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On the complexity of the absorption spectrum of molecular nitrogen

M.O. Vieitez [a], T.I. Ivanov [a], W. Ubachs [a], B.R. Lewis [b], C.A. de Lange [a,*]

[a] Department of Physics and Astronomy, Laser Centre, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
[b] Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia

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Abstract

The spectral properties of molecular nitrogen are crucial to a better understanding of radiative-transfer phenomena and activated N/N_2 chemistry in the Earth's upper atmosphere. Excited states of N_2 are difficult to access experimentally, and analysis of its electric dipole-allowed spectrum is notoriously complex. In this paper, we give an overview of these complexities and of the power of extreme ultraviolet ionization spectroscopy in unraveling many of the observed features. Some illustrative examples from our own research will be discussed.

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1. Introduction

The importance of molecular nitrogen as the most abundant species in the Earth's atmosphere is evident. The strong absorption bands in the range 80–100 nm shield the Earth's surface from the extreme ultraviolet (XUV) part of the solar radiation [1]. In fact, even the entire troposphere and stratosphere are free from this hazardous radiation that penetrates only some ~150 km above the Earth's surface. Absorption of the short-wavelength light leads to molecular dissociation, and for N_2 this process is *via* predissociation, with ground- and excited-state atoms as products. Clearly, an understanding of the spectroscopy of N_2 in this wavelength range is essential for a better understanding of radiative-transfer phenomena and activated N/N_2 chemistry in the Earth's upper atmosphere. Similar processes are expected to take place in our solar system in the upper atmospheres of Jupiter, Saturn and its moon Titan, and Triton, the largest moon of Neptune [2].

Molecular nitrogen, N_2, together with the isoelectronic carbon monoxide CO, is one of the most stable molecules in nature. The electronic configuration of homonuclear N_2 in its $X^1\Sigma_g^+$ ground state is:

$$\left(1s\sigma_g\right)^2\left(1s\sigma_u\right)^2\left(2s\sigma_g\right)^2\left(2s\sigma_u\right)^2\left(2p\pi_u\right)^4\left(2p\sigma_g\right)^2,$$

corresponding to a triple chemical bond. For $^{14}N^{15}N$, the g (*gerade*) and u (*ungerade*) symmetry assignments for the orbitals hold only in approximation. The triple chemical bond explains the large dissociation limit of N_2 (78 714 cm^{-1} [3]). Removal of an electron from the highest occupied molecular orbital leads to the lowest $X^2\Sigma_g^+$ ionic state, with configuration

$$\left(1s\sigma_g\right)^2\left(1s\sigma_u\right)^2\left(2s\sigma_g\right)^2\left(2s\sigma_u\right)^2\left(2p\pi_u\right)^4\left(2p\sigma_g\right)^1,$$

and an ionization energy of 125 666.959 cm^{-1} [4]. As a result, excited electronic states of molecular nitrogen are high lying and not easily accessible by normal experimental means.

Focusing on optical transitions involving the ground state, the weak spin-forbidden $A\ ^3\Sigma_u^+–X^1\Sigma_g^+$ Vegard–Kaplan bands, the weak symmetry-forbidden $a'\ ^1\Sigma_u^-–X^1\Sigma_g^+$ Ogawa–Tanaka–Wilkinson–Mulliken and $a\ ^1\Pi_g–X^1\Sigma_g^+$ Lyman–Birge–Hopfield bands have been observed, both in emission and absorption in the (far) ultraviolet (UV) [3]. The weakness of these bands implies that N_2 is optically transparent in the visible and UV regions of the spectrum. The much stronger one-photon electric-dipole-allowed absorption features in the N_2 spectrum involve transitions to valence and Rydberg states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry from the ground state and are found in the extreme ultraviolet.

In this paper, we shall focus on the complexities of the electric-dipole-allowed spectrum of molecular nitrogen and on the role that XUV ionization spectroscopy can play in unraveling them. The N_2 spectrum, situated in the energy range just above 100 000 cm^{-1},

* Corresponding author.
E-mail address: cdelange@few.vu.nl (C.A. de Lange).

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displays many irregularities due to strong global vibronic Rydberg-valence interactions between the singlet ungerade states. Other local and accidental perturbations in the rotational structure are also evident in many places, generally arising from heterogeneous interactions that are usually significantly dependent on the isotopomer involved. All these interactions strongly affect vibronic and rotational intensities, and can result in vibronic and rotational quantum interferences. Another key process is predissociation, which is mediated through the spin-orbit interaction with triplet states. This coupling between the singlet and triplet manifolds is another source of spectral complexity. The rate of predissociation in molecular nitrogen is often sufficiently slow not to wash out the rotational structure in highly-excited states completely, but, at the same time sufficiently fast to allow the observation of line broadening of individual rotational transitions. Because of its excellent spectral resolution, XUV-laser spectroscopy is eminently suitable for resolving this rotational structure and for determining the degree of line broadening and the corresponding rate of predissociation. Various illustrative examples derived from our research in Amsterdam will be discussed.

2. The complexity of the spectrum

The dipole-allowed absorption spectrum of molecular nitrogen in the XUV shows a very complex behavior. Initially, it was thought that the many bands in the spectrum were due to transitions involving a large number of excited electronic states [3], but later it was found that they arose as a result of Rydberg-valence and Rydberg–Rydberg interactions between a limited number of singlet ungerade states lying at excitation energies just above 100 000 cm^{-1} [5,6,7]. There are two valence states involved, one of $^1\Sigma_u^+$ and one of $^1\Pi_u$ symmetry (designated as $b'\,^1\Sigma_u^+$ and $b^1\,\Pi_u$, respectively). The relevant Rydberg states belong either to the series converging on the lowest $X^2\Sigma_g^+$ ionization limit ($np\sigma_u\, c'_{n+1}\,^1\Sigma_u^+$ and $np\pi_u\, c_n\,^1\Pi_u$, with principal quantum number $n \geq 3$), or the $ns\sigma_g\, o_n\,^1\Pi_u$ series, converging on the $A\,^2\Pi_u$ ionic limit of N_2^+. The relevant electronic configurations of the lowest-lying singlet states are:

$b'\,^1\Sigma_u^+ \ldots (2s\sigma_u)^2(2p\pi_u)^3(2p\sigma_g)^2(2p\pi_g)^1$ valence
$b^1\Pi_u \ldots (2s\sigma_u)^1(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g)^1$ valence
c'_4 or $c'\,^1\Sigma_u^+ \ldots (2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^1(3p\sigma_u)^1$ Rydberg
c_3 or $c^1\Pi_u \ldots (2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^1(3p\pi_u)^1$ Rydberg
o_3 or $o^1\Pi_u \ldots (2s\sigma_u)^2(2p\pi_u)^3(2p\sigma_g)^2(3s\sigma_g)^1$ Rydberg.

Potential-energy curves of these states, together with the C, C', F and G states of triplet character (to be discussed later), are presented in Fig. 1. They have the following configurations:

$C^3\Pi_u \ldots (2s\sigma_u)^1(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g)^1$ valence
$C'^3\Pi_u \ldots (2s\sigma_u)^2(2p\pi_u)^3(2p\sigma_g)^1(2p\pi_g)^2$ valence
$F^3\Pi_u \ldots (2s\sigma_u)^2(2p\pi_u)^3(2p\sigma_g)^2(3s\sigma_g)^1$ Rydberg
$G^3\Pi_u \ldots (2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^1(3p\pi_u)^1$ Rydberg.

We note, in particular, that the configurations listed above for the b, b', and C valence states are those predominating at smaller internuclear distances R. As R increases, other configurations become important [8], as evidenced by the unusual shapes of the potential-energy curves for these states in Fig. 1.

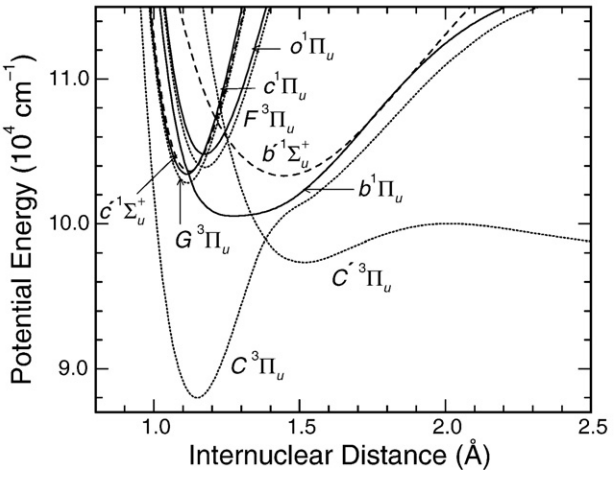

Fig. 1. Potential-energy curves for the ungerade singlet states that govern the dipole absorption spectrum, and the triplet (C, C', F and G) electronic states that govern the predissociation behavior of N_2. Full lines: $^1\Pi_u$ states. Dashed lines: $^1\Sigma_u^+$ states. Dotted lines: $^3\Pi_u$ states.

A detailed understanding of the spectroscopy in this energy region has long been hampered by the complex nature of the observed spectra. In a benchmark paper by Stahel et al. [9], a model of Rydberg-valence interactions was developed that provides a quantitative explanation for the energy-level perturbations, the seemingly erratic behavior of the rotational constants, and the observed band intensities that deviate strongly from Franck–Condon predictions, due to vibronic quantum-interference effects. In particular, the homogeneous vibronic interactions between states of $^1\Sigma_u^+$ symmetry (the b' valence and the c'_4 and c'_5 Rydberg states) and between states of $^1\Pi_u$ symmetry (the b valence and the c_3 and o_3 Rydberg states) were treated [9]. These global perturbations have been crucial in understanding the key features of the allowed optical absorption spectrum of N_2. Later, Spelsberg and Meyer put forward a quantitatively improved model, based on *ab initio* calculations [10]. Edwards et al. [11] extended the model by incorporating heterogeneous interactions to treat the mixing of states with different symmetries. These rotationally-dependent perturbations are local in character, and experimental methods to study such interactions usually require rotational resolution. These perturbations may cause shifts in rotational energy levels and can affect rotational transition intensities and predissociation line widths. Similar to what has been observed in the case of vibronic levels, such interactions may also give rise to rotational quantum interferences.

Photodissociation can occur directly, by photoexcitation from a bound state to a repulsive state or to a bound state above its dissociation limit. Dissociation can also be indirect, when photoexcitation takes place from a bound state to another bound state, which in turn 'predissociates' through a perturbative interaction with the continuum of another electronic state. The importance of predissociation phenomena in the lowest-lying electric-dipole accessible states of the abundant $^{14}N_2$ and its rarer stable isotopomers, $^{14}N^{15}N$ and $^{15}N_2$, has been apparent for