Absorption spectra and isotope shifts of the (2, 0), (3, 1), and (8, 5) bands of the $A^2\Pi_u$–$X^2\Sigma_g^+$ system of $^{15}N_2^+$ in near infrared*

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The high-resolution absorption spectra of the (2, 0), (3, 1), and (8, 5) bands of the $A^2\Pi_u$–$X^2\Sigma_g^+$ system of $^{15}N_2^+$ have been recorded by using velocity modulation spectroscopy technique in the near infrared region. The rotational constants of the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of $^{15}N_2^+$ were derived from the spectroscopic data. The isotope shifts of these bands of the $A^2\Pi_u$–$X^2\Sigma_g^+$ system of $^{14}N_2^+$ and $^{15}N_2^+$ were also analyzed and discussed.

Keywords: molecular constants, absorption spectrum, isotope shift, $^{15}N_2^+$

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1. Introduction

Molecular nitrogen is the most abundant diatomic molecule in the atmosphere of the Earth and plays a critical role in the evolution of life on the Earth. The spectral investigations of N_2 and its ion N_2^+ play a significant role in atmospheric and astrophysical studies. N_2 and N_2^+ were observed in the auroral emission and comet tails. The abundance ratios of $^{15}N/^{14}N$ can be estimated for lunar samples, solar wind, and meteoritic samples.[1]

In the early 1950s, Meinel[2,3] first observed the $A^2\Pi_u$–$X^2\Sigma_g^+$ system of $^{14}N_2^+$ in the aurora glow. In the following decades, the spectra of the A–X system of $^{14}N_2^+$ have been thoroughly investigated in the laboratory by using several spectroscopic techniques, such as emission grating spectroscopy,[4] laser induced fluorescence,[5] velocity modulation spectroscopy,[6] or Fourier transform emission spectroscopy.[7] However, the spectroscopic investigations of $^{15}N_2^+$ are scarce and fragmentary.

In 1988, Reddy *et al.*[8] studied the $B^2\Sigma_u^+$–$X^2\Sigma_g^+$ system of $^{15}N_2^+$ and obtained the rotational constants of the vibration levels $v = 0$–1 of the X state. Boudjarane *et al.*[9] determined the hyperfine parameters of the ground and excited states of the B–X transition of the (1, 2) band of $^{15}N_2^+$. Later, they[10] gave the molecular parameters for the excited and perturbed states of $^{15}N_2^+$ and $^{14}N_2^+$ by combining their LIF data for the B–X band and the Fourier-transform (FT) emission data for the A–X system. In 1997, they[11] extended the study of the B–X system to the (0, 1) band, identified 80 rotational lines and removed the strong correlation between the X and B states to determine the uncorrelated values of the excited B and perturbed A states by combining the LIF data of the B–X system and FT emission data of the A–X system. Until now, only Bernard *et al.*[12] investigated the (0, 0), (0, 1), (1, 2), (1, 0), (2, 1), (2, 0), and (3, 1) bands of the A–X system of $^{15}N_2^+$, and gave the rotational constants and molecular equilibrium parameters for the A and X states and the isotope shifts between $^{15}N_2^+$ and $^{14}N_2^+$

In the present work, we report the spectra of the (8, 5), (3, 1), and (2, 0) bands of the A–X system of $^{15}N_2^+$, derive the related molecular constants of these states from the experimental spectroscopic data, and give the isotope shifts of these states between $^{15}N_2^+$ and $^{14}N_2^+$.

2. Experiment

The experimental setup has been described in detail in our previous work.[13] The $^{15}N_2^+$ cations were generated by discharging the mixture gases of $^{15}N_2$ and helium. The absorption signal of molecular ions was observed with two forms of modulation which were the phase modulation of the optical field at the radio frequency 480 MHz and the velocity modulation at the audio frequency of 23 kHz acting on the same absorption medium together. The axial electric field imposed a modulation on the drifting velocity of ions. The frequency modulated laser beam at 480 MHz passed through the discharge absorption cell. The output signal from the detector was demodulated by a double balance mixer at a frequency of 480 MHz and then by a lock-in amplifier at the reference frequency of 23 kHz. The laser wavenumber was recorded by an attached wavemeter with a resolution of 0.001 cm^{-1} and was calibrated using a published molecular I_2 line.[14] The absolute wavenumbers were determined to an accuracy of approximately ± 0.006 cm^{-1}.

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3. Results and discussion

A portion of the observed spectra and the corresponding assignments of the (2, 0) band of the $A^2\Pi_u$–$X^2\Sigma_g^+$ system of $^{15}N_2^+$ are shown in Fig. 1. The observed line shape of a single transition is the second derivative of a Gaussian type. In the present work, the spectra of $^{15}N_2^+$ in the range of 12294.0 cm^{-1}–12731.2 cm^{-1} were recorded. However, there are gaps in the spectra in the range of 12342.8 cm^{-1}–12406.1 cm^{-1} and 12583 cm^{-1}–12600 cm^{-1} due to the fluctuation of the output energy of our laser.

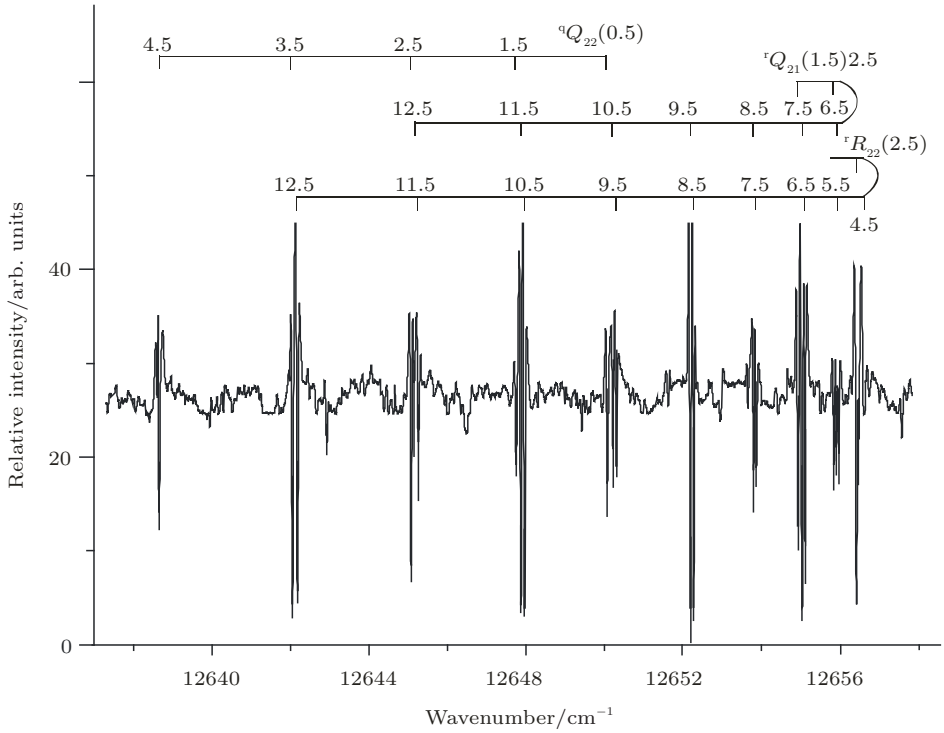


Fig. 1. A portion of the Doppler-limited absorption spectra of $^qQ_{22}$, $^rQ_{21}$, and $^rR_{22}$ lines of the (2, 0) band of $A^2\Pi_u$–$X^2\Sigma_g$ system of $^{15}N_2^+$.

3.1. Rotational analysis

The ground state, $^2\Sigma_g^+$, of $^{15}N_2^+$ belongs to the Hund's case (b). The levels with a given value of the rotational quantum number N are split into two components, F_1 ($J = N + 1/2$) and F_2 ($J = N - 1/2$), due to the electron spin-rotation coupling. The parities of the rovibronic functions are given following the definitions of Brown and Carrington.[15] The excited state, $^2\Pi_u$, obeys the Hund's case (a) at low J values. Each Ω is split into two components: $\Omega = 1/2(F_2)$ and $\Omega = 3/2(F_1)$. The $\Omega = 1/2$ energy level higher than that of the $\Omega = 3/2$ due to the negative coupling constant A_v. For each Ω, a certain J level will split into two sublevels with inverse parities due to the Λ-doubling.

In the present work, all the 12 branches ($^rR_{11}$, $^sR_{21}$, $^qR_{12}$, $^rR_{22}$, $^qQ_{11}$, $^rQ_{21}$, $^pQ_{12}$, $^qQ_{22}$, $^pP_{11}$, $^qP_{21}$, $^oP_{12}$, and $^pP_{22}$) of each band system were observed and analyzed to obtain the molecular constants for each vibration level. The $^sR_{21}$ branch of the (8, 5) band has not be measured in this work. The assignment of the transitions follows the selection rules: $\Delta J = 0$, e↔f; and $\Delta J = \pm 1$, e↔e or f↔f. The transitions are labelled as: $^{\Delta N}\Delta J_{F'F''}(J'')$.

The Pgopher program[16] was used to fit the experimental data to get the molecular constants of the (8, 5), (3, 1), and (2,0) bands of the $A^2\Pi_u$–$X^2\Sigma_g^+$ system of $^{15}N_2^+$. In total, 677 rotational transition lines were assigned and fitted with the same weight, and shown in supplement part. The band labels, rotational J numbers of the observed lines, and the residual of the band origin are given in Table 1. The molecular constants of A_v, B_v, D_v, p_v, q_v, A_{Dv}, and γ_v of the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of $^{15}N_2^+$ are listed in Table 2 and Table 3, respectively. Here, A_v is the spin–orbit constant, B_v is the molecular rotational constant, D_v is the centrifugal distortion constant, A_{Dv} is the centrifugal distortion correction to A_v, p_v and q_v are Λ-doubling parameters, and γ_v is the spin-rotation parameter.

In Table 2, comparing our experimental results with other published ones, our molecular constants, B_v and D_v of the $X^2\Sigma_g^+$ state are in agreement with those of Reddy *et al.*[8] and Bernard *et al.*[12] except for γ_v values. For example, the experimental values of the γ parameter for the $v = 0$ of the $X^2\Sigma_g^+$ state from Reddy *et al.*,[8] Bernard *et al.*[12] and our values are $-1.83(4) \times 10^{-2}$ cm^{-1}, $0.9026(68) \times 10^{-2}$ cm^{-1}, and $0.8921(38) \times 10^{-2}$ cm^{-1}, respectively. We fitted the experimental data of Reddy *et al.* using Pgopher program, and gave a γ value of $0.22(47) \times 10^{-2}$ cm^{-1} which is dif-

ferent with Reddy's result. Bernard *et al.* pointed out that Reddy's estimated value of $\gamma''_{v=0} = -1.83(4) \times 10^{-2}$ cm^{-1} of the X state is from the analysis of the B–X system, the $\gamma'_{v=0} = 1.1(9) \times 10^{-3}$ cm^{-1} in the upper state, $B^2\Sigma_u^+$, is not statistically significant within 2σ limits. The γ' and γ'' parameters are strongly correlated in the $^2\Sigma$–$^2\Sigma$ transitions and only the γ'–γ'' can be determined with confidence,[17] thus Reddy's result of the γ in the $X^2\Sigma_g^+$ state is not realistic. However, in the $A^2\Pi$–$X^2\Sigma$ transition, the γ in $^2\Sigma$ state does not correlate significantly with any parameter in the upper $^2\Pi$ state, so it can be properly determined in experiment. The values of the spin-rotation parameter, γ of Bernard's and ours are in agreement with each other, Reddy's and the "Fit" results are inconsistent with that of Bernard's and ours.

Table 1. Summary of the observed bands in the $A^2\Pi_u$–$X^2\Sigma_g$ system of $^{15}N_2^+$

Band	Number of lines	J_{max}	J_{min}	Residual/cm^{-1}
(8, 5)	194	23.5	3.5	0.0042
(3,1)	251	30.5	0.5	0.0033
(2, 0)	232	27.5	0.5	0.0039

Table 3 lists the molecular constants A_v, B_v, D_v, p_v, and q_v of the $A^2\Pi$ state. Our experimental A_{Dv} values of the $v = 2$ and 3 in the $A^2\Pi$ state are different with those of Bernard's[12] both in magnitude and sign. The A_{Dv} value is determined by how the p_v and q_v values have been associated. In Bernard's paper, they assumed that the $^2\Sigma^+$ state interaction with the $A^2\Pi$ state,[12] and fixed the A_{Dv} values as 0.38 for both $v = 2$ and 3 of the $A^2\Pi$.

Table 2. The molecular constants (in unit cm^{-1}) of the $X^2\Sigma_g$ state of $^{15}N_2^+$. Numbers in parentheses represent one standard deviation for the last digit.

		B_v	$10^2 \times \gamma_v$	$10^5 \times D_v$
$v = 0$	This work	1.7945214(216)	0.8921(38)	0.49786(217)
	Ref. [8]	1.79520(8)	−1.83(4)	0.55(1)
	Ref. [12]	1.794654(31)	0.9026(68)	0.4919(31)
	Fit[a]	1.794880(16)	0.22(47)	0.5122(16)
	Cal.[b]	1.7945780		0.51516729
$v = 1$	This work	1.7777513(197)	0.8595(34)	0.52581(259)
	Ref. [8]	1.77817(8)	−1.88(4)	0.56(1)
	Ref. [12]	1.777578(24)	0.9204(94)	0.5007(38)
	Fit[a]	1.777877(19)	0.23(50)	0.519(23)
	Cal.[b]	1.7769190		0.52315877
$v = 5$	This work	1.7081041(298)	0.8744(49)	0.56358(392)
	Ref. [8]	1.70783(23)		0.40(6)
	Ref. [12]			
	Fit[a]	1.70613	−0.69(53)	0.02(13)
	Cal.[b]	1.7045286		0.53413072

[a] The values are the fitted with the experimental data in Ref. [8] using Pgopher program. [b] The values are the calculated results from the our previous experimental data of $^{14}N_2^+$ in Ref. [18].

Table 3. The molecular constants (in unit cm^{-1}) of the $A^2\Pi_u$ state of $^{15}N_2^+$. Numbers in parentheses represent one standard deviation for the last digit.

		A_v	$10^4 \times A_{Dv}$	B_v	$10^5 \times D_v$	$10^2 \times p_v$	$10^3 \times q_v$
$v = 2$	This work	−74.61012(95)	−0717(31)	1.5857622(215)	0.49994(218)	0.4596(64)	−0.3087(26)
	Ref. [12]	−74.6295(14)	0.38	1.585968(31)	0.4908(55)	0.458(21)	−0.277(19)
	Cal.[a]			1.5845389	0.5152805	0.46097784	−0.2894188
$v = 3$	This work	−74.62301(67)	−0611(28)	1.5689646(187)	0.52381(228)	0.5086(66)	−0.3053(33)
	Ref. [12]	−74.6172(23)	0.38	1.568934(41)	0.5062(97)	0.459(32)	−0.279(25)
	Cal.[a]			1.566883	0.52109336	0.51754985	−0.3153018
$v = 8$	This work	−74.5405(12)	1.047(47)	1.4828593(309)	0.56042(419)	0.8554(86)	−0.4527(45)
	Cal.[a]			1.4774718	0.53256205	0.87565253	−0.4719069

[a] The values are calculated from the fitted parameter of $^{14}N_2^+$ from Ref. [18].

3.2. Isotope shifts

The observed isotope shifts of the (2, 0), (3, 1), and (8, 5) bands of the A–X system of $^{15}N_2^+$ were obtained directly from the differences between our observed lines of $^{15}N_2^+$ and the reported experimental lines[18] of $^{14}N_2^+$ of this Meniel system.

The calculated isotope shifts were determined using the following expression:

$$\begin{aligned}\Delta\nu &= \nu^{14}_{v',v''} - \nu^{15}_{v',v''} \\ &= (1-\rho)\left[\omega'_e\left(v'+\frac{1}{2}\right) - \omega''_e\left(v''+\frac{1}{2}\right)\right] - (1-\rho^2)\left[\omega'_e\chi'_e\left(v'+\frac{1}{2}\right)^2 - \omega''_e\chi''_e(v''+\frac{1}{2})^2\right] \\ &\quad + (1-\rho^3)\left[\omega'_e\gamma'_e\left(v'+\frac{1}{2}\right)^3 - \omega''_e\gamma''_e\left(v''+\frac{1}{2}\right)^3\right] + \cdots, \end{aligned} \tag{1}$$

where ν is the transition frequency, v is the vibrational quantum number, "$\prime$"and "$\prime\prime$" refer to the upper and lower states, ω_e, $\omega_e\chi_e$, and $\omega_e\gamma_e$ are the equilibrium molecular constants. The value of the isotope parameter, $\rho = [\mu(^{14}N_2^+)/\mu(^{15}N_2^+)]^{1/2} = 0.96619433$.[19]

The observed and calculated band origins and isotope shifts of the (2, 0), (3, 1), and (8, 5) bands of the A–X system of $^{14}N_2^+$ and $^{15}N_2^+$ are listed in Table 4. The band origins of $^{14}N_2^+$ and $^{15}N_2^+$ are obtained from our previous[18] and the present experimental results, respectively. The measured isotope shifts (labbled with E_{xpt}) are extracted from the experimental values of the band origins of $^{14}N_2^+$ and $^{15}N_2^+$ directly. The calculated isotope shifts are calculatedusing equation (1) with several experimental equilibrium molecular constants.[7,18,20] The observed values of the isotope shifts are in agreement with those of the calculated.

Table 4. Band origins of the $A^2\Pi_u$–$X^2\Sigma_g$ system of $^{14}N_2^+$ and $^{15}N_2^+$, and the isotope shifts of $^{15}N_2^+$.

Band	Band origin/cm^{-1}		Isotope Shift, Δv ($^{14}N_2^+$–$^{15}N_2^+$)/cm^{-1}			
	$^{14}N_2^+$	$^{15}N_2^+$	Expt[a]	Cal.[b]	Cal.[c]	Cal.[d]
(2, 0)	12731.1454(12)	12613.1830(15)	117.9633 (27)	117.5779	117.5772	117.5792
(3, 1)	12369.7392(13)	12265.9195(9)	103.8197(22)	103.4257	103.4233	103.4280
(8, 5)	12615.3400(24)	12517.4288(21)	97.9112(45)	97.6758	97.6453	97.6838

[a] These values were extracted from experimental values between our observed lines of $^{15}N_2^+$ and the reported experimental results of $^{14}N_2^+$ listed in Table 3 and Table 4 of Ref. [18]. [b] These values were calculated with Eq. (1) using the molecular constants in Table 5 of Ref. [18]. [c] These values were calculated with Eq. (1) using the molecular constants in Table 5 of Ref. [20]. [d] These values were calculated with Eq. (1) using molecular constants in Table IV of Ref. [7].

4. Conclusion

The high-resolution rotational spectra of the (2, 0), (3, 1), and (8, 5) bands of the Meinel system $A^2\Pi_u$–$X^2\Sigma_g^+$ of $^{15}N_2^+$ have been recorded by using velocity modulation spectroscopy technique in this work. In total, 677 transition lines were assigned, rotational structures of these bands were analyzed, and the molecular constants of the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states were estimated and compared with other reported values. Also, the related isotope shifts of the A–X system of $^{15}N_2^+$ and $^{14}N_2^+$ were determined and discussed.

References

[1] Clayton R N 1977 *CNO Isotopes in Astrophysics* (Boston: Reidel)
[2] Meinel A B 1950 *Astrophys. J.* **112** 562
[3] Meinel A B 1951 *Astrophys. J.* **113** 583
[4] Douglas A E 1953 *Astrophys. J.* **117** 380
[5] Miller T A, Suzuki T and Hirota E 1984 *J. Chem. Phys.* **80** 4671
[6] Gudernan C S, Martner C C and Saykally R J 1985 *Chem. Phys. Lett.* **122** 108
[7] Ferguson D W, Rao K N, Martin P A and Guelachvili G 1992 *J. Mol. Spectrosc.* **153** 599
[8] Reddy S P and Prasad C V V 1988 *Astrophys. J.* **331** 572
[9] Boudjarane K, Lacoursière J and Larzillière M 1994 *J. Chem. Phys.* **101** 10274
[10] Boudjarane K, Alikacem A and Larzillière M 1996 *Chem. Phys.* **211** 393
[11] Boudjarane K, Shy J T and Larzillière M 1997 *J. Phys. Chem. A* **101** 6712
[12] Bernard A, Larzillière M, Effantin C and Ross A J 1993 *Astrophys. J.* **413** 829
[13] Deng L H, Zhu Y Y, Li C L and Chen Y Q 2012 *J. Chem. Phys.* **137** 054308
[14] Gerstenkorn S, Verges J and Chevilard J 1982 *Atlas du spectred'absorption de la molecule d'iode* (11000 cm^{-1}–14000 cm^{-1}) (Orsay: CNRS II)
[15] Brown J and Carrington A 2003 *Rotational Spectroscopy of Diatomic Molecules* (New York: Cambridge University Press)
[16] Western C M PGOPHER, A program for simulating rotational, vibrational and electronic spectra (University of Bristol)
[17] Gottscho R A, Field R W, Dick K W and Bemesch W 1979 *J. Mol. Spectrosc.* **74** 435
[18] Zhang Y P, Deng L H, Zhang J and Chen Y Q 2015 *Chin. J. Chem. Phys.* **28** 134
[19] National Institutes of Standards and Technology, Physics Laboratory, "Atomic Weights and Isotopic Compositions for All Elements", ⟨http://physics.nist.gov/cgi-bin/Compositions/stand_alone.pl?ele=&all=all⟩
[20] Tarsitano C G and Oka T 2003 *J. Mol. Spectrosc.* **219** 263