$ and $\Delta R = 0.005\text{ a.u.}$ for the grid spacing. The propagation lasted for 5 ps in all the dynamical calculations. The lifetimes of the excited vibrational singlet states are estimated by a linear fit for the logarithm of their time-dependent population, $|C_{ng}(t)|^2$, assuming a unimolecular exponential decay.

The interaction with the light field is governed by the transition dipole moment $\mu_{nk}(R)$ between the ground $X^1\Sigma_g^+$ and excited singlet electronic states. An explicit time-profile for the VUV light field is used with a very long duration

$$E(t) = \epsilon_p E_{\text{max}} \exp\left(-\frac{(t-t_p)^2}{2\sigma_p^2}\right) \left[\cos(\omega_p t) - \frac{t-t_p}{\omega_p \sigma_p^2} \sin(\omega_p t) \right] \quad (1)$$

Here ϵ_p is the polarization direction of the light field, set along the internuclear axis so as to access the $^1\Sigma_u^+$ states and perpendicular to the internuclear axis to reach the $^1\Pi_u$ states. E_{max} is the maximum amplitude of the field; t_p and σ_p are the time at which the pulse is centered and the width of the Gaussian envelope of the field.

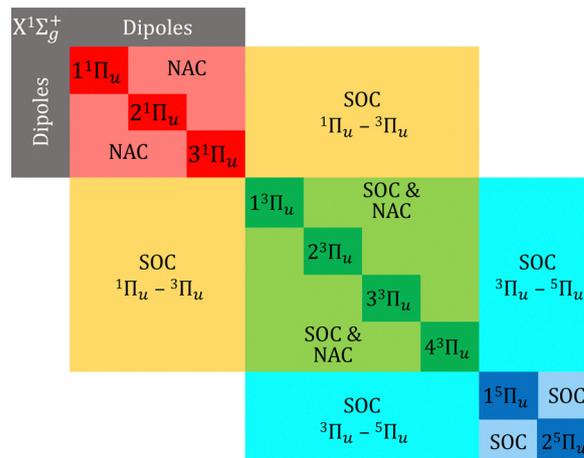


Fig. 3 A schematic representation of the Hamiltonian which includes the ground electronic state $X^1\Sigma_g^+$, singlet $^1\Pi_u$, triplet $^3\Pi_u$ and quintet $^5\Pi_u$. The singlet $^1\Pi_u$ states are coupled by X/Y components of the transition dipole moments with the ground state $X^1\Sigma_g^+$ (the dark-grey block). In the calculations, such a block is comprised by more excited states, and it is formed for each internuclear N–N grid point from 1.0 to 7.5 a.u. with the grid spacing of 0.005 a.u., 1301 blocks in total for each time point along 5 ps propagation. The same structure of Hamiltonian is applied to the singlet $^1\Sigma_u^+$ states which are coupled by Z components of the transition dipole moments with the ground state $X^1\Sigma_g^+$.

Duration of the pulse is set to be long enough to selectively excite specific vibrational levels of the singlet states, $\sigma_p = 160\text{ fs}$, $t_p = 1200\text{ fs}$ and $E_{\text{max}} = 0.0001\text{ a.u.}$ The carrier frequency ω_p is varied from $108\,000$ to $116\,000\text{ cm}^{-1}$ according to the energy of the vibrational levels obtained by diagonalization in the singlets manifold. The choice of this energy range is determined by the thresholds of two dissociation channels.

Given all the above information, the Hamiltonian can be represented as a sparse square matrix, as shown in Fig. 3. The potential energies of the electronic states form diagonal elements, and the various coupling terms are off-diagonal ones. These terms can link states of the same symmetry and multiplicity (nonadiabatic or spin-orbit couplings, shown in light-red, light-green, and light-blue) or states of different multiplicity (yellow and cyan off-diagonal blocks).

Results and discussion

VUV optically excited and dissociative states of N_2

The N_2 molecule dissociates indirectly and the excited $^1\Sigma_u^+$ and $^1\Pi_u$ singlets are the (rather narrow) doorways in the population transfer from the ground $X^1\Sigma_g^+$ state to the dissociative electronic states.⁸² For both types of the singlets, there are two bound (Rydberg-type) and one delocalized (valence-type) states. However, the $^1\Pi_u$ states all are lower-lying and are stronger mixed by nonadiabatic interaction in the energy range of $100\,000$ – $107\,000\text{ cm}^{-1}$ while the $^1\Sigma_u^+$ states are more energetically separated from one another and from $2^3\Pi_u$ and $3^3\Pi_u$ states, see Fig. 4(a) and 5(b).

Triplet $^3\Pi_u$ states are believed to be the main doorway to the single photon VUV dissociation of the N_2 molecule in the energy below $116\,000\text{ cm}^{-1}$. Three distinct dissociation channels can be

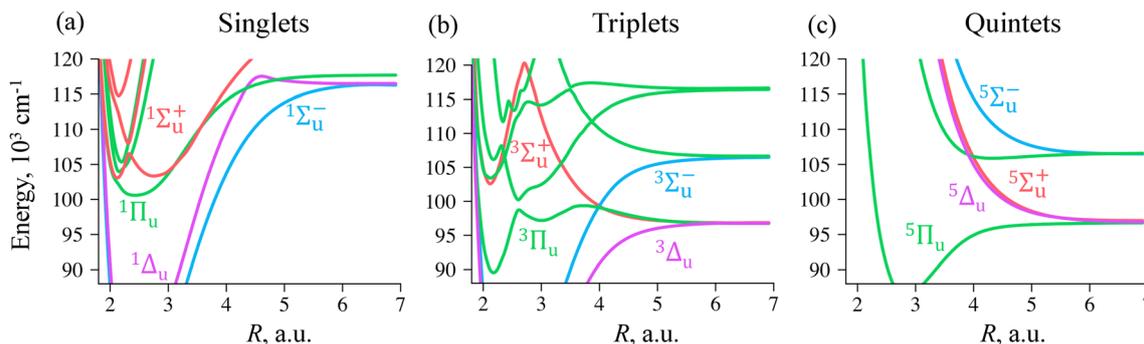


Fig. 4 Potential energy curves of singlet (a), triplet (b) and quintet (c) multiplicity color-coded according to the symmetry of the states: $^1\Sigma_u^+$, $^3\Sigma_u^+$ and $^5\Sigma_u^+$ are in orange-red; $^1\Sigma_u^-$, $^3\Sigma_u^-$, $^5\Sigma_u^-$ are in light-blue; $^1\Pi_u$, $^3\Pi_u$, $^5\Pi_u$ are in mint green; $^1\Delta_u$, $^3\Delta_u$, $^5\Delta_u$ are in magenta.

seen in the energy range from 90 000 to 120 000 cm^{-1} and two lower ones are labeled as “Channel 1” and “Channel 2” in Fig. 2. The triplet states are composed of bound parts when the internuclear distance, R , is shorter than 2.7 a.u., the repulsive one from $R > 3.5$ a.u. and dissociative ones, $R > 6$ a.u. Among the other triplets,

$^2^3\Sigma_u^+$ also has a distinctive structure: in the short-range distances, it is very energetically close to the singlet $^1\Pi_u$ state and mirrors its shape, Fig. 4(b). The other triplets and quintet states are primarily repulsive: there are no avoided crossings or other distinctions in their manifold, Fig. 4(b) and (c).

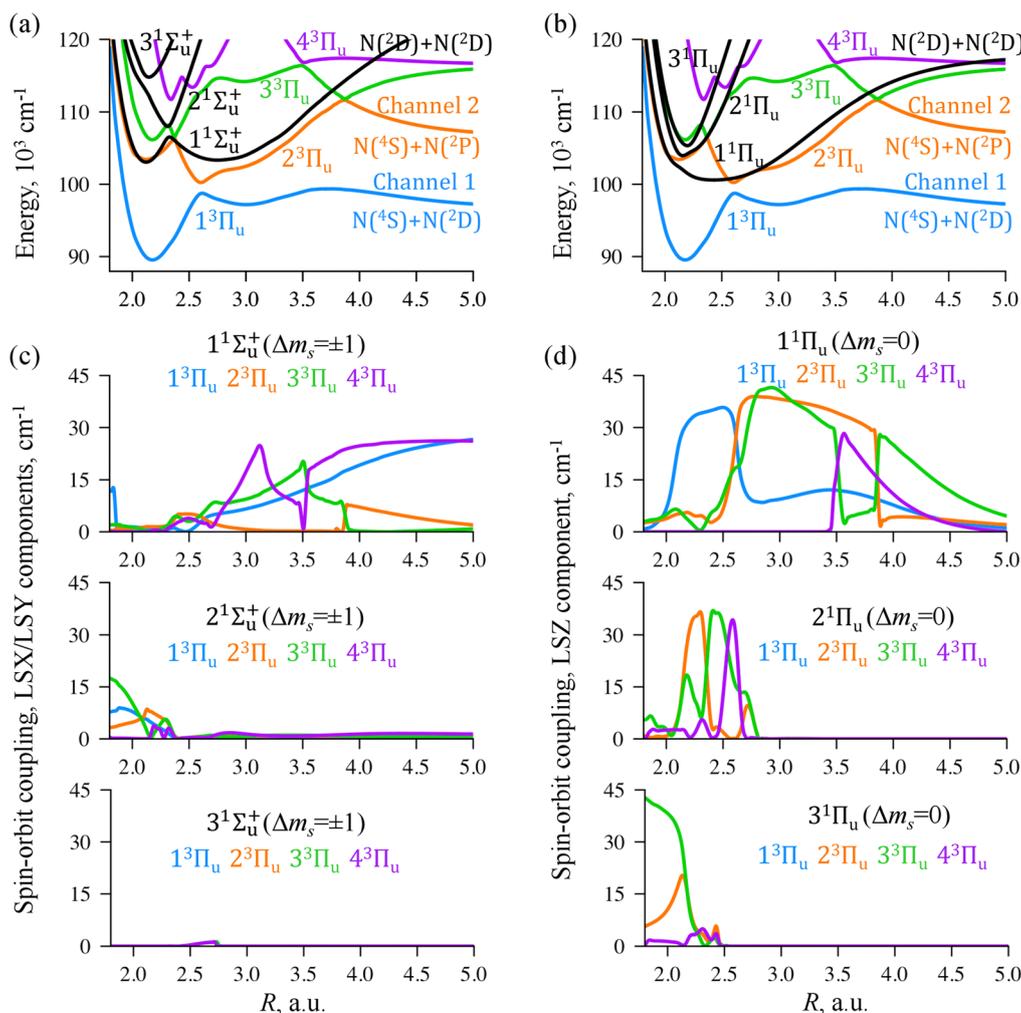


Fig. 5 (a) Potential energy curves of $^1\Sigma_u^+$ (in black) and $^3\Pi_u$ (color-coded in the figure) and the absolute values of the spin-orbit coupling terms between them; (b) $^1\Pi_u$ and (in black) and $^3\Pi_u$ (color-coded in the figure) and the spin-orbit coupling terms between them. Sudden changes in the spin-orbit coupling curves determined by changes in the character of the adiabatic triplet $^3\Pi_u$ states at avoided crossings at 2.6, 3.5, 3.9 a.u.

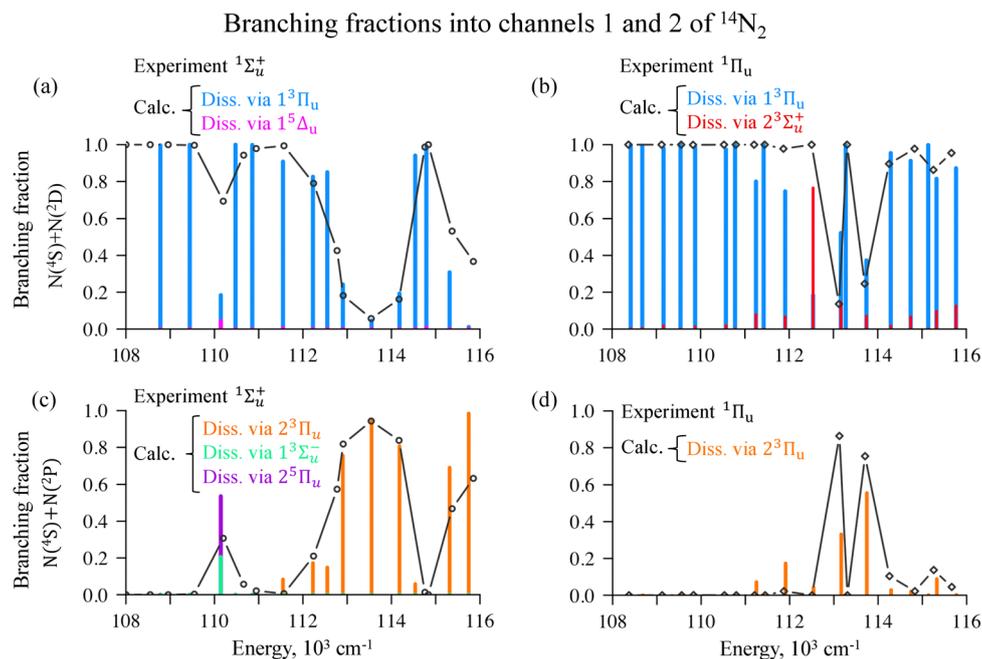


Fig. 6 Experimental (black line)⁴² and calculated (histograms color-coded in the figure) branching fractions in Channel 1 (panels a and b) and in Channel 2 (panels c and d) obtained by exciting vibronic levels of $^1\Sigma_u^+$ (panels a and c) or $^1\Pi_u$ (panels b and d) states of the $^{14}\text{N}_2$ molecule.

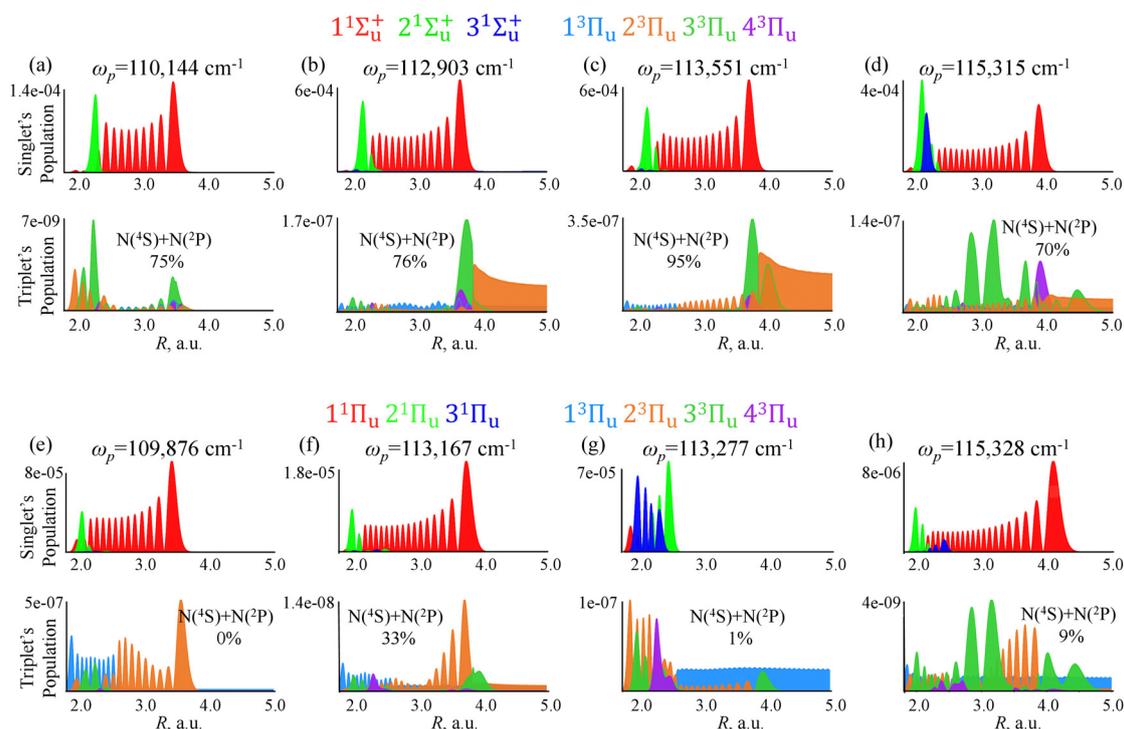


Fig. 7 Population redistribution in the singlet and triplet manifolds at 5 ps obtained by exciting vibronic levels of $^1\Sigma_u^+$ (panels a–d) or $^1\Pi_u$ (panels e–h) states of the $^{14}\text{N}_2$ molecule. ω_p is the carrier frequency of the exciting pulse (eqn (1)). Top two rows show population of four selected $^1\Sigma_u^+$ vibronic singlet and correspondingly populated triplet $^3\Pi_u$ states. Each column compares the dynamics for the two singlets at similar energy range. The branching fraction into $\text{N}(^4\text{S}) + \text{N}(^2\text{P})$ (Channel 2) is indicated in the figure for each energy.

The link between the excited states of different multiplicity is the spin–orbit coupling. The shape of the potentials

predominantly affects the magnitude and sign of the spin–orbit induced transfer from the singlet to the triplet states.

Fig. 5 shows the results of quantum chemical calculations for the spin-orbit coupling terms between $^1\Sigma_u^+$ and $^3\Pi_u$ (panels a and c) and $^1\Pi_u$ and $^3\Pi_u$ states (panels b and d). All three lowest $^1\Pi_u$ adiabatic states are stronger connected to the $^3\Pi_u$ states: the coupling of 42 cm^{-1} against of 30 cm^{-1} in the case of $^1\Sigma_u^+-^3\Pi_u$. The delocalized $^1\Pi_u$ state exits to the higher $N(^2D) + N(^2D)$ channel and so is coupled to $^3^3\Pi_u$ even in the region of its avoided crossing at 4 a.u.

The singlets are also coupled to other triplet states: $^1\Sigma_u^+$ can interact with $^3\Sigma_u^-$ while $^1\Pi_u$ interacts with $^3\Sigma_u^+$, $^3\Sigma_u^-$ and $^3\Delta_u$. However, our computations provide rather small couplings among the states mentioned above and the largest is of 12 cm^{-1} between $^1\Pi_u$ and $^2^3\Sigma_u^+$ states, see Fig. S5–S8 of the ESI.†

Energy dependence in photodissociation branching fractions. The non-statistical character of the dissociation of N_2 was noted already in 1988 by Helm and Cosby³⁷ and the experiment of Song *et al.*⁴² confirmed a non-monotonic energy dependence in the dissociation branching fractions. These experimental works showed a non-monotonic dependence of the dissociation branching on the total VUV excitation energy and suggested the presence of different pathways to dissociation determined by the initial excited vibronic level of the singlet states. The experimental results for $^1\Sigma_u^+$ and $^1\Pi_u$ states are significantly different (black lines in Fig. 6):

(1) In the case of $^1\Sigma_u^+$, there is an early opening of Channel 2 at $110\,000\text{ cm}^{-1}$ which is absent for $^1\Pi_u$;

(2) Above the avoided crossing between $^2^3\Pi_u$ and $^3^3\Pi_u$ where the triplet repulsive potential is available (from $112\,000$ to $115\,000\text{ cm}^{-1}$) there are oscillating changes in branching for $^1\Pi_u$ and a smooth change for $^1\Sigma_u^+$;

(3) In both cases, a drop is present at $115\,000\text{ cm}^{-1}$, but then for excited $^1\Sigma_u^+$ there is a preferable branching into Channel 2 while for $^1\Pi_u$ the branching is favored into Channel 1.

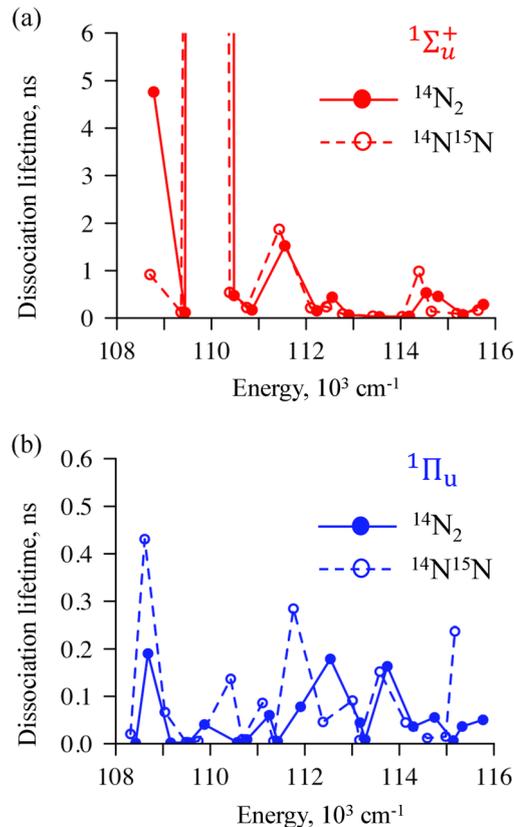


Fig. 9 Calculated predissociation lifetimes obtained by exciting vibronic levels of $^1\Sigma_u^+$ (panel a) or $^1\Pi_u$ (panel b) states of the $^{14}N_2$ (full circles) or $^{14}N^{15}N$ (empty circles) molecule.

To investigate an intricate pathway of electronic subsystem on its way from excitation of a particular vibronic level of

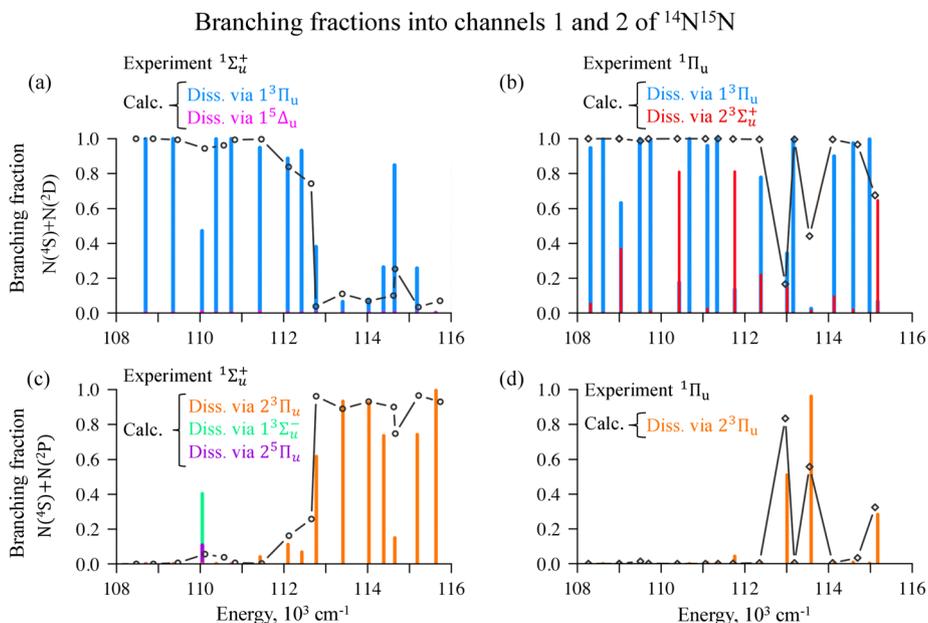


Fig. 8 Experimental (black line with circles)⁴³ and calculated (histograms are color-coded in the figure) branching fractions in Channel 1 (panels a and b) and in Channel 2 (panels c and d) obtained by exciting vibronic levels of $^1\Sigma_u^+$ (panels a and c) or $^1\Pi_u$ (panels b and d) states of the $^{14}N^{15}N$ molecule.

singlets to dissociation, we performed quantum dynamical calculations on a grid of the N–N internuclear coordinate. These calculations are based on the results of *ab initio* quantum chemical computations at CASSCF/MRCI level. The states of triplet and quintet multiplicity of *u* parity from 90 000 to 120 000 cm⁻¹ were included in the Hamiltonian, more details are given in section “Computational details”.

Fig. 6 shows the computed branching fractions into Channel 1 and Channel 2 *versus* the experimental data. The calculations have captured key features of the experiment and therefore allow us to deliver a detailed explanation on the questions pointed above.

Both Channel 1 and Channel 2 are accessible in the energy range from 108 000 to 116 000 cm⁻¹ and, statistically, up to electronic degeneracies, one would expect to see the dissociation primarily into the lowest in energy channel. However, at some energies the molecule dissociates into the higher exit. Fig. 6 shows the branching into Channel 1 in panels (a) and (b) for ¹Σ_u⁺ and ¹Π_u, respectively. Various electronic states of triplet and quintet multiplicity feed the channels, and all the significantly contributing states (more than 5% of the total dissociation) are depicted in Fig. 6. The major contributor to the dissociation is the ³Π_u triplet states: ¹³Π_u leads to Channel 1 (the blue columns in Fig. 6) and ²³Π_u leads to Channel 2 (the orange columns in Fig. 6). When ¹Σ_u⁺ states are excited, ¹³Σ_u⁻, ¹³Δ_u and ²³Π_u contribute at 110 000 cm⁻¹ only, Fig. 6(c). When ¹Π_u states are excited, ²³Σ_u⁺ plays a major role due to a higher spin–orbit coupling comparing with ¹³Σ_u⁻ and ¹³Δ_u (Fig. S7 of ESI†).

Channel 1 is preferable at lower energies almost up to 113 000 cm⁻¹ with an exception at 110 000 cm⁻¹ exclusively for the excited ¹Σ_u⁺. At the higher energies, the picture becomes more complicated due to a competition between the channels. To understand the origin of these oscillations, one should look closely at the dynamics of the wave packet. Employing ultraslow laser pulses, which are narrow in energy, one can reach a particular vibronic level and so the population will not redistribute after the pulse is over but will slightly decrease with time due to a slow dissociation. There is a discussion on this in ref. 65, 83 and 84. This allows us to examine the wave packet redistribution when the pulse is already over, but the molecule is far from being fully dissociated, as we show in the snapshots of the dynamics at 5 ps in Fig. 7. We have selected four energy levels for both ¹Σ_u⁺ and ¹Π_u where drastic changes can be seen in the branching ratio. Let us first note the similarity between the branching starting from the vibronic states of the two singlets, ¹Σ_u⁺ are presented in the top row and ¹Π_u in the bottom row in the Fig. 7.

There are clear differences between the two singlet states. Under excitation of ¹Σ_u⁺ at 110 144 cm⁻¹, Channel 2 opens. As one can see in Fig. 7(a), the population of the triplets ³Π_u is very low and so even other low populated states become important. In a previous study,⁷³ we proposed that the reason of this low population is the notably long lifetime of the excited singlet state.

The next difference in the branching is a rapid change at 113 277 cm⁻¹ for ¹Π_u. The upper panel in Fig. 7(g) shows the

singlet vibronic state ¹Π_u which is of Rydberg type. Unlike Rydberg ²¹Σ_u⁺ and ³¹Σ_u⁺ states, localized ²¹Π_u and ³¹Π_u are strongly coupled to ³Π_u triplets at short distances (see the bottom panel of Fig. 5(d)), so ¹Π_u Rydberg singlet state is effectively populating the bound triplet, see the bottom panel in Fig. 7(g).

The third difference is at 115 300 cm⁻¹ where ¹Σ_u⁺ occurs to be in resonance with the repulsive ³Π_u potential while ¹Π_u is primarily coupled to the bound ³Π_u. However, both singlets contribute to Channel 2 at 113 000 cm⁻¹ which is just above the avoided crossing between ²³Π_u and ³³Π_u states.

The principal similarity of the two singlet states is the dissociation into Channel 2 at 113 000 cm⁻¹: the repulsive triplet ³Π_u is accessible here for both singlets and the prompt dissociation occurs (Fig. 7(b) and 7(f)). At other lower energies, Channel 1 is almost always preferable and also at 115 000 cm⁻¹ when the triplet is trapped (a rapid decrease at 115 000 cm⁻¹ in Fig. 6(c) and (d)).

Predissociation lifetimes and isotope effect in photodissociation branching fractions. The recent experiment of ref. 43 showed the mass effect in the branching, which is primarily seen in the fraction of the products exiting in Channel 2. The results of the computations along with the experimental data⁴³ are depicted for the isotopomer ¹⁴N¹⁵N in Fig. 8. While the main branching fraction changes are the same for ¹⁴N₂ and ¹⁴N¹⁵N, the theory predicts a significant change in the contribution of the triplet states, in particular, ²³Σ_u⁺ state into Channel 2: even the small mass difference influence the resonance between the singlet and triplet states and makes the population transfer easier.

Another characteristic of the photodissociation is the predissociation singlet lifetime which indicates how fast or slow the initial wave packet will be transferring from the excited singlet state to the dissociation product channel *via* the triplets.

Fig. 9 presents the calculated lifetimes for both ¹Σ_u⁺ (Fig. 9a) and ¹Π_u (Fig. 9b) of the two isotopomers. A key result is that the *Y*-axes is ten-times larger for ¹Σ_u⁺: because of a weaker coupling, these states dissociate much more slowly. In particular, at the specific energy of 110 144 cm⁻¹ the singlets ¹Σ_u⁺ will take much longer to decay.

Conclusions

Photodissociation is the most direct way to obtain a chemically reactive nitrogen, however, the atomic composition of dissociation products cannot be easily predicted if more than one product channel is accessible. Combining the results of accurate experiments and state-of-art computer modelling, a better understanding of energy-dependence in the dissociation of N₂ and its fractionation mechanism has been achieved. Our simulations show that the character of singlets, valence or Rydberg, and the strength of their spin–orbit coupling to the triplets determine the efficiency of population transfer and therefore predissociation lifetime. As a result of stronger coupling, excited ¹Π_u states dissociate much faster than ¹Σ_u⁺. However,

we also found the repulsive shape of the triplet $^3\Pi_u$ potentials is in control of the prompt dissociation from 112 000 to 115 000 cm^{-1} . For some energies, contribution of other states – $2^3\Sigma_u^+$, $3\Sigma_u^-$, $2^5\Pi_u$ – have been found significant.

Therefore, the route to producing reactive $\text{N}(^2\text{D})$ is not straightforward and the fraction will be especially low when it is the vibronic levels of $^1\Sigma_u^+$ above 115 000 cm^{-1} that are excited. The somewhat lower in energy vibronic states of $^1\Pi_u$ symmetry are on the contrary better coupled to the bound $^3\Pi_u$ triplets and dissociative $2^3\Sigma_u^+$ which allows $\text{N}(^2\text{D})$ to be the more favourable product. Shielding of the VUV light in the upper atmosphere can therefore play a major role in the preferential formation of the reactive $\text{N}(^2\text{D})$ atoms.

Author contributions

NG (conceptualization; formal analysis; investigation; visualization; writing – original draft; writing – review & editing), KK (formal analysis; investigation; writing – review & editing), FR (formal analysis; investigation; writing – review & editing), RDL (conceptualization; formal analysis; funding acquisition; investigation; supervision; writing – review & editing).

Conflicts of interest

There are no conflicts to declare.

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