Vibronic and Rydberg series assignments in the vacuum ultraviolet absorption spectrum of nitrous oxide

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ABSTRACT

We report a comprehensive photoabsorption study of nitrous oxide (N_2O) in the vacuum ultraviolet (45,000–95,000 cm^{-1}) region using synchrotron radiation. The observed spectrum comprises of a few valence transitions and low lying Rydberg series converging to the two spin–orbit components ($^2\Pi_{1/2,3/2}$) of the ground state of N_2O^+. Spectral analysis is aided by extensive quantum chemical calculations of vertical excited states, oscillator strengths and potential energy curves using the time dependent density functional theory. Vibronic bands observed in the first absorption system (45,000–60,000 cm^{-1}) are assigned to hot band progressions in v'_2 originating from $v''=1$ or 2. New insights into the assignment of the well-formed progression of bands in the $X^1\Sigma^+ \rightarrow C^1\Pi$ system (60,000–72,000 cm^{-1}) are afforded by consideration of the Renner–Teller interaction. A set of molecular vibrational parameters ($\omega_2=467$ cm^{-1}, $x_{22}=-2.9$, $\varepsilon=-0.24$) for the $C^1\Pi$ state are derived from a fitting of the experimental data. The $3p\pi^1\Sigma^+$ state at $\sim77,600$ cm^{-1} shows a large quantum defect (0.96) which is explained as arising due to mixed valence–Rydberg character. In the 85,000–95,000 cm^{-1} region, a number of absorption features are observed with greater clarity than in earlier photoabsorption studies and assigned to Rydberg series of type $nl\lambda$ ($n=3,4$; $l=s,p,d$; $\lambda=\sigma,\pi,\delta$) and accompanying vibronic bands. This work has resulted in clarification of several discrepancies in earlier Rydberg series assignments. Additionally, the $3p\pi$ $^3\Sigma^-$ Rydberg state at 85,788 cm^{-1}, the valence transition $7\sigma \rightarrow 3\pi$ ($^1\Pi$) at 87,433 cm^{-1} and the $3d\lambda$ Rydberg series in the 91,700–92,600 cm^{-1} region are assigned for the first time.

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1. Introduction

There has been continued interest in the nitrous oxide (N_2O) molecule due to its important role in atmospheric and astrophysical processes [1–5]. For example, the isotopic fractionation of nitrogen atoms in the upper atmosphere has been ascribed to the UV photodissociation dynamics of N_2O [3 and references therein]. Photodissociation of N_2O is known to produce metastable species such as O (^1S,^1D) which participate in important atmospheric photochemical reactions. Recent studies show that nitrous oxide is the single largest anthropogenic threat to the ozone layer in the 21st century and also has a very high global warming potential [1]. It has been found to be involved in the catalytic destruction of ozone in the stratosphere and to be the main source of odd nitrogen which regulates the ozone layer, and also could be the only

interstellar compound in which the N atom uses all five valence electrons [4]. The availability of synchrotron radiation and equivalent electron impact sources in recent times has served as an impetus for studies of photo-induced molecular processes, enabling measurements over wide spectral ranges and providing a wealth of data regarding the nature and properties of excited electronic states. Nitrous oxide is a case in point, understanding of its excited state structure and dynamics being greatly enhanced by studies carried out using a variety of experimental techniques [3–25] as well as theoretical calculations [26–35]. Nevertheless, a thorough understanding of the excited states of this molecule still remains a challenging problem.

The electronic absorption spectrum of N_2O spans a wide energy region, from the UV region (45,000 cm^{-1}) and extending deep into the vacuum ultraviolet (VUV) region. In the VUV region, a number of electronic transitions comprising of both valence transitions and Rydberg series converging to the lowest two ionization limits at ~ 12.89 and 12.91 eV (103,963 and 104,097 cm^{-1}) [17] are observed. The first VUV absorption spectrum of nitrous oxide was reported by Duncan in 1936 [6] and subsequently revisited by Sponer and Teller [7], Zelikoff et al. [8] and Tanaka et al. [9]. Early work on nitrous oxide is well summarized in the review by Rabalais et al. [10]. The only synchrotron radiation based photoabsorption study of this molecule was by Nee et al. [11] who reported absolute cross sections up to the first ionization potential, but no new spectral assignments were given. Additionally, there have also been a number of reports on the electronic spectrum of N_2O, focusing on specific aspects in small energy regions. For instance, photodissociation of N_2O through its first absorption band (45,000–60,000 cm^{-1}) has received much attention in recent years due to its atmospheric implications [3,12–14,26–31]. In the 60,000–72,000 cm^{-1} region, after the initial work by Zelikoff et al. [8], there have been very few studies [15,16]. Vibronic assignments of the extensive and well formed progression of bands in this region are still incompletely understood. Towards the higher energy side of this progression ($> 75,000$ cm^{-1}), the absorption spectrum is dominated by Rydberg transitions. The Rydberg states of nitrous oxide have been studied by several authors using a variety of techniques like photoabsorption spectroscopy [9,11,15,17, 18], resonance enhanced multiphoton ionization (REMPI) [19–22] and electron impact/electron energy loss spectroscopy [23–25]. Assignments of Rydberg series and accompanying vibronic structures reported in these papers are at wide variance with each other and a clear set of assignments is still not available. For example, the strong sharp band at $\sim 84,900$ cm^{-1} has been assigned to the origin of the $3p\sigma\,^1\Pi$ transition in some works [17,24], and to the 3^1_0 vibronic band of $3p\sigma\,^1\Pi$ by others [19,20]. Although some of these discrepancies were resolved in the work by Cossart-Magos et al. [17], still several issues in assignments of transitions in the 85,000–95,000 cm^{-1} region remain unresolved. From a theoretical perspective, the electronic spectroscopy of nitrous oxide presents many challenges with additional complications introduced due to perturbations like Renner–Teller coupling and spin–orbit splitting. There

have been a wide range of theoretical studies covering various aspects like geometry and stability of its three isomers [26], photodissociation dynamics [27–31], excited electronic states [32–35], etc. A special mention must be made about the work by Hopper [34] which remains one of the most comprehensive theoretical studies of the electronic structure of nitrous oxide till date. Also worth citing are the frozen core calculations by Cossart-Magos et al. [17] which have helped in assigning many Rydberg transitions.

Despite this large volume of experimental and theoretical work, there remain several unresolved issues in the excited state electronic structure of nitrous oxide. The present work attempts to improve the understanding of the excited state structure of N_2O by carrying out a detailed reinvestigation of its VUV absorption spectrum. The photoabsorption spectrum of N_2O is recorded in the wavelength region 45,000–95,000 cm^{-1} using synchrotron radiation. Ab initio calculations are used to aid the spectral analysis. Details of the experiment, computations and results obtained are discussed in the ensuing sections.

2. Methodology

2.1. Experimental

VUV photoabsorption studies were carried out using the Photophysics beamline coupled to the 450 MeV storage ring Indus-1 at Raja Ramanna Centre for Advanced Technology, Indore, India. Details of the experimental setup have been described in earlier papers [36,37]. Briefly, synchrotron radiation is dispersed by a 1 m Seya-Namioka monochromator with 2400 l/mm grating (resolving power ~ 1000) and made to pass through a 25 cm long stainless steel gas cell. The experimental resolution is ~ 6 meV (~ 48 cm^{-1}) at 6 eV and ~ 12 meV (~ 97 cm^{-1}) at 12 eV. The cell is fitted with lithium fluoride windows, which limit the transmission to > 1050 Å. Nitrous oxide of stated purity 99.9% procured from M/s. Alchemie Gases is used without further purification and introduced into the cell through a system of Swagelok valves. The transmitted intensity is detected using a sodium salicylate coated window and UV–visible photomultiplier tube. The measured intensity without sample serves as the reference or I_0 and the intensity with sample introduced serves as I. Using the Beer–Lambert law, a plot of $\ln(I_0/I)$ versus wavelength, scanned in steps of 0.5 Å generates the absorption spectrum. Spectra are recorded at several pressures in the range 0.001–10 mbar, measured using capacitance gauges. Due to the widely varying absorption cross sections in different wavelength regions, optimum pressures used also differ from region to region. The optimum pressures for obtaining clear absorption features in the sub-regions 50,000–62,000 cm^{-1}, 62,000–72,000 cm^{-1} and 72,000–95,000 cm^{-1} are found to be ~ 10 mbar, 0.1 mbar and 0.001 mbar respectively. We however do not observe any noticeable change in the spectra when the pressure is varied in the neighborhood of these optimum pressures. The synchrotron beam current is recorded simultaneously at every step in order to normalize the data with respect to the decay in beam