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ABSTRACT

Photoabsorption spectra of $^{14}\text{N}^{15}\text{N}$ were recorded at high resolution with a vacuum-ultraviolet Fourier-transform spectrometer fed by synchrotron radiation in the range of 81–100 nm. The combination of high column density ($3 \times 10^{17} \text{ cm}^{-2}$) and low temperature (98 K) allowed for the recording of weak spin-forbidden absorption bands' exciting levels of triplet character. The triplet states borrow intensity from $^1\Pi_u$ states of Rydberg and valence character while causing their predissociation. New predissociation linewidths and molecular constants are obtained for the states $C^3\Pi_u(v=7, 8, 14, 15, 16, 21)$, $G^3\Pi_u(v=0, 1, 4)$, and $F^3\Pi_u(v=0)$. The positions and widths of these levels are shown to be well-predicted by a coupled-Schrödinger equation model with empirical parameters based on experimental data on $^{14}\text{N}_2$ and $^{15}\text{N}_2$ triplet levels.

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I. INTRODUCTION

The vacuum-ultraviolet (VUV) photoabsorption spectrum of molecular nitrogen is of importance to studies of terrestrial atmospheric physics,^{1,2} planetary physics,^{3–5} and astrophysics.^{6–8} It is also of fundamental interest in molecular physics in view of the benchmark perturbation phenomena occurring in this diatomic molecule. Early investigations of the dipole-allowed absorption spectrum of N_2 revealed the perturbations between singlet states of valence and Rydberg character,^{9–11} giving rise to intensity-interference effects in the vibronic spectrum, even extending into details of the rotational fine structure.^{12,13} Interactions between the singlet manifolds and the triplet manifolds, induced by spin-orbit coupling, were found to cause strong predissociation effects in the excited states, however, in most cases, still allowing for resolved rotational structure.¹⁴

Over the decades, a large number of spectroscopic investigations of N_2 have been performed, focusing on the predissociation phenomenon, and using a variety of advanced techniques, such as tunable narrowband extreme ultraviolet (XUV) laser spectroscopy,^{15–17} picosecond pump-probe experiments,^{18,19} electron-impact excitation,^{20,21} synchrotron absorption studies,^{22–25} synchrotron fluorescence-excitation studies,²⁶ detection of dissociation products in charge-exchange studies,^{27,28} as well as upon VUV-laser excitation,²⁹ and the spectroscopic study of infrared transitions within the triplet system.^{30,31}

A framework of coupled-channel Schrödinger equations (CSEs) was developed^{32–36} to provide a description of the absorption spectrum of molecular nitrogen, including Rydberg-valence electrostatic interactions and singlet-triplet spin-orbit interactions. Through this description, a comprehensive explanation is provided for the spectral perturbations as well as the predissociation

phenomena.^{37–39} Based on the CSE-framework, the full absorption spectrum and dissociation cross section of N_2 have been calculated,⁶ as well as the electron-impact XUV emission spectrum.⁴⁰ In principle, the CSE model is applicable to all isotopologues of nitrogen through mass scaling of the molecular parameters involved, and in some cases, it has been applied to $^{14}N^{15}N$ and $^{15}N_2$,^{41–43} comparing with data from XUV laser excitation. One application resulted in the calculation of the isotopically selective dissociation of nitrogen in the interstellar radiation field.⁸

The most complete investigation of the absorption spectrum of $^{14}N^{15}N$ was performed using VUV Fourier-Transform (FT) spectroscopy, analyzing in detail 25 singlet-singlet bands of this isotopologue⁴⁴ and identifying perturbations in the level structure of singlet states caused by a parallel manifold of optically forbidden states of triplet character. The present study is an extension of this, whereby triplet states are observed directly by using an increased gas column density and by recording absorption at lower temperatures. The motivation of the present work is to test the ability of a CSE model, developed by Lewis *et al.*³⁴ with reference to the $^{14}N_2$ and $^{15}N_2$ isotopologues, and to predict the triplet spectrum of $^{14}N^{15}N$. In the longer term, the new experimental data on the $^3\Pi_u$ states of $^{14}N^{15}N$ presented here,⁴⁵ together with similar planned measurements on $^{15}N_2$, will enable the improvement and extension of the CSE model of N_2 predissociation, with particular application to studies of isotopic fractionation.

II. EXPERIMENTAL DETAILS

High-resolution absorption spectra of $^{14}N^{15}N$ were recorded with the VUV-FT instrument installed at the DESIRS beam line of the SOLEIL synchrotron.^{46,47} This instrument is based on a wave-front interferometer that allows the extension of the FT technique into the deep VUV. Spectral coverage is determined by the undulator synchrotron radiation source, delivering a bandwidth of about 5 nm illuminating the FT instrument. The $^{14}N^{15}N$ gas flows continuously through a 100 mm-long windowless absorption cell with capillaries at both ends, thus providing a condition

of quasistatic gas pressure inside the cell. The absolute frequency calibration is based on the intrinsically linear frequency scale generated by the FT spectrometer and from the comparison of selected H_2 and Ar I lines appearing in the spectrum with high-precision reference data. The specific absorption lines used are Ar I at 95 399.833 cm^{-1} ,⁴⁸ H_2 at 99 755.399, 101 668.268, 101 746.449, and 101 825.295 cm^{-1} ,⁴⁹ and H_2 at 107 114.785 and 105 549.599 cm^{-1} .⁵⁰ The estimated absolute calibration uncertainty is 0.004 cm^{-1} , but individual $^{14}N^{15}N$ line wavenumbers have greater uncertainties due to fitting errors of ~ 0.02 cm^{-1} or more for lines that are blended or saturated.

Our experimental and analysis procedures are similar to those previously adopted by Heays *et al.*⁴⁴ except that measurements were performed with the cell externally cooled by a flowing liquid-nitrogen jacket and employing $\sim 300\times$ greater column density. The optically allowed transitions to $^1\Pi_u$ and $^1\Sigma_u^+$ states previously studied⁴⁴ are then completely saturated in our spectra near their bandheads, but the targeted forbidden transitions' exciting $^3\Pi_u$ levels are now measurable, e.g., Fig. 1 showing $b^1\Pi_u(v=0) \leftarrow X^1\Sigma_g^+(v=0)$ and $C^3\Pi_u(v=7) \leftarrow X^1\Sigma_g^+(v=0)$. The main advantage of using cooled gas is the reduced spectral congestion from singlet-state absorption due to fewer thermally populated ground state rotational levels. Additionally, the profiles of predissociation-broadened $^3\Pi_u \leftarrow X^1\Sigma_g^+$ bands are more revealing, with their oscillator strengths concentrated into $J'' \lesssim 10$ transitions.

The population distribution of $^{14}N^{15}N$ ground-state rotational levels was assumed to correspond to a mixture of room-temperature (295 K) and cold gases, with the column density, N_i , of each, and the cold-gas rotational temperature determined by a fit to the unsaturated rotational transitions of the $b(0) \leftarrow X(0)$ (Fig. 1) and $b(1) \leftarrow X(0)$ bands.⁵¹ The resulting best-fit values are $N_{room} = (2.2 \pm 0.3) \times 10^{15}$ cm^{-2} , $N_{cold} = (3.9 \pm 0.6) \times 10^{17}$ cm^{-2} , and $T_{cold} = 98 \pm 5$ K. The absolute N_i calibration was made with reference to $b(0) \leftarrow X(0)$ and $b(1) \leftarrow X(0)$ f -values determined by Heays *et al.*⁴⁴ and has an estimated 15% uncertainty, arising from a combination of the estimated uncertainty of Heays *et al.*⁴⁴ and our own fitting errors. The cooled-gas temperature uncertainty was estimated

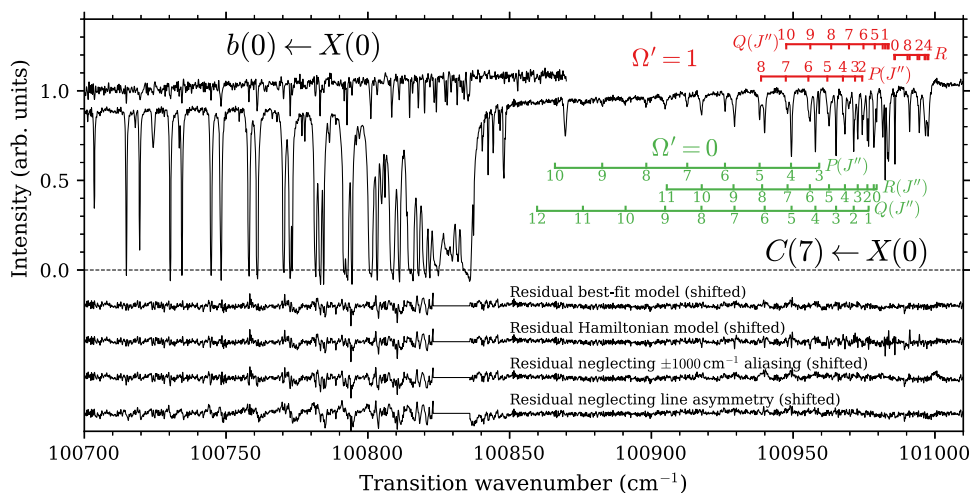


FIG. 1. Absorption spectra showing $b(0) \leftarrow X(0)$ and $C(7) \leftarrow X(0)$. Upper spectrum: room-temperature low-column-density spectrum analyzed by Heays *et al.*⁴⁴ Lower spectrum: liquid- N_2 -cooled spectrum. Also indicated are the residual errors of models fitted to the lower spectrum under various assumptions discussed in the text.

subjectively based on its range, giving a good quality-of-fit to the $b(v) \leftarrow X(0)$ spectrum. The assumed two-temperature model fits the spectrum quite well, and we found no benefit from adopting more complicated temperature profiles. Contributions to the experimental spectra from species other than the desired $^{14}\text{N}^{15}\text{N}$ were found, inevitably from cold $^{14}\text{N}_2$ and $^{15}\text{N}_2$, yielding, e.g., weak lines overlapping $b(0) \leftarrow X(0)$ in Fig. 1, and from the room-temperature H_2 contaminant, e.g., at $100\,870\text{ cm}^{-1}$ in Fig. 1.

The 98 K Doppler width of $^{14}\text{N}^{15}\text{N}$ resonances amounts to 0.14 cm^{-1} FWHM (full-width at half-maximum) at $105\,000\text{ cm}^{-1}$. Spectra were recorded at a setting of the VUV-FT instrument, giving rise to an unapodized sinc-shaped instrumental line shape with width 0.215 cm^{-1} FWHM. Several nonideal instrumental effects were included in the modeling of the total instrumental broadening function. Asymmetric line shapes are evident in spectral regions near highly saturated bandheads of $^1\Pi_u \leftarrow X(0)$ and $^1\Sigma_u^+ \leftarrow X(0)$ transitions where the near-zero recorded intensity appears to locally interfere with the frequency-dependent FT phase correction.^{52,53} This effect was modeled phenomenologically by the convolution of the ideal instrumental function with the following equation:

$$F_{\text{asym}}(\nu) = \begin{cases} 1, & \text{if } \nu = 0, \\ a/\nu, & \text{otherwise,} \end{cases} \quad (1)$$

where ν is the wavenumber gap from the line center and the parameter a was fitted to each spectral region studied. An example of the degradation of the model fit to the measured spectra from neglecting this asymmetry is shown in Fig. 1, but this effect is significant only for those $^3\Pi_u \leftarrow X(0)$ bands overlapped by strong singlet-state excitation.

A second nonideal instrumental effect appears as a weak aliasing of the experimental spectrum shifted by $\pm 1000\text{ cm}^{-1}$, where the aliasing is additive for one sign and subtractive for the other. This is due to a periodic error in the stepping system of the FT translation⁵² and was handled by counteracting the aliasing through the addition and subtraction of $\pm 1000\text{ cm}^{-1}$ -shifted copies of the experimental spectrum, with best-fit correction magnitude determined separately for each spectral-region studied. Neglecting this aliasing introduces a significant model error near $101\,000\text{ cm}^{-1}$ in Fig. 1, which is due to the negative aliasing of the strong $b(2) \leftarrow X(0)$ absorption at $+1000\text{ cm}^{-1}$. The magnitude of this correction is 1%–3% of the measured intensity, and second-order corrections were deemed unnecessary.

Finally, an additional phenomenological Gaussian-shaped broadening was included in the instrumental broadening, with width 0.1 cm^{-1} FWHM, as found necessary for this instrument by Heays *et al.*⁴⁴ Full information could not be retrieved from the experimental spectrum in heavily saturated regions, even with these corrections, as is evident in the residual error of the best-fit model shown in Fig. 1 where the worst affected portions were neglected from model fitting (zero residual).

III. SPECTRAL ANALYSIS METHODS

Molecular parameters summarizing the observed $^3\Pi_u$ states were extracted by fitting model spectra to the experimental absorption measurements. Each observed $^{14}\text{N}^{15}\text{N}$ line was assigned a

transition wavenumber, ν_i ; a line f -value, according to the definition of Morton and Noreau,⁵⁴ f_i ; and a predissociation linewidth, Γ_i .⁵⁵ Resulting temperature-dependent line cross sections were computed according to

$$\sigma_i(\nu; T) = \left(\frac{e^2 \cdot 10^2}{4\epsilon_0 m_e c^2} \right) f_i \alpha_{J_i''}(T) V(\nu - \nu_i, \Gamma_i, \Gamma_D(T)), \quad (2)$$

where σ_i is in cm^2 , T is the temperature in kelvin, and e , ϵ_0 , m_e , and c are the usual physical constants. The parenthesized prefactor has the numerical value of $8853 \times 10^{-13}\text{ cm}$. In Eq. (2), V is a unit-area Voigt function centered on ν_i with Lorentzian width Γ_i and Gaussian (Doppler) width $\Gamma_D(T)$ and $\alpha_{J_i''}(T)$ is the Boltzmann population of ground-state rotational level J_i'' .

A total absorption opacity was constructed, allowing for absorption by $^{14}\text{N}^{15}\text{N}$ lines at 98 K and 295 K, together with contaminants,

$$\tau(\nu) = \sum_i N_{98\text{K}} \sigma_i(\nu; 98\text{K}) + N_{295\text{K}} \sigma_i(\nu; 295\text{K}) + \sum_j \tau_j^{\text{int}} V(\nu - \nu_j, \Gamma_j, \Gamma_{Dj}), \quad (3)$$

using the $^{14}\text{N}^{15}\text{N}$ column densities discussed in Sec. II. The second summation in Eq. (3) accounts for any $^{14}\text{N}_2$, $^{15}\text{N}_2$, or H_2 contaminant lines using their fitted frequencies, integrated optical depths, τ_j^{int} , and line shapes.

This opacity was converted into an absorption spectrum,⁵⁶

$$I(\nu) = [I_0(\nu) e^{-\tau(\nu)}] * F(\nu), \quad (4)$$

for a direct pointwise comparison with the experimental spectrum. Here, the incoming intensity of synchrotron radiation, $I_0(\nu)$, was fitted to a slowly varying function of ν and the ideal absorption spectrum broadened by convolution with the instrumental function, $F(\nu)$, described in Sec. II.

The Q-branch rotational transitions of strong and unblended $^3\Pi_u \leftarrow X^1\Sigma_g^+$ bands were modeled individually, and their $P(J' + 1)$ and $R(J' - 1)$ transition pairs with a common upper-state term value and linewidth, different ground-state $X(v = 0, J'')$ term values, and different oscillator strengths. Ground-state energy levels were computed from the Dunham coefficients of Le Roy *et al.*⁵⁷

It was not possible to fit parameters to the individual rotational lines of the weak or broadened features observed experimentally. Instead, smaller sets of parameters were optimized, controlling an effective Hamiltonian matrix representing all upper-state levels. For this purpose, the Hund's case-(a) Hamiltonian of Brown and Merer⁵⁸ was adopted, fully specified in their Table 1 for the case of a $^3\Pi$ state, and a standard Hamiltonian was used to represent the observed $^1\Pi$ and $^1\Sigma$ levels,

$$T_{1\Sigma} = T + BJ(J + 1) - D[J(J + 1)]^2 \quad (5)$$

and

$$T_{1\Pi} = T + BJ(J + 1) - D[J(J + 1)]^2 + qJ(J + 1), \quad (6)$$

where the parameter q is only included for f -parity levels. The spin-orbit mixing of case-(a) $^3\Pi_u$ and $^1\Pi_u$ states is restricted to their $\Omega = 1$ levels of common ef parity and is modeled with an interaction matrix element ξ , treated as a free parameter for each pair

of interacting electronic-vibrational levels. The mixed-level energies and mixing-coefficients are then computed by diagonalizing the full Hamiltonian matrix of $^3\Pi_{u\Omega}$ and $^1\Pi_{u1}$ levels.

The absorption strength of $^3\Pi_u \leftarrow X^1\Sigma_g^+(0)$ transitions is borrowed from nearby $^1\Pi_u \leftarrow X^1\Sigma_g^+(0)$ transitions through their mutual spin-orbit coupling.⁵⁹ We model the rotational line strengths of the $^1\Pi_u \leftarrow X^1\Sigma_g^+(0)$ transitions using an empirical electronic-vibrational transition moment and Hönl-London rotational-line-strength factors.⁶⁰ Mixing coefficients from the Hamiltonian-matrix diagonalization are then used to generate the full rotational structure of the observed mixed $^3\Pi_u \sim ^1\Pi_u \leftarrow X^1\Sigma_g^+$ spectrum.

Ω labels are assigned to the observed $^3\Pi_u$ levels forming continuous *ef*-parity rotational progressions based on their dominant character at low J . The relative contribution of nominal Ω -levels to the observed absorption depends on their admixture of pure $\Omega = 1$ character and is controlled by J and the diagonal spin-orbit constant A . Sufficiently large- A and low- J states are of nearly unmixed Ω character, and transitions to the central $\Omega = 1$ levels appear strongly. For increasing J , these transitions weaken and the higher- and lower-energy triplet levels are more readily excited. An example of this phenomenon is given in a detailed study on the $E^1\Pi \sim k^3\Pi$ interaction in isotopologues of CO.⁶¹ Other level and intensity patterns may occur where the magnitudes of A and the rotational constant B are comparable,⁵⁸ e.g., as found for the $C^3\Pi_u(v=7)$ level.

The spin-orbit borrowing of absorption intensity is reciprocated by a sharing of dissociation proclivity. However, while the source of the intensity is always the dipole-allowed $^1\Pi_u \leftarrow X(0)$ transition, both the $^3\Pi_u$ and $^1\Pi_u$ levels have nonzero inherent predissociation widths, prior to mixing, which are derived from different multichannel dissociation pathways, although ultimately involving the $C'^3\Pi_u$ valence state. This can lead to interference effects and J -dependent linewidths. Here, we adopt a hybrid procedure to fit the experimental $^3\Pi_u \leftarrow X(0)$ band cross sections, empirically modeling the dissociation linewidth of $^3\Pi_u$ effective-Hamiltonian levels by means of an imaginary energy, $i\Gamma$,⁶¹ mixing the $^3\Pi_u$ and $^1\Pi_u$ levels with the ξ parameter, and using the results of previous work to treat the $^1\Pi_u \leftarrow X(0)$ transition.⁴⁴ This approach is necessary since, as implied above, it is not usual to find simultaneous consistency between the two-state modeled linewidths and the corresponding intensity sharing due to the inherent multilevel nature of the interaction. It should be noted, however, that the independently fitted $^3\Pi_u$ experimental linewidths determined here are meaningful and very suitable for comparison with the CSE computations.

IV. CSE MODELING

A semiempirical CSE model of the interacting C , C' , F , and $G^3\Pi_u$ states of N_2 was developed by Lewis *et al.*³⁴ in order to reproduce the energy levels, rotational constants, and predissociation broadening of all experimentally observed levels. This dataset consisted of $^{14}N_2$ levels between 88 900 and 111 000 cm^{-1} , i.e., as high as $v = 3$ for the $F^3\Pi_u$ and $G^3\Pi_u$ states and $v = 18$ for $C^3\Pi_u$, together with a few additional levels of $^{15}N_2$. The parameters of their model are the diabatic potential-energy curves, $V_i(R)$, of the $^3\Pi_{u1}$ states, reproduced in Fig. 2, and the electrostatic interaction energies

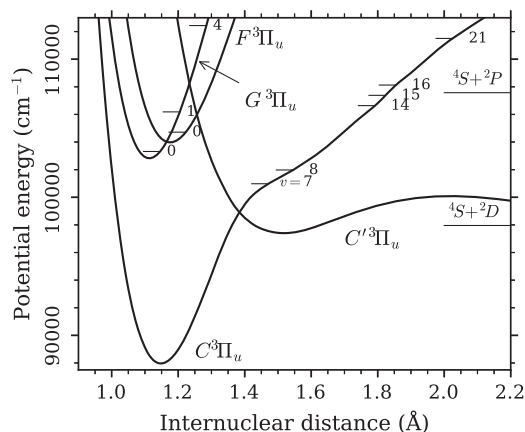


FIG. 2. Potential-energy curves of $^3\Pi_u$ states (after Ref. 34), referenced to $X^1\Sigma_g^+(v=0, J=0)$ of $^{14}N^{15}N$ and with the newly observed levels indicated.

mixing them. Together, the parameters form an R -dependent potential matrix

$$\mathbf{V}(R) = \begin{pmatrix} V_C(R) & 798 & 0 & 0 \\ 798 & V_{C'}(R) & 315 & 1175 \\ 0 & 315 & V_F(R) & 1115 \\ 0 & 1175 & 1115 & V_G(R) \end{pmatrix}, \quad (7)$$

where R is the internuclear distance and the off-diagonal interaction energies are in cm^{-1} . Coupled radial vector wavefunctions, $\chi(R)$, are solutions to a coupled-channel Schrödinger equation,

$$\frac{d^2}{dR^2}\chi(R) = \frac{-2\mu}{\hbar^2}\chi(R)[E - \mathbf{V}(R)], \quad (8)$$

where μ is the molecular reduced mass. These wavefunctions exist for all energies, E , lying above the dissociation energy of $C'^3\Pi_u$, which provides the predissociation mechanism. Detailed descriptions of the CSE method applied to the predissociative coupling of bound and unbound states, and a method for solving Eq. (8), have been given previously.^{62–64}

The model of Lewis *et al.*³⁴ is restricted to $^3\Pi_{u\Omega=1}$ states and considers neither the fine-structure splittings leading to separate $\Omega = 0$ and 2 states nor the spin-orbit interactions involving $^1\Pi_u$ levels. Some of these details have been considered elsewhere.^{36,44,59}

The potential-energy curves and interaction energies in Eq. (7) were optimized by Lewis *et al.*³⁴ to best match the available $^{14}N_2$ and $^{15}N_2$ level data but are independent of nuclear mass and also applicable to $^{14}N^{15}N$. We utilize and test this mass-independence by adopting the CSE model of Lewis *et al.*³⁴ unchanged and computing its predictions for $^{14}N^{15}N$ by the substitution of the correct reduced mass in Eq. (8).

Elements of the vector wavefunction in Eq. (8),

$$\chi(R; E) = \begin{pmatrix} \chi_C(R; E) \\ \chi_{C'}(R; E) \\ \chi_F(R; E) \\ \chi_G(R; E) \end{pmatrix}, \quad (9)$$

constitute R -dependent mixing coefficients of the four coupled electronic states. Radially integrating the bound-state coefficients gives E -dependent overall mixing coefficients,

$$c_i(E) = \int_0^{R_{\max}} |\chi_i(R; E)|^2 dR, \quad (10)$$

with $i = C, G, \text{ or } F$, that show resonant structure near the vibrational eigenenergies that would occur if these states were not coupled to

the C' continuum and truly bound. The central energies and widths of these coupled-state resonances are then directly comparable with the experimentally determined level energies and linewidths. We fit Fano line shapes to the $c_i(E)$ spectrum in order to make this comparison. The choice of the outer integration limit, R_{\max} , in Eq. (10) is not significant as long as it extends beyond the classically allowed region of all bound states.

Computed level energies, predissociation linewidths, and rotational constants are given in Table I. The potential-energy curves in

TABLE I. Experimental molecular constants of $^{14}\text{N}^{15}\text{N}^3\Pi_u$ levels and those computed from the CSE model.^a

Level	T_{00}^b	T_{00}^{CSE}	B^c	B^{CSE}	A^c	Γ	Γ^{CSE}	$f_v \times 10^{4d}$
C(6)		99 733.2		1.110			0.33	
C(7) ^e	100 979.9(1)	100 981.8	1.361 3(3)	1.364	3.69(2)	0.11(2) ^f	0.09	0.24(4)
C(8) ^g	101 980(5)	101 970.7	1.3	1.279	2	60(15)	55	1.9(4)
C(9)		102 781		1.31			142	
C(10)		103 543		1.32			167	
C(11)		104 307		1.24			111	
C(12)		105 090.3		1.194			56	
C(13)		105 870.3		1.150			21	
C(14)	106 639.4(3)	106 639.6	1.18(2)	1.151	−14	0.61(3)	0.62	0.09(3)
C(15) ^h	107 384.86(1)	107 380.5	1.105 2(2)	1.101	−13.03(1)	0.02(1) ^f	0.00	0.067(19)
C(16) ⁱ	108 130(4)	108 130.0	1.27(5)	1.143	−14	22(2)	16	0.41(6)
C(17)		108 852.6		1.085			59	
C(18)		109 543.6		1.050			30	
C(19)		110 211.7		1.049			69	
C(20)		110 820 ^j		1.07 ^j			45 ^j	
C(21)	111 503(20)	111 477.6	1.0	1.009	−18	64(15)	78	4.2(11)
C(22)		112 081.1		0.953			72	
G(0) ^k	103 320.4(1)	103 320.8	1.804(3)	1.822	−8.0(2)	0.11(1)	0.09	0.18(3)
G(1)	106 184(20)	106 139.6	1.7(4)	1.780	−8	19(8)	9.8	0.12(3)
G(2)		107 961.3		1.713			68	
G(3)		110 740 ^j		1.77 ^j			250 ^j	
G(4)	112 440(5)	112 519.9	1.8(2)	1.699	−8	32(5)	24	0.57(9)
F(0) ^l	104 718.42(7)	104 717.5	1.75(2)	1.747	−21.64(7)	0.4(1)	0.44	0.074(11)
F(1)		106 550.4		1.654			16	
F(2)		108 608		1.69			140	
F(3)		109 870		1.74			167	
F(4)		111 727.2		1.682			28	

^aAll are in cm^{-1} apart from Γ (cm^{-1} FWHM) and f_v (dimensionless). Estimated 1σ uncertainties are given in parentheses in units of the least-significant digit.

^b $\Omega = 1$ and $J = 0$ term origin, from adding $(2B - 4\lambda/3 - 2\gamma)$ to the Hamiltonian term in Ref. 58, referenced to an $X(v = 0, J = 0)$ energy zero.

^cEntries without uncertainties are assumed values.

^dA 15% uncertainty is assigned to f -values of well-resolved bands, corresponding to the overall column-density calibration uncertainty. Larger uncertainties are estimated for poorly resolved or fitted bands.

^eResults of a two-state deperturbation with $b(0)$ with additional parameters: $\lambda_{C(7)} = 1.37(3)$, $\gamma_{C(7)} = -0.007(1)$, and $\sigma_{C(7)} = 0.695(8) \text{ cm}^{-1}$. $T_{b(0)} = 100 832.33(4)$, $B_{b(0)} = 1.400 74(6)$, $D_{b(0)} = 2.62(2) \times 10^{-5}$, and $\xi_{C(7)\sim b(0)} = 16.5(2) \text{ cm}^{-1}$.

^fWidth at $J = 1$.

^gResults of a two-state deperturbation with $b(2)$ with additional parameters: $T_{b(2)} = 102 138.71(1)$, $B_{b(2)} = 1.342 26(6)$, $D_{b(2)} = 1.64(2) \times 10^{-5}$, and $\xi_{C(8)\sim b(2)} = 17(1) \text{ cm}^{-1}$.

^hResults of a two-state deperturbation with $b(9)$ with additional parameters: $\lambda_{C(15)} = 0.474(7)$, $\sigma_{C(15)} = 0.490(8)$, $T_{b(9)} = 107 644.87(1)$, $B_{b(9)} = 1.200 0(1)$, $D_{b(9)} = 2.01(6) \times 10^{-5}$, $H_{b(9)} = 3.35(8) \times 10^{-8}$, $q_{b(9)} = 2.31(2) \times 10^{-5}$, and $\xi_{C(15)\sim b(9)} = 6.5(1) \text{ cm}^{-1}$.

ⁱResults of a two-state deperturbation with $b(10)$ with additional parameters: $T_{b(10)} = 108 262.4(1)$, $B_{b(10)} = 1.168 6(1)$, $D_{b(10)} = 1.54(3) \times 10^{-5}$, and $\xi_{C(16)\sim b(10)} = 8(1) \text{ cm}^{-1}$.

^jEstimated value from closely coupled C(20) and G(3) resonances.

^kResults of a two-state deperturbation with $b(4)$ with additional parameters: $q_{G(0)} = -0.037(2)$, $T_{b(4)} = 103 517.2(3)$, $B_{b(4)} = 1.374(4)$, $D_{b(4)} = 5.1(15) \times 10^{-5}$, $H_{b(4)} = 1.1(15) \times 10^{-8}$, $q_{b(4)} = 1.4(5) \times 10^{-4}$, and $\xi_{G(0)\sim b(4)} = 1.8(7) \text{ cm}^{-1}$.

^lAdditional parameter: $\lambda = 0.28(8) \text{ cm}^{-1}$.

Eq. (7) correspond to virtual $J = 0$ levels, and the rotational constant is computed from the difference between the $J = 5$ and $J = 0$ CSE level energies, i.e., $B = (T_5 - T_0)/30$, where the rotationally excited level is computed using a potential matrix with diagonal elements modified according to

$$V_{ii}(R; J) = V_{ii}(R; J = 0) + \frac{\hbar^2 J(J+1)}{2\mu R^2}, \quad (11)$$

with $J = 5$.

V. RESULTS AND DISCUSSION

In the present study, $^{14}\text{N}^{15}\text{N}$ states with excitation energies between 100 900 and 112 600 cm^{-1} are investigated under high column-density conditions to reveal the forbidden $^3\Pi_u \leftarrow X^1\Sigma_g^+$ spectrum. In Subsections V A–V J, we discuss the observed absorption bands terminating on $C^3\Pi_u(v = 7, 8, 14\text{--}16, 21)$, $G^3\Pi_u(v = 0\text{--}1, 4)$, and $F^3\Pi_u(v = 0)$.

Molecular constants determined for the observed $^3\Pi_u$ levels are listed in Table I, and line lists for all observed transitions are provided in the supplementary material. The band oscillator strengths, f_v , in Table I, are computed by summing the f -values of all rotational transitions weighted by their lower-level thermal populations and are then only strictly applicable at 98 K. The listed term origins, T_{00} , refer to virtual $\Omega = 1$, $J = 0$ triplet-state levels and differ from the Hamiltonian terms of Ref. 58 as described in the table footnotes.

A. $C^3\Pi_u(v = 7)$

We assign a well-resolved band appearing in our spectrum near 101 000 cm^{-1} to $C(7) \leftarrow X(0)$, following its observed location in $^{14}\text{N}_2$ and $^{15}\text{N}_2$.³⁸ The spectrum is plotted in Fig. 1 with lines assigned to six rotational branches accessing e - and f -parity levels of the $\Omega = 0$ and 1 substates. The band occurs 150 cm^{-1} higher in energy than the bandhead of $b(0) \leftarrow X(0)$, no doubt the principal perturbation partner from which $C(7) \leftarrow X(0)$ borrows its absorption intensity. The observed $C(7) \leftarrow X(0)$ lines are less predissociation broadened than that found in other isotopologues, where they are entirely rotationally blended.³⁸

The observed spectrum was fitted to an effective Hamiltonian model for $C(7)$ and $b(0)$, coupled by a spin-orbit interaction. The fitted parameters for $C(7)$ are listed in Table I and include a nonzero Λ -doubling parameter, o ,⁵⁸ to account for e - and f -parity splitting up to 0.5 cm^{-1} . The interaction energy, chosen to reproduce the observed $C(7) \leftarrow X(0)$ intensity borrowing, does not provide a satisfactory value for the $b(0)$ predissociation broadening, underestimating this by a factor of 10 for low- J levels when compared with the measured and calculated widths of Heays *et al.*⁴⁴ An initial model that included an empirical J -dependent linewidth for $b(0)$, following Heays *et al.*,⁴⁴ was used for the Hamiltonian model fit shown in Fig. 1. However, this model does not fully explain the observed line shapes of the $C(7) \leftarrow X(0)$ transitions. In the finally adopted model, the term energy and linewidth for each $C(7)$ rotational level were allowed to vary individually, while retaining the Hamiltonian-derived line strengths. The corresponding best-fit shown in Fig. 1 is then quite satisfactory, and the resulting J -dependent $C(7)$ predissociation widths are plotted in Fig. 3.

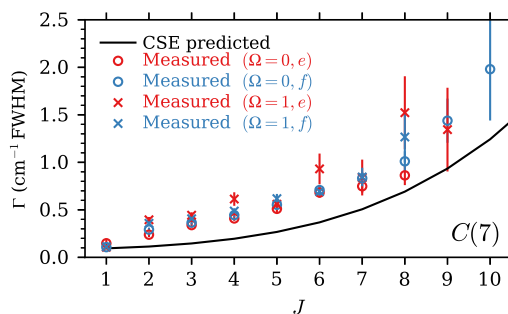


FIG. 3. Rotational variation of the predissociation linewidth for $C(7)$. Symbols: experimental, this work. Curve: CSE computations using the model of Ref. 38.

The deduced band origins and rotational constants, T and B , respectively, are appropriately intermediate to those determined by Lewis *et al.*³⁸ in observations of $C(7)$ in $^{14}\text{N}_2$ and $^{15}\text{N}_2$. However, the $^{14}\text{N}^{15}\text{N}$ diagonal spin-orbit constant, $A = 3.69 \pm 0.01 \text{ cm}^{-1}$, is found to be significantly smaller than the rough 11 cm^{-1} value found previously for both homonuclear species, although there is a significant uncertainty in these previous estimates that were derived from rotationally unresolved spectra. A small spin-orbit constant is consistent with the known strong internuclear-distance-dependence in the principal configuration of $C^3\Pi_u$,³⁵ leading to a zero-crossing of A as a function of the vibrational level near $v = 7$. The energy ordering of $C(7)$'s pure Hund's case (a) Ω -substates is affected by the smallness of A and has the unusual sequence $\Omega = 0, 2$, and 1. Spin-rotation coupling thoroughly mixes the pure case (a) levels, even by $J = 4$, but with near-zero admixture of pure $\Omega = 1$ into the series of intermediate levels nominally labeled $\Omega = 2$. No transitions to this $\Omega = 2$ series are then observed in our spectrum because all intensity of forbidden absorption into $C^3\Pi_u$ arises from spin-orbit mixing of its pure $\Omega = 1$ levels with $b^1\Pi_u$.

B. $C^3\Pi_u(v = 8)$

Absorption due to $C(8) \leftarrow X(0)$ was observed in $^{14}\text{N}_2$ by Lewis *et al.*,³⁸ and we find a similar feature in our $^{14}\text{N}^{15}\text{N}$ spectrum, centered at 101 950 cm^{-1} , and overlapped by $b(2) \leftarrow X(0)$ absorption lines, as shown in Fig. 4. The rotational structure of $C(8) \leftarrow X(0)$ is completely blended, and the red-degraded bandhead of $b(2) \leftarrow X(0)$ is totally saturated. Apparent nonzero intensity in the bandhead region is due to the locally unreliable phase correction of the measured interferogram where the true intensity is zero. Furthermore, the residual room-temperature $^{14}\text{N}^{15}\text{N}$ gas outside the cooled sample chamber contributes to the high- J ' lines at energies below 101 920 cm^{-1} , and contaminating H_2 lines appear in a few locations in the spectrum, e.g., at 101 825 cm^{-1} .

We constructed a local-perturbation model consisting of $C(8)$, $b(2)$, and their spin-orbit interaction, with fitted parameters given in Table I. The resulting modeled and experimental absorption spectra are compared in Fig. 4. This model was optimized with concurrent comparison to the unsaturated spectrum recorded by Heays *et al.*⁴⁴ in order to better fit the $b(2) \leftarrow X(0)$ bandhead.

Only a few Hamiltonian parameters could be independently fitted to the unresolved $C(8) \leftarrow X(0)$ absorption, and we, therefore,

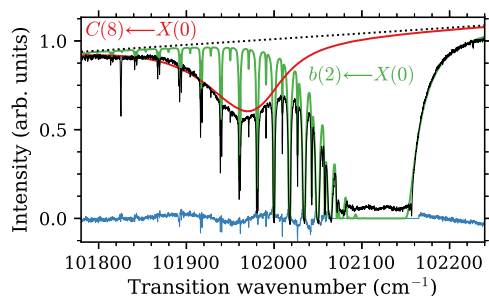


FIG. 4. Black curve: absorption spectrum showing $C(8) \leftarrow X(0)$ and $b(2) \leftarrow X(0)$. Red curve: $C(8) \leftarrow X(0)$ absorption computed from the two-level deperturbation model. Green curve: $b(2) \leftarrow X(0)$ model absorption. Blue trace: residual error of the deperturbation model. Dotted line: the frequency-dependent synchrotron radiation intensity.

fixed the $C(8)$ diagonal spin-orbit constant to $A = 2 \text{ cm}^{-1}$, consistent with the values calculated for $^{14}\text{N}_2$ and $^{15}\text{N}_2$ by Ndome *et al.*,³⁵ although the model fit is insensitive to any reasonably small choice of A . We also assume no $C(8)$ centrifugal distortion and J - and Ω -independent predissociation broadening. A freely varied rotational constant $B = 1.44 \text{ cm}^{-1}$ was found, but this parameter is only weakly constrained by the experimental spectrum and ultimately a fixed value $B = 1.3 \text{ cm}^{-1}$ was assumed, given the values computed for $^{14}\text{N}_2$ and $^{15}\text{N}_2$ by Lewis *et al.*³⁴ The fitted predissociation linewidth of $C(8)$ is $\Gamma = 60 \pm 15 \text{ cm}^{-1}$ FWHM, with the uncertainty estimated by considering a range of values that plausibly fit the experimental spectrum. Similarly, subjective uncertainties were also evaluated for the term origin of $C(8)$ and the $C(8) \sim b(2)$ spin-orbit interaction energy.

The interaction between $b(2)$ and $C(8)$, optimized to best match the intensity borrowed by $C(8) \leftarrow X(0)$, also results in the correct 0.6 cm^{-1} FWHM line broadening for transitions to low- J $b(2)$ levels. Higher- J $b(2)$ levels are known to have decreasing predissociation widths,⁴⁴ but this effect is not reproduced by our two-level model. The imperfect quality-of-fit of the modeled $C(8) \leftarrow X(0)$ band profile evident in Fig. 4 is another indication that more than two interacting states are contributing to the observed $C(8)$ level.

C. $C^3\Pi_u(v = 14)$

Figure 5 shows a spectrum of $C(14) \leftarrow X(0)$ and overlying lines of $^{14}\text{N}^{15}\text{N}$ $b(8) \leftarrow X(0)$ and $^{14}\text{N}_2$ $b'(4) \leftarrow X(0)$, with steeply rising absorption at lower energy due to the $^{14}\text{N}^{15}\text{N}$ bandhead of $b'(4) \leftarrow X(0)$. After accounting for this contamination, P - and R -branch lines from $C(14) \leftarrow X(0)$, having $J' < 4$ and the correct energy combination differences to originate from common e -parity upper levels, are evident in the spectrum. Additional lines are observed from the Q -branch connecting with the corresponding f -levels, with Λ -doubling up to 0.1 cm^{-1} . A common linewidth was fitted to all of these transitions, and f -values with assumed linear-in- $J'(J' + 1)$ dependences fitted separately to each branch are plotted in Fig. 6.

We assigned the observed absorption to $C(14) \leftarrow X(0)$ due to its appearance midway between the corresponding band origins in $^{14}\text{N}_2$ and $^{15}\text{N}_2$.³⁴ Absorption is only observed to one Ω -component,

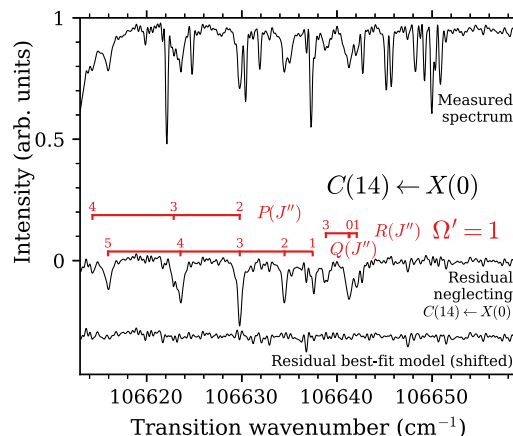


FIG. 5. Spectrum showing $C(14) \leftarrow X(0)$ absorption and overlapping $^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}_2$ contamination. The residual error after modeling this spectrum is shown, and for a model neglecting $C(14) \leftarrow X(0)$, to highlight its rotational structure.

with $\Omega = 2$ ruled out by the observance of a $J = 1$ level. The strongest low-rotation transitions will occur for $\Omega' = 1$ because of a direct admixture of this state with the $^1\Pi_u$ manifold, but with spin-rotation mixing, sharing this intensity with nominal $\Omega' = 0$ and 2 transitions at higher J . The observed decrease in f -value with J is then consistent with an $\Omega = 1$ upper state.

Molecular parameters fitted to the observed transitions to $C(14) \Omega = 1$ levels are given in Table I, with an assumed spin-orbit constant of $A = -14 \text{ cm}^{-1}$ in accordance with previous observations of this and nearby $C(v)$ levels for other isotopologues.³⁸

A summation of f -values for all observed $C(v = 14, \Omega = 1) \leftarrow X(0)$ transitions gives a value of 3.6×10^{-6} . Assuming $C(14) \leftarrow X(0)$ borrows intensity from a remote $^1\Pi_u \leftarrow X(0)$ transition, we computed f -values for transitions to all $C(v = 14, \Omega)$ levels. Then, a whole-band f -value extrapolated from the experimentally observed transitions is 9.0×10^{-6} .

D. $C^3\Pi_u(v = 15)$

The $C(15) \leftarrow X(0)$ band has not been observed previously for any isotopologue and provides a test of the CSE model when interpolating both v and reduced mass. The upper trace in Fig. 7 shows

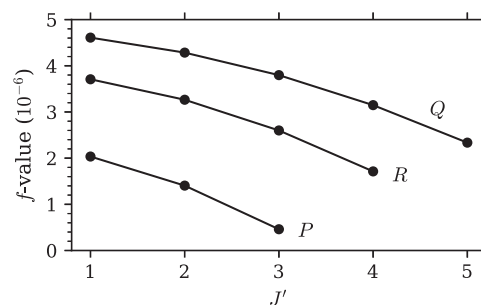


FIG. 6. Experimental effective band f -values from observed branches of $C(v = 14, \Omega = 1) \leftarrow X(0)$, constrained to formulas, $f_v(J') = f_v(0) + \text{const.} \times J'(J' + 1)$.

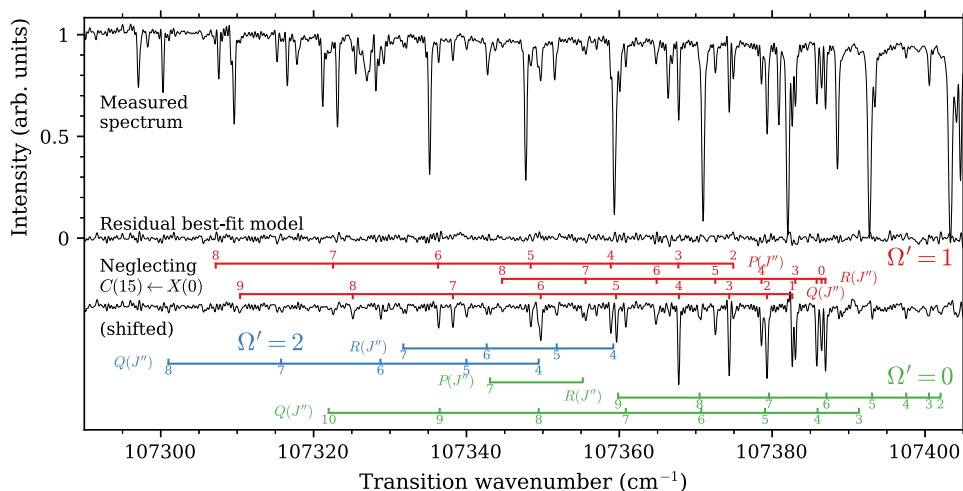


FIG. 7. Spectrum showing $C(15) \leftarrow X(0)$ absorption, overlapping $^{14}\text{N}^{15}\text{N}$ transitions, and contamination from $^{14}\text{N}_2$, $^{15}\text{N}_2$, and H_2 . The residual error after modeling this spectrum is shown, and for a model neglecting $C(15) \leftarrow X(0)$, to highlight its rotational structure.

the measured absorption spectrum of $C(15) \leftarrow X(0)$, together with lines attributable to $b(9) \leftarrow X(0)$ and $o_3(1) \leftarrow X(0)$, weak contamination from the $^{14}\text{N}_2$ and $^{15}\text{N}_2$ bands $b'(5) \leftarrow X(0)$ and $b(9) \leftarrow X(0)$, and a few H_2 contaminant lines.

The $C(15)$ level was modeled in tandem with $b(9)$ and a spin-orbit mixing between them, with all model parameters listed in Table I. The resultant $C(15) \leftarrow X(0)$ lines are strongest for transitions to the upper state $\Omega' = 1$ levels, but with weaker transitions to $\Omega' = 0$ and $\Omega' = 2$ also evident in the spectrum. The best-fit model residual is plotted in Fig. 7 as well as a residual neglecting all $C(15) \leftarrow X(0)$ absorption to distinguish this from overlapping absorption. The observation of all $C(15)$ Ω -levels allows for a determination of both diagonal spin-orbit and spin-spin parameters, A and λ , respectively.

The two-level model adopted here reproduces the wavenumbers and strengths of the $C(15) \leftarrow X(0)$ lines to experimental precision but does not contain the necessary physics to constrain their predissociation broadening. We fitted the latter independently while assuming Ω - and ef -parity-independence, with the resulting J -dependence plotted in Fig. 8. These fitted widths are principally constrained by the strong $\Omega' = 1$ transitions.

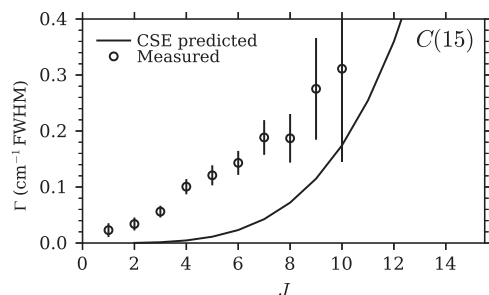


FIG. 8. Rotational variation of the predissociation linewidth for $C(15)$. Symbols: experimental, this work. Curve: CSE computations using the model of Ref. 38.

E. $C^3\Pi_u(v = 16)$

A broad absorption feature shown in Fig. 9 at $108\,120\text{ cm}^{-1}$ is assigned to $C(16) \leftarrow X(0)$, based on the CSE model prediction and the known location of this band in $^{14}\text{N}_2$.³⁸ The saturated bandhead of $b(10) \leftarrow X(0)$ occurs at $108\,260\text{ cm}^{-1}$, showing some phase-error distortion, and higher- J'' lines also overlap $C(16) \leftarrow X(0)$. Some further weak or intermediate strength lines are due to contamination from $^{15}\text{N}_2$. The $^{14}\text{N}^{15}\text{N}$ spectrum was treated with a two-level model including $C(16)$, $b(10)$, and a mutual spin-orbit interaction. The strength of this mixing controls the intensity borrowing of $C(16) \leftarrow X(0)$ and how much of the predissociation broadening of $C(16)$ is transferred to $b(10)$. The spin-orbit constant of $C(16)$ was fixed near the value computed by Ndome *et al.*,³⁵ $A = -14\text{ cm}^{-1}$, and assumptions of zero centrifugal distortion and J -independent line broadening made. The absorption strength and profile of $C(16) \leftarrow X(0)$ are quite well fitted, as shown in Fig. 9, as is the line broadening of $b(10) \leftarrow X(0)$. All fitted constants are given in Table I where uncertainties

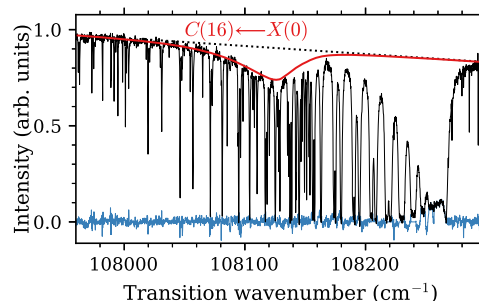


FIG. 9. Black curve: absorption spectrum showing $C(16) \leftarrow X(0)$ and $b(10) \leftarrow X(0)$. Red curve: $C(16) \leftarrow X(0)$ computed using a two-level deperturbation model. Blue curve: residual error of the full deperturbation model. Saturated $b(10) \leftarrow X(0)$ lines are excluded from this residual. Dotted line: background synchrotron radiation intensity.

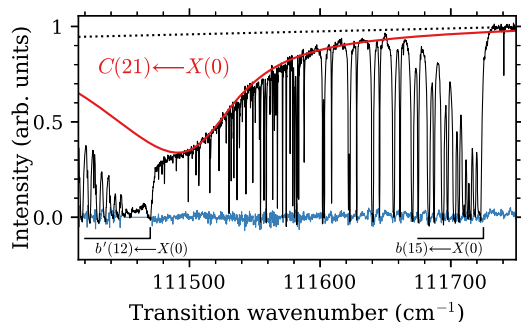


FIG. 10. Black curve: absorption spectrum showing a broad $C(21) \leftarrow X(0)$ feature, embedded under strong singlet bands, with additional overlapping narrow lines due to $^{14}\text{N}_2$. Red curve: fitted model $C(21) \leftarrow X(0)$ contribution. Blue curve: residual error after modeling the spectrum. Dotted line: background synchrotron radiation intensity.

of the T , B , and Γ parameters for $C(16)$ and the spin-orbit mixing parameter ξ have been estimated manually with trial models.

F. $C^3\Pi_u(v=21)$

A broad absorption feature shown in Fig. 10 is assigned to $C(21) \leftarrow X(0)$ based on its close coincidence with the CSE-predicted band origin. There is strong absorption due to $b'(12) \leftarrow X(0)$, obscuring much of the observed forbidden band, and only two molecular parameters for $C(21)$, T , and Γ could be fitted using the experimental spectrum. For this fit, a spin-orbit constant of $A = -18 \text{ cm}^{-1}$ was assumed, following the values predicted for high $C(v)$ levels by Ndomé *et al.*,³⁵ and a rotational constant $B = 1 \text{ cm}^{-1}$ was fixed near the predicted value of the CSE model.

G. $C^3\Pi_u(v=0)$

A spectrum of $G(0) \leftarrow X(0)$ is plotted in Fig. 11, and line parameters are fitted to all nine of the expected rotational branches, with a common linewidth found for the entire spectrum. This

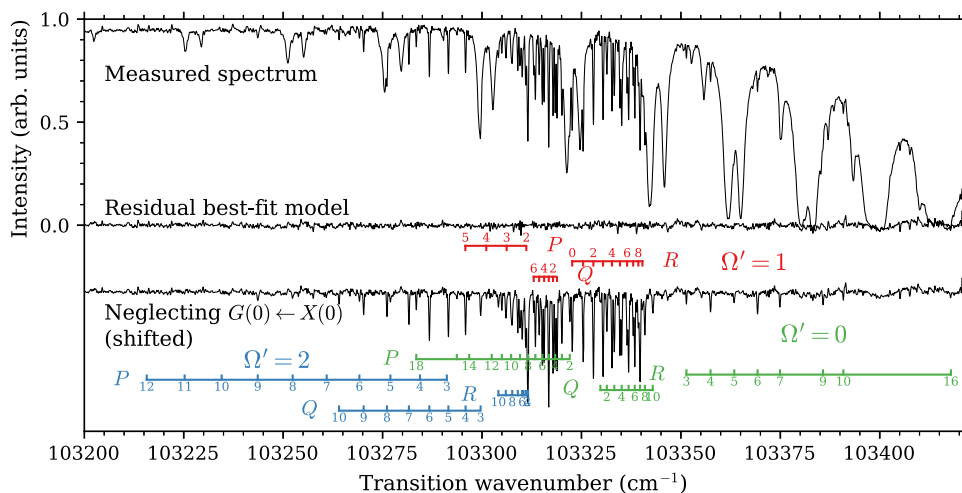


FIG. 11. Spectrum and line assignments showing $G(0) \leftarrow X(0)$. Saturated and broadened lines are due to $b(4) \leftarrow X(0)$ and contaminating H_2 . The residual error after modeling this spectrum is shown, and for a model neglecting $G(0) \leftarrow X(0)$, to highlight its rotational structure.

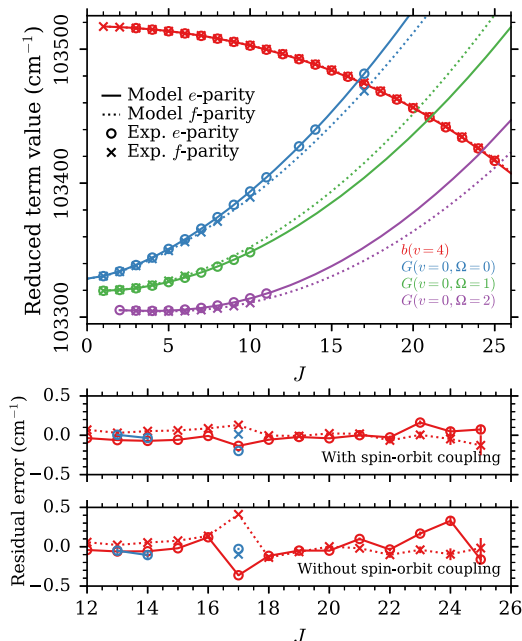


FIG. 12. Upper figure: experimental term values of $G(0)$ and $b(4)$, reduced by the subtraction of $1.5 \times J(J + 1)$, are shown as symbols and term values computed from an effective Hamiltonian model as curves. Lower figures: residual errors of effective Hamiltonian models, with and without the inclusion of $b(4) \sim G(0)$ spin-orbit coupling.

band borrows strength principally through the interaction between $G(0)$ and $b(4)$. We simultaneously fit a low-pressure spectrum of $b(4)$ measured by Heays *et al.*⁴⁴ to properly characterize this interaction.

A near-degeneracy of $G(0)$ $\Omega = 0$ *ef*-parity levels with $b(4)$ occurs at $J = 17$, leading to a perturbation of $b(4)$ energies, and the appearance of extra $Q(17)$, $R(16)$, and $P(18)$ lines is attributable to $G(0) \leftarrow X(0)$. Similar $b(4)$ energy shifts also occur where it crosses

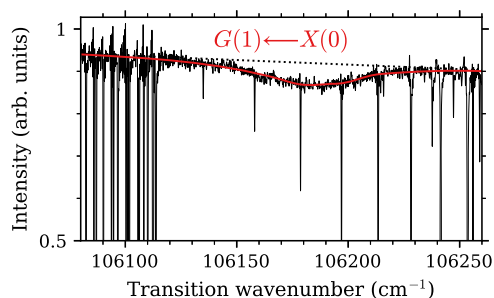


FIG. 13. Black curve: absorption spectrum showing $G(1) \leftarrow X(0)$. Narrow overlapping features are due to $c'_4(1) \leftarrow X(0)$ from $^{14}\text{N}^{15}\text{N}$ and contaminating $b(7) \leftarrow X(0)$ lines from $^{14}\text{N}_2$. Red curve: modeled $G(1) \leftarrow X(0)$ absorption. Dotted line: the frequency-dependent synchrotron radiation intensity.

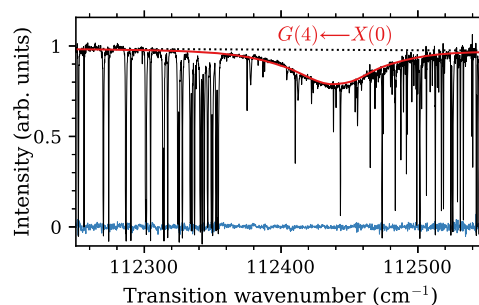


FIG. 14. Black curve: absorption spectrum showing $G(4) \leftarrow X(0)$. Narrow overlapping features are due to $b(16) \leftarrow X(0)$ absorption from $^{14}\text{N}^{15}\text{N}$ and $b(7) \leftarrow X(0)$ absorption from $^{14}\text{N}_2$ as well as H_2 contamination. Red curve: modeled $G(4) \leftarrow X(0)$ absorption. Blue trace: residual error of the deperturbation model. Dotted line: the frequency-dependent synchrotron radiation intensity.

the $\Omega = 1$ and 2 levels of $G(0)$ near $J = 21$ and 25, respectively, but without the occurrence of observable extra lines in our spectra.

The experimental energy levels of $G(0)$ and $b(4)$ are plotted in Fig. 12, along with term values computed from an effective Hamiltonian model that includes these states and their spin-orbit interaction. The fitted parameters of this model are given in Table 1, and its residual error is shown in Fig. 12. A trial model neglecting the spin-orbit interaction of $b(4)$ and $G(0)$ fails to account for the observed $b(4)$ levels at all three crossing points, with residual errors up to 0.5 cm^{-1} demonstrated in Fig. 12. Then, the $\Omega = 1$ and 2 sublevels of $G(0)$ between their observed levels and $b(4)$ crossings are likely to be well-interpolated by the two-level Hamiltonian model.

Figure 11 provides an instructive example of the $^3\Pi_u \sim ^1\Pi_u$ mixing complexities discussed at the end of Sec. III. There is an extremely small $G(0) \sim b(4)$ mixing, yet it is large enough to provide all of the observed $G(0) \leftarrow X(0)$ oscillator strength. However, the same mixing has essentially no effect on the unmixed $G(0)$ and $b(4)$ level widths, 0.11 cm^{-1} FWHM and 1.46 cm^{-1} FWHM,⁴⁴ respectively. As evidenced by the CSE model of Lewis *et al.*,³⁴ employed here, the $G(0)$ width is explicable using only a manifold of the coupled F , G , C , and $C'^3\Pi_u$ states. Similarly, the widths of the low $b(v)$

levels, including $b(4)$, are explicable using a CSE model containing only the b , c , $o^1\Pi_u$ manifold, together with the C and dissociative $C'^3\Pi_u$ states.⁵⁹ Remarkably, despite all predissociation in this region being derived from the $^3\Pi_u$ route, the $G(0)$ level plays no measurable part in the predissociation of $b(4)$.

H. $C'^3\Pi_u(v = 1)$

A broad absorption feature, shown in Fig. 13, is observed in the VUV-FT spectrum near 106180 cm^{-1} , close to the position of a similar broad feature in the absorption spectrum of cooled $^{14}\text{N}_2$, which has been assigned as $G(1) \leftarrow X(0)$.³⁸ Principally on the basis of intensity considerations, we assign this feature to $G(1) \leftarrow X(0)$ in $^{14}\text{N}^{15}\text{N}$, but note that this assignment may not be quite as robust as others in this work. A band model has been constructed in order to constrain the term origin and predissociation linewidth of $G(1)$, assuming a fixed spin-orbit constant, $A = -8 \text{ cm}^{-1}$, in accord with the value deduced for $G(0)$, as well as zero centrifugal distortion, and J -independent predissociation broadening. The intensity of $G(1) \leftarrow X(0)$ is due to spin-orbit interaction with one or more nearby $^1\Pi_u$ levels, and this is approximated with a two-level model comprising

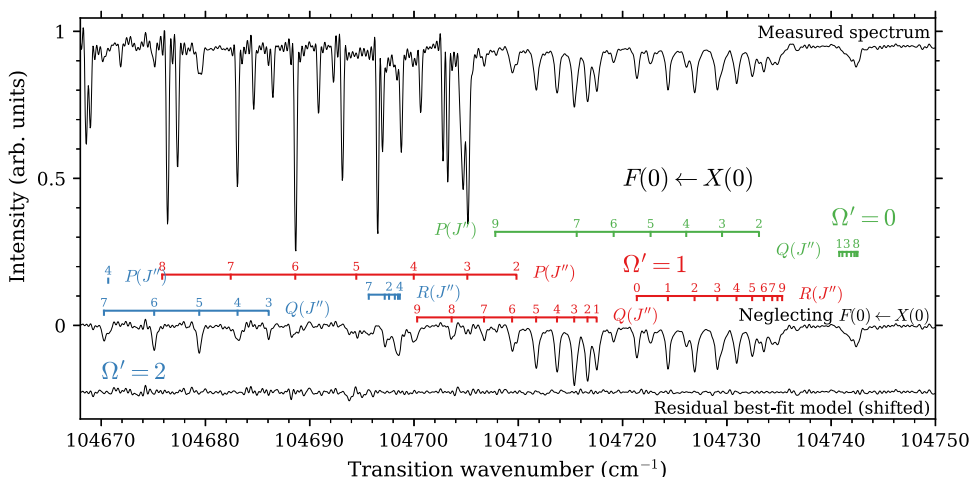


FIG. 15. Spectrum showing $F(0) \leftarrow X(0)$ absorption and overlapping $^{14}\text{N}_2$ and H_2 contamination. The residual error after modeling this spectrum is shown, and for a model neglecting $F(0) \leftarrow X(0)$, to highlight its rotational structure.

$G(1)$ spin-orbit mixed with $b(7)$ (term origin of $106\,045\text{ cm}^{-1}$). The fitted term origin, rotational constant, and predissociation linewidth for $G(1)$, with uncertainties subjectively estimated following the consideration of a range of parameter values, are given in Table I, with the best-fitting model spectrum indicated in Fig. 13.

I. $G^3\Pi_u(v=4)$

A diffuse feature centered at $112\,450\text{ cm}^{-1}$ is assigned to $G(4) \leftarrow X(0)$ absorption, since it occurs in the region of the CSE-predicted wavenumber for this band. Its spectrum is plotted in Fig. 14 together with an effective Hamiltonian simulation. In this model, the intensity-borrowing of $G(4) \leftarrow X(0)$ is attributed to the spin-orbit coupling of $G(4)$ with a single remote $^1\Pi_u$ level, approximating the multilevel interactions mixing $^1\Pi_u$ and singlet manifolds.

We assume a spin-orbit constant $A = -8\text{ cm}^{-1}$, in common with resolved observations of other $G(v)$ levels and isotopologues, and then finding a rotational constant $B = 1.76(1)\text{ cm}^{-1}$, consistent with expectation for a $G(v)$ or $F(v)$ Rydberg level. An equally good fit to the experimental data is obtained by assuming that the observed absorption corresponds to an $F(v)$ level with $A = -20\text{ cm}^{-1}$. This assignment, however, requires a large deviation from any reasonable energy extrapolation of $F(v)$ levels, known up to $v = 3$ in both $^{14}\text{N}_2$ and $^{15}\text{N}_2$.³⁴ We rule out an assignment to a high- v C -state level because the required rotational constant of $B \simeq 1\text{ cm}^{-1}$ is incompatible with a good fit to the spectrum in Fig. 14.

J. $F^3\Pi_u(v=0)$

Eight rotational branches accessing levels with J' up to 10 are observed near $104\,700\text{ cm}^{-1}$ and attributed to $F(0) \leftarrow X(0)$ absorption, with intensity borrowed from the nearby $b(5) \leftarrow X(0)$ band. The observed transitions, shown in Fig. 15, were used to determine the molecular parameters for $F(0)$ listed in Table I and are well described by rotation-independent predissociation broadening.

VI. COMPARISON WITH THE CSE MODEL

A comparison between the experimental and CSE-computed $^3\Pi_u$ molecular parameters and linewidths for $^{14}\text{N}^{15}\text{N}$ is made in Table I. Most term origins are in agreement within a few cm^{-1} apart from the $G(1)$ and $G(4)$ levels, where the energy discrepancies are significantly in excess of the corresponding predissociation linewidths. Strictly speaking, the $G(4)$ region is above the energy range of applicability of the present CSE model and the new experimental data here should enable future model improvement. While the experimental and model terms are in excellent agreement for $C(14)$ and $C(16)$, the $\sim 4\text{ cm}^{-1}$ difference for $C(15)$ is surprisingly large for such a narrow resonance, especially since the model has been optimized using precisely known narrow resonances, $C(14)$ for $^{14}\text{N}_2$ and $C(16)$ for $^{15}\text{N}_2$.³⁸ Clearly, the present observation of $C(15)$ in $^{14}\text{N}^{15}\text{N}$ should enable further constraint of the CSE model in this energy region. Computed rotational constants are within 1% of the experimental values, or within the experimental uncertainty where this is larger, apart from $C(14)$, marginally, and $C(16)$. The difference for $C(16)$ probably reflects the difficulty in fitting

rotational constants and determining their uncertainties using diffuse spectra.

A comparison between experimental and modeled predissociation widths for all isotopologues is presented in Fig. 16, with $^{14}\text{N}_2$ and $^{15}\text{N}_2$ models and experimental widths taken from the collation of Lewis *et al.*³⁴ Collectively, experimental studies of the various isotopologues have observed all levels with energies below $110\,000\text{ cm}^{-1}$ and widths below 20 cm^{-1} FWHM, respectively, with two broader bands, $C(8)$ and $C(21)$, identified here. The difficulty of studying weak, diffuse bands amidst the dense allowed singlet spectrum of N_2 explains this selection.

The multiple order-of-magnitude oscillation of C -state predissociation linewidths with vibrational level, evident in Fig. 16, is somewhat reminiscent of predissociation induced by an outer-limb-crossing repulsive state,⁶⁰ a role played in this case by $C^3\Pi_u$. However, the present case is much more complicated than the textbook perturbative crossing due to the relatively large $C \sim C'$ interaction, configurational mixing in the C state, which leads to the unusual shape of its potential-energy curve, and the multistate nature of the predissociation. In particular, Rydberg-valence and Rydberg-Rydberg interactions mixing the predissociated $^3\Pi_u$ bound states have the potential to produce interference effects in the width matrix elements, which can profoundly affect level widths, especially in the energy region above $G(0)$ and $F(0)$. The experimental level widths in Fig. 16 are very well reproduced by the CSE model, including where a reduced-mass interpolation is made to $^{14}\text{N}^{15}\text{N}$ levels. In particular, deep width minima for $C^3\Pi_u$ are predicted correctly at $v = 7$ and $v = 15$.

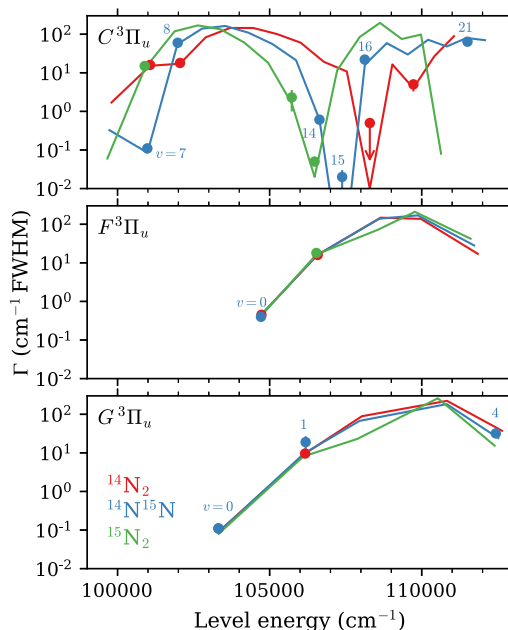


FIG. 16. Comparison between experimental and CSE-modeled $^3\Pi_u$ predissociation linewidths for isotopologues of N_2 . Symbols: experimental values for $^{14}\text{N}^{15}\text{N}$ (present work), $^{14}\text{N}_2$, and $^{15}\text{N}_2$ (Ref. 34). Line vertices: CSE computations using the model of Ref. 38.

The computed widths in Table I and Fig. 16 are for virtual $J = 0$ levels. We observe $C(7)$ and $C(15)$ in $^{14}\text{N}^{15}\text{N}$ to have J -dependent linewidths and these are compared with an excited- J CSE calculation in Figs. 3 and 8, respectively. The monotonically increasing linewidths of $C(7)$ are well predicted by the CSE model, no doubt because this level was found by Lewis *et al.*³⁴ in both $^{14}\text{N}_2$ and $^{15}\text{N}_2$, and was included in their CSE-model fitting.³⁸ Furthermore, the monotonic increase with J of the $C(15)$ widths is also predicted by the model, albeit with a lesser slope. It is unsurprising that the CSE widths for these two levels are a little lower than the experimental values, given that the CSE model includes only the strong electrostatic interactions with no spin-orbit or rotational couplings. The effects of this approximation will be mostly noticeable for the narrowest levels, where the electrostatic contribution will be very close to zero.

The predissociation widths for the lowest Rydberg levels, $G(0)$ and $F(0)$, are also very well predicted by the model. However, the CSE model of Lewis *et al.*,³⁴ which is employed here to describe the $^3\Pi_u$ states, is mostly limited in the energy region of $F(2)$, $G(2)$, and above, since it is based on experimental data having at least 50 cm^{-1} energy uncertainty in that region. Furthermore, the model does not include the next-highest $^3\Pi_u$ valence state, $III^3\Pi_u$,³⁸ which will definitely affect levels above $\sim 112\,000\text{ cm}^{-1}$. As stated above, the present experimental data, particularly for $G(4)$, will improve that situation, allowing refinement of the model potential-energy curves and electrostatic couplings. To best accomplish that future task, it will be preferable to include not only direct $^3\Pi_u$ data for all isotopologues but also indirect experimental constraints on further unobserved $^3\Pi_u$ levels due to their spin-orbit interaction with optically excited $^1\Pi_u$ and $^1\Sigma_u^+$ states, which show resultant level broadening.⁴⁴ The result will be a multichannel model including triplet and singlet states coupled by electrostatic, spin-orbit, and rotational interactions.

VII. CONCLUSIONS

Ten spin-forbidden vacuum-ultraviolet bands of $^{14}\text{N}^{15}\text{N}$ have been observed and spectroscopically analyzed in a direct photoabsorption experiment, specifically the $v = 7, 8, 14, 15, 16$, and 21 levels of $C^3\Pi_u$, $v = 0, 1$, and 4 levels of $G^3\Pi_u$, and $v = 0$ level of $F^3\Pi_u$. Assignment of the observed bands was made with the aid of wavenumbers and linewidths predicted using a coupled Schrödinger-equation model of electrostatically coupled $^3\Pi_u$ states, originally designed to reproduce a database of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ $^3\Pi_u$ levels. In turn, the new $^{14}\text{N}^{15}\text{N}$ data provide a convincing demonstration of the predictive power of the CSE model in terms of mass and energy interpolation. When combined with our previous experimental study of $^{14}\text{N}^{15}\text{N}$ singlet states, the present work provides a sound basis for a general refinement and extension of the CSE model of N_2 spectroscopy and predissociation.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for a line-by-line listing of all modeled transitions' frequencies, oscillator strengths, and linewidths fit to the experimental spectra. For the rotationally blended bands that are modeled with effective Hamiltonians lines, these are listed as far as $J'' \leq 15$. Also provided are excited-state

rotational level energies and widths deduced from the observed transitions.

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REFERENCES

- 1 J. Bishop, M. H. Stevens, and P. D. Feldman, *J. Geophys. Res.* **112**, A10312, <https://doi.org/10.1029/2007ja012389> (2007).
- 2 X. Liu, A. N. Heays, D. E. Shemansky, B. R. Lewis, and P. D. Feldman, *J. Geophys. Res.* **114**, D07304, <https://doi.org/10.1029/2008jd010403> (2009).
- 3 J. I. Lunine, Y. L. Yung, and R. Lorenz, *Planet. Space Sci.* **47**, 1291 (1999).
- 4 M. H. Stevens, *J. Geophys. Res.* **106**, 3685, <https://doi.org/10.1029/1999ja000329> (2001).
- 5 P. Lavvas, M. Galand, R. V. Yelle, A. N. Heays, B. R. Lewis, G. R. Lewis, and A. J. Coates, *Icarus* **213**, 233 (2011).
- 6 X. Li, A. N. Heays, R. Visser, W. Ubachs, B. R. Lewis, S. T. Gibson, and E. F. van Dishoeck, *Astron. Astrophys.* **555**, A14 (2013).
- 7 X. Li, T. J. Millar, C. Walsh, A. N. Heays, and E. F. van Dishoeck, *Astron. Astrophys.* **568**, A111 (2014).
- 8 A. N. Heays, R. Visser, R. Gredel, W. Ubachs, B. R. Lewis, S. T. Gibson, and E. F. van Dishoeck, *Astron. Astrophys.* **562**, A61 (2014).
- 9 H. Lefebvre-Brion, *Can. J. Phys.* **47**, 541 (1969).
- 10 K. Dressler, *Can. J. Phys.* **47**, 547 (1969).
- 11 P. K. Carroll and C. P. Collins, *Can. J. Phys.* **47**, 563 (1969).
- 12 S. A. Edwards, W.-Ü. L. Tchang-Brillet, J.-Y. Roncin, F. Launay, and F. Rostas, *Planet. Space Sci.* **43**, 67 (1995).
- 13 M. O. Vieitez, T. I. Ivanov, J. P. Sprengers, C. A. de Lange, W. Ubachs, B. R. Lewis, and G. Stark, *Mol. Phys.* **105**, 1543 (2007).
- 14 W. Ubachs, L. Tashiro, and R. N. Zare, *Chem. Phys.* **130**, 1 (1989).
- 15 P. F. Levelt and W. Ubachs, *Chem. Phys.* **163**, 263 (1992).
- 16 W. Ubachs, I. Velchev, and A. de Lange, *J. Chem. Phys.* **112**, 5711 (2000).
- 17 M. Sommariva and F. Merkt, *J. Electron Spectrosc. Relat. Phenom.* **151**, 31 (2006).
- 18 W. Ubachs, R. Lang, I. Velchev, W.-Ü. L. Tchang-Brillet, A. Johansson, Z. S. Li, V. Lohnygin, and C.-G. Wahlström, *Chem. Phys.* **270**, 215 (2001).
- 19 J. P. Sprengers, A. Johansson, A. L'Huillier, C.-G. Wahlström, B. R. Lewis, and W. Ubachs, *Chem. Phys. Lett.* **389**, 348 (2004).
- 20 J. M. Ajello, G. K. James, B. O. Franklin, and D. E. Shemansky, *Phys. Rev. A* **40**, 3524 (1989).
- 21 M. A. Khakoo, C. P. Malone, P. V. Johnson, B. R. Lewis, R. Laher, S. Wang, V. Swaminathan, D. Nuyujukian, and I. Kanik, *Phys. Rev. A* **77**, 012704 (2008).
- 22 K. P. Huber and C. Jungen, *J. Chem. Phys.* **92**, 850 (1990).
- 23 G. Stark, P. L. Smith, K. P. Huber, K. Yoshino, M. Stevens, and K. Ito, *J. Chem. Phys.* **97**, 4809 (1992).
- 24 G. Stark, K. P. Huber, K. Yoshino, M. C. Chan, T. Matsui, P. L. Smith, and K. Ito, *Astrophys. J.* **531**, 321 (2000).
- 25 G. Stark, K. P. Huber, K. Yoshino, P. L. Smith, and K. Ito, *J. Chem. Phys.* **123**, 214303 (2005).
- 26 C. Y. R. Wu, D. L. Judge, M.-H. Tsai, Y.-C. Lin, T.-S. Yih, J.-I. Lo, H.-S. Fung, Y.-Y. Lee, B. R. Lewis, A. N. Heays, and S. T. Gibson, *J. Chem. Phys.* **136**, 044301 (2012).
- 27 H. Helm, I. Hazell, and N. Bjerre, *Phys. Rev. A* **48**, 2762 (1993).

- ²⁸A. B. van der Kamp, P. C. Cosby, and W. J. van der Zande, *Chem. Phys.* **184**, 319 (1994).
- ²⁹Y. Song, H. Gao, Y. C. Chang, D. Hammouténe, H. Ndome, M. Hochlaf, W. M. Jackson, and C. Y. Ng, *Astrophys. J.* **819**, 23 (2016).
- ³⁰H. Kanamori, S. Takashima, and K. Sakurai, *J. Chem. Phys.* **95**, 80 (1991).
- ³¹T. Hashimoto and H. Kanamori, *J. Mol. Spectrosc.* **235**, 104 (2006).
- ³²S. T. Gibson and B. R. Lewis, *J. Electron Spectrosc. Relat. Phenom.* **80**, 9 (1996).
- ³³V. E. Haverd, B. R. Lewis, S. T. Gibson, and G. Stark, *J. Chem. Phys.* **123**, 214304 (2005).
- ³⁴B. R. Lewis, A. N. Heays, S. T. Gibson, H. Lefebvre-Brion, and R. Lefebvre, *J. Chem. Phys.* **129**, 164306 (2008).
- ³⁵H. Ndome, M. Hochlaf, B. R. Lewis, A. N. Heays, S. T. Gibson, and H. Lefebvre-Brion, *J. Chem. Phys.* **129**, 164307 (2008).
- ³⁶A. N. Heays, Ph.D. thesis, The Australian National University, Canberra, Australia, 2011.
- ³⁷B. R. Lewis, S. T. Gibson, J. P. Sprengers, W. Ubachs, A. Johansson, and C.-G. Wahlström, *J. Chem. Phys.* **123**, 236101 (2005).
- ³⁸B. R. Lewis, K. G. H. Baldwin, J. P. Sprengers, W. Ubachs, G. Stark, and K. Yoshino, *J. Chem. Phys.* **129**, 164305 (2008).
- ³⁹B. R. Lewis, K. G. H. Baldwin, A. N. Heays, S. T. Gibson, J. P. Sprengers, W. Ubachs, and M. Fujitake, *J. Chem. Phys.* **129**, 204303 (2008).
- ⁴⁰A. N. Heays, J. M. Ajello, A. Aguilar, B. R. Lewis, and S. T. Gibson, *Astrophys. J., Suppl. Ser.* **211**, 28 (2014).
- ⁴¹J. P. Sprengers, W. Ubachs, K. G. H. Baldwin, B. R. Lewis, and W.-Ü. L. Tchang-Brillet, *J. Chem. Phys.* **119**, 3160 (2003).
- ⁴²J. P. Sprengers, E. Reinhold, W. Ubachs, K. G. H. Baldwin, and B. R. Lewis, *J. Chem. Phys.* **123**, 144315 (2005).
- ⁴³M. O. Vieitez, T. I. Ivanov, C. A. de Lange, W. Ubachs, A. N. Heays, B. R. Lewis, and G. Stark, *J. Chem. Phys.* **128**, 134313 (2008).
- ⁴⁴A. N. Heays, G. D. Dickenson, E. J. Salumbides, N. de Oliveira, M. Roudjane, D. Joyeux, L. Nahon, B. R. Lewis, and W. Ubachs, *J. Chem. Phys.* **135**, 244301 (2011).
- ⁴⁵In this paper, we have indicated the u/g inversion symmetry quantum label even though $^{14}\text{N}^{15}\text{N}$ is a heteronuclear species, due to the smallness of the perturbation attributable to this symmetry breaking relative to our experimental precision.
- ⁴⁶N. de Oliveira, M. Roudjane, D. Joyeux, D. Phalippou, J.-C. Rodier, and L. Nahon, *Nat. Photonics* **5**, 149 (2011).
- ⁴⁷N. de Oliveira, D. Joyeux, M. Roudjane, J.-F. Gil, B. Pilette, L. Archer, K. Ito, and L. Nahon, *J. Synchrotron Radiat.* **23**, 887 (2016).
- ⁴⁸I. Velchev, W. Hogervorst, and W. Ubachs, *J. Phys. B* **32**, L511 (1999).
- ⁴⁹D. Bailly, E. Salumbides, M. Vervloet, and W. Ubachs, *Mol. Phys.* **108**, 827 (2010).
- ⁵⁰J. Philip, J. Sprengers, T. Pielage, C. de Lange, W. Ubachs, and E. Reinhold, *Can. J. Chem.* **82**, 713 (2004).
- ⁵¹In this work, the spectroscopic notation is usually abbreviated where this is unambiguous, e.g., $C^3\Pi_u(v' = 7) \leftarrow X^1\Sigma_g^+(v'' = 0)$ to $C(7) \leftarrow X(0)$.
- ⁵²R. C. M. Learner, A. P. Thorne, and J. W. Brault, *Appl. Opt.* **35**, 2947 (1996).
- ⁵³J. W. Brault, *Mikrochim. Acta* **93**, 215 (1987).
- ⁵⁴D. C. Morton and L. Noreau, *Astrophys. J., Suppl. Ser.* **95**, 301 (1994).
- ⁵⁵Radiative lifetimes are too long to lead to measurable broadening.
- ⁵⁶In this work, we use the term “absorption spectrum” in its general sense, throughout. Strictly, the model fitting to the experimental data is performed in the transmittance space.
- ⁵⁷R. J. Le Roy, Y. Huang, and C. Jary, *J. Chem. Phys.* **125**, 164310 (2006).
- ⁵⁸J. M. Brown and A. J. Merer, *J. Mol. Spectrosc.* **74**, 488 (1979).
- ⁵⁹B. R. Lewis, S. T. Gibson, W. Zhang, H. Lefebvre-Brion, and J. M. Robbe, *J. Chem. Phys.* **122**, 144302 (2005).
- ⁶⁰H. Lefebvre-Brion and R. W. Field, *The Spectra and Dynamics of Diatomic Molecules* (Elsevier, Amsterdam, 2004).
- ⁶¹P. Cacciani, W. Hogervorst, and W. Ubachs, *J. Chem. Phys.* **102**, 8308 (1995).
- ⁶²F. H. Mies, *Mol. Phys.* **41**, 953 (1980).
- ⁶³L. Torop, D. G. McCoy, A. J. Blake, J. Wang, and T. Scholz, *J. Quant. Spectrosc. Radiat. Transfer* **38**, 9 (1987).
- ⁶⁴B. R. Johnson, *J. Chem. Phys.* **69**, 4678 (1978).