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A new linelist for the $A^3\Pi$–$X^3\Sigma^-$ transition of the NH free radical

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ABSTRACT

A new linelist for the $A^3\Pi$–$X^3\Sigma^-$ electronic transition of NH has been prepared using line positions from the literature and calculated line intensities. High level *ab initio* calculations were performed with the `MOLPRO` program to obtain the *A*–*X* transition dipole moment function. Potential energy curves and line strengths were calculated with Le Roy's `RKR1` and `LEVEL` programs. Line intensities and Einstein A values were calculated with Western's `PGOPHER` program after converting the Hund's case (b) output of `LEVEL` to Hund's case (a) input needed for `PGOPHER`. The Herman–Wallis effect is included in the Einstein A calculations of the bands for the levels with $v' = 0-2$ and $v'' = 0-6$.

1. Introduction

The NH radical plays an important role in astrophysics. The bands of the $A^3\Pi$–$X^3\Sigma^-$ transition were first detected in a laboratory spectrum in 1893 [1]. The first astronomical observation of the NH *A*–*X* system was made in the spectrum of the Sun [2]. In 1940, the *A*–*X* system of NH was detected in the Comet Cunningham [3]. The $A^3\Pi$–$X^3\Sigma^-$ transition of NH was first recorded in the interstellar medium in 1991, towards the stars HD 27778 and HD 24398 and again in 1997 towards the star HD 149757 [4,5]. In 2009, interstellar NH abundances were calculated using the lines of the *A*–*X* system recorded towards the stars HD 149757, HD 170740, HD 154368 and HD 169454 [6].

NH is also frequently detected in the infrared spectra of cool stars. The infrared vibration-rotation lines of NH in oxygen-rich M giant stars, including α Orionis, were analyzed in order to obtain nitrogen abundances [7,8]. In 1986, nitrogen abundances for six additional stars were calculated using the observed infrared spectra [9].

In stellar atmospheres, although the formation of N-bearing molecules is strongly dominated by N_2 [10], molecular transitions are an excellent indicator of N abundances. Despite its dependence on carbon abundance, the CN molecule in the red and near infrared spectral regions is preferentially used by stellar spectroscopists because a higher stellar signal is obtained.

With the advent of a new generation of spectrographs such as UVES mounted on the VLT [11], the observation of the short wavelength region of the spectrum has become accessible. Indeed, the *A*–*X* transition of NH has been observed in stars and notably in metal-poor stars [12,13]. Spite et al. [13] noticed a systematic discrepancy in the N abundance derived from NH compared to the value derived from CN. They suspected that the NH *A*–*X* linelist needed revision, which we provide in the present paper.

The assignment of the 0–0 and 1–1 bands of the *A*–*X* system was carried out in the 1930s from emission spectra [14]. In 1959, the 0–0 and 1–0 bands were recorded in absorption [15] and in 1966 and 1970 several additional bands were analyzed [16,17]. In 1986, the *A*–*X* system of NH was measured with a precision of ± 0.0002 cm^{-1} for the 0–0, 1–1, 2–2, 0–1, 1–2, 1–0 and 2–1 bands [18]. These measurements improved on the previously available line positions by more than two orders of magnitude. The vibration-rotation lines in the infrared region were re-analyzed using solar spectra as well as IR laboratory spectra [19,20].

The $A^3\Pi$–$X^3\Sigma^-$ system recorded by Brazier et al. [18] used a copper hollow cathode discharge of helium with added nitrogen and hydrogen. The *A*–*X* spectrum was recorded with the Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory at Kitt Peak [18].

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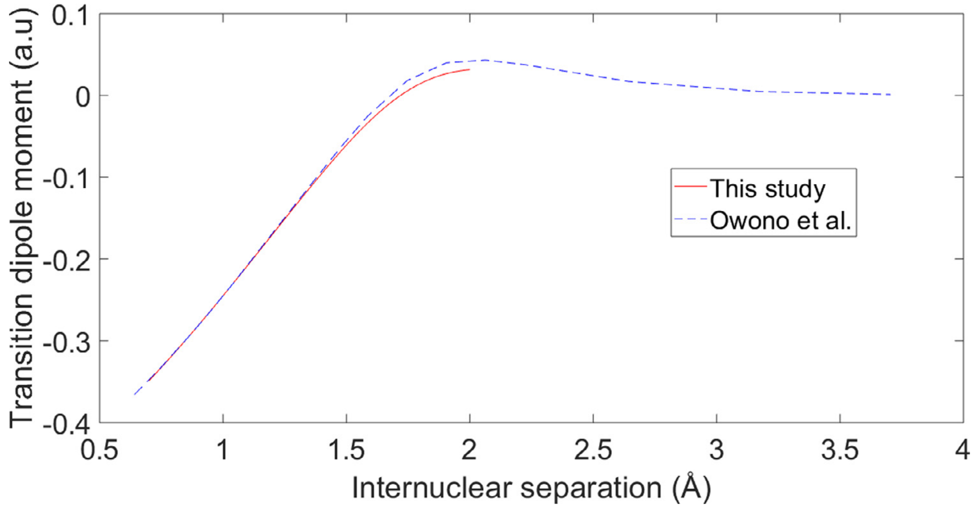

Fig. 1. Calculated transition dipole moment function for NH $A^3\Pi$–$X^3\Sigma^-$ compared with the TDMF calculated by Owono et al. [29].

2. Method

2.1. Experimental data

The spectroscopic constants for $A^3\Pi$ and $X^3\Sigma^-$ states were obtained from Ram and Bernath [20] based on Brazier et al. [18] for the A–X transition and Ram et al. [19] for the infrared vibration-rotation and pure rotation lines. The X state constants from Ram and Bernath [20] were also used by Brooke et al. [21] for the vibration-rotation line intensity analysis. The Brazier et al. A–X spectrum [18] will be used for comparison with our new linelist. We do not include ^{15}NH in our analysis because it was not detected in the spectrum of Brazier et al. [18].

2.2. Transition dipole moment function calculations

`MOLPRO 2012` [22] was used to perform *ab initio* calculations of the transition dipole moment function of the $A^3\Pi$–$X^3\Sigma^-$ transition. To calculate the transition moment, the multireference configuration interaction (MRCI) method was used with the aug-cc-pwCV5Z basis set. The wavefunctions utilized for the MRCI calculations were obtained from state-averaged CASSCF (Complete Active Space Self-Consistent Field) calculations with the $A^3\Pi$ and $X^3\Sigma^-$ states having equal weights. All the electrons were included in the correlation treatment. The active space included the 2-5a$_1$, 1-2b$_1$, 1-2b$_2$ and 1a$_2$ orbitals in the C$_{2v}$ point symmetry group used by `MOLPRO`. The TDMF (transition dipole moment function) points were calculated for internuclear distances between 0.7 Å and 2 Å in steps of 0.02 Å as expectation values. The calculated TDMF is provided as supplementary data.

2.3. Potential functions

The potential energy curves of the $A^3\Pi$ and $X^3\Sigma^-$ states were calculated employing Le Roy's `RKR1` program [23]. The `RKR1` program produces classical turning points of the potential energy curves using the first order semi-classical Rydberg–Klein–Rees procedure. The `RKR1` program requires vibrational and rotational constants as the input in order to perform the calculations. The molecular constants required for the $X^3\Sigma^-$ state were obtained from Ram and Bernath [20] and for the $A^3\Pi$ state from Brazier et al. [18] (Table 1). The dissociation energy for the ground state ($D_0 = 27,409 \pm 13\,\text{cm}^{-1}$) was obtained using the enthalpy of formation of N, H and NH at 0 K from the Active Thermochemical Tables [24] and for the excited state using a thermochemical cycle ($D_0 = 16,874 \pm 13\,\text{cm}^{-1}$). The error in the dissociation energy was calculated by propagation of the errors in the enthalpies given in the tables.

Table 1
Equilibrium constants for $A^3\Pi$ and $X^3\Sigma^-$ States of NH (cm^{-1}).

Constant	$X^3\Sigma^-$	$A^3\Pi$
D_e	29,030	18,465.5
T_e	–	29,790.5
ω_e	3282.220(15)	3231.70
$\omega_e x_e$	78.513(15)	98.48
$\omega_e y_e$	0.1341(61)	–
$\omega_e z_e$	−0.0066(11)	–
B_e	16.667704(29)	16.681963(8)
α_e	0.649670(91)	0.712880(35)
γ_e	−0.001674(71)	−0.016160
δ_e	−0.000067(25)	–
ϵ_e	−0.0000633(24)	–

2.4. Transition dipole moment matrix elements and the “Herman–Wallis effect”

The calculated potential energy curves (Fig. 2) were used as input for Le Roy's `LEVEL` program [25]. The `LEVEL` program generates vibrational wavefunctions by solving the 1-D Schrödinger equation and then uses them with a specified transition dipole moment function (TDMF) to calculate transition dipole moment matrix elements (TDMMEs). `LEVEL` does not include electron spin in its calculations which corresponds to Hund's case (b). In `LEVEL` the total angular momentum quantum number J ($\vec{J} = \vec{N} + \vec{S}$) is actually the quantum number N (total angular momentum except electron spin) [25]. The matrix elements provided by `LEVEL` include the rotational dependence that originates from the J-dependent centrifugal term in the 1-D vibrational Schrödinger equation (i.e. the vibrational wavefunctions depend on J). These TDMMEs are transformed into Hund's case (a) using the method of Brooke et al. [21] and then input into Western's `PGOPHER` [26] to calculate the linelist.

When a diatomic molecule is rotating, it increases its bond length as a result of the centrifugal force [27]. Therefore the vibrational wavefunctions of the molecule change due to rotation and this affects the molecular properties. In particular, infrared line intensities can no longer be separated into a vibrational part times a Hönl-London factor [28]. This mechanical effect of the vibration-