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ABSTRACT

We present a comprehensive revisited experimental high-resolution vacuum ultraviolet (VUV) photoabsorption spectrum of ammonia, NH₃, covering for the first time the full 5.4–10.8 eV energy-range, with absolute cross sections determined. The calculations on the vertical excitation energies and oscillator strengths were performed using the equation-of-motion coupled cluster method restricted to single and double excitation levels and used to help reanalyze the observed Rydberg structures in the photoabsorption spectrum. The VUV spectrum reveals several new features that are not previously reported in the literature, with particular reference to the vibrational progressions of the ($\tilde{D}^1E' \leftarrow \tilde{X}^1A_1'$), the ($\tilde{F}^1E' \leftarrow \tilde{X}^1A_1'$), and the ($\tilde{G}^1A_2'' \leftarrow \tilde{X}^1A_1'$) absorption bands. In addition, new Rydberg members have been identified in ($nda_1' \leftarrow 1a_2''$)($\tilde{D}''^1A_2'' \leftarrow \tilde{X}^1A_1'$), where $n > 3$ has not been reported before as well as in ($nde'' \leftarrow 1a_2''$)($\tilde{F}^1E' \leftarrow \tilde{X}^1A_1'$) and in ($nsa_1' \leftarrow 1a_2''$)($\tilde{G}^1A_2'' \leftarrow \tilde{X}^1A_1'$). The measured absolute photoabsorption cross sections have been used to calculate the photolysis lifetime of ammonia in the Earth's atmosphere (0–50 km).

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I. INTRODUCTION

Ammonia, NH₃, has attracted increasing attention of the international community as a relevant molecule in the interstellar medium and dense molecular clouds¹ in planetary atmospheres^{2,3} including the Earth for its role in local chemical reactions with other trace gases leading to fine particulate formation and eventually global climate change.⁴ Amongst many other areas, it is also of interest in the chemistry and kinetics of the surface nitridation process in the semiconductor plasma industry⁵ and synthesis of ammonia directly from air and water under ambient conditions.⁶

NH₃ and its isotopologues have been comprehensively explored by experimental and theoretical methods, the former investigating photoabsorption^{2,3,7–32} and photodissociation,^{8,10,15,33–38}

photon and multiphoton ionization,^{17,23,27,39–42} photoelectron spectroscopy,^{15,39,43–48} and electron energy loss and electron impact spectroscopies;^{47,49–55} the latter on the electronic-state spectroscopy of valence, Rydberg and lowest ionic states,^{56–65} and analytical representations of the ground state potential energy surfaces.^{66–68}

Experimental methods include ultraviolet absorption spectra in the regions 240–190 nm (5.17–6.53 eV),²¹ 230–85 nm (5.39–14.58 eV),¹⁸ 225–105 nm (5.51–11.81 eV),⁷ and 220–80 nm (5.64–15.49 eV),¹⁶ assignment of the lowest five electronic transitions with their related vibrational patterns and rotational analysis in the region 220–110 nm (5.64–11.27 eV),^{19,28} and cross section values in the 240–120 nm (5.17–10.33 eV),³¹ 235–185 nm (5.28–6.70 eV),³⁰ 225–210 nm (5.51–5.90 eV),² 225–175 nm (5.51–7.08 eV),³

220–140 nm (5.64–8.86 eV),²² 220–105 nm (5.64–11.81 eV),²⁷ 144–110 nm (8.61–11.27 eV),²⁶ and 122–106 nm (10.16–11.70 eV)¹⁷ regions. We note special attention to the lowest-lying absorption band ($\tilde{A}$ state) of ammonia with contributions exploring the vibronic structure and UV Raman scattering by Ziegler^{38,69} and the absorption spectra of NH_3 and ND_3 in cold molecular jets with vibrational band progressions up to 14 quanta of the umbrella bending (or out-of-plane bending) mode, ν_2 .²⁹ Additionally, Li and Vidal¹² performed fluorescence investigations of the vibronic bands of the $\tilde{B}^1E''$ state by detecting the fluorescence from the predissociation fragments. Assignment and characterization of the electronic states in the 5.7–9.3 eV energy range have been reported in multiphoton spectroscopy measurements by Nieman and Colson,^{41,42} together with rotational analyses of expansion-cooled ammonia.⁴⁰ The spectroscopy of ammonia Rydberg states converging to the first ionization energy has been reviewed by Ashfold and co-workers,²⁵ whereas Langford *et al.*¹⁴ identified ten new Rydberg origins with principal quantum numbers up to $n = 8$ in multiphoton ionization studies. Electron impact spectroscopy studies include the work of Harsbarger and co-workers in the $\tilde{A} \leftarrow \tilde{X}$ band,⁵⁵ and $\tilde{B} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ ⁵⁴ bands. Furlan *et al.*⁵³ explored singlet excited states in the 5.50–11.0 eV energy range also discussing the classification of the Rydberg series, while Burton *et al.*^{50,51} reported absolute dipole oscillator strengths for the $\tilde{A} \leftarrow \tilde{X}$ transition. The He(I) photoelectron spectrum of Edvardsson *et al.*¹⁵ relevant to this work obtained an adiabatic ionization energy for the $\tilde{X}^2A_1'$ state of 10.186 eV in good agreement with the Branton *et al.*^{44,45} value of 10.14 eV as well as from the zero kinetic energy photoelectron spectrum of Reiser *et al.*,⁴⁸ whereas the photoionization data of Loch and co-workers⁴³ report a value of 10.072 eV.

As far as theoretical methods are concerned, these include studies on the vibronic nature of the $\tilde{A} \leftarrow \tilde{X}$ electronic absorption and of the lowest energy photoelectron spectrum of ammonia,⁵⁶ vertical and adiabatic transition energies of the lowest ns , np , and nd members of Rydberg series,⁵⁷ Jahn-Teller distortions related to the ionization from the $1e$ orbital exhibiting a complex and diffuse vibronic structure,^{15,58} the Franck-Condon factors for the $\tilde{A} \leftarrow \tilde{X}$ transition allowed to obtain the symmetric stretching frequency, ν_1' , of the upper state to be $(2900 \pm 50) \text{ cm}^{-1}$ (0.359 eV)⁵⁹ and are in good agreement with the experimental values of Dobber *et al.*³⁹ and Miller *et al.*,⁴⁶ and vertical excitation energies of the electronic states by configuration interaction (CI) methods^{57,61,63} and the complete active-space self-consistent field (CASSCF) method.²² Vibrational band centers of NH_3 and its isotopologues have been calculated based on high level *ab initio* potential energy surfaces,⁶⁷ while a new analytical representation for the lowest adiabatic potential energy surface of ammonia allows reproduction of the vibrational spectrum with significantly higher accuracy.⁶⁶

In Sec. II, we present a brief summary of the structure of NH_3 , and in Sec. III, we present the computational details of the calculations used to help the interpretation of experimental data. In Sec. IV, a description of the experimental methodology is given. Section V includes a comprehensive description of the electronic-state spectroscopy of ammonia in the 5.4–10.8 eV photon energy region and compares the present data with other absolute photoabsorption cross sections. The data have been used to calculate the photolysis rates of NH_3 from 20 to 50 km altitude in the Earth's

atmosphere. We finish with Sec. VI by including a brief summary and conclusions.

II. BRIEF SUMMARY OF THE STRUCTURE AND PROPERTIES OF AMMONIA

In this section, we are particularly interested in giving a brief description of the NH_3 electronic structure relevant for the features observed in the photoabsorption spectrum, as well as to help assessing the role of the main molecular states involved in the excitation process. Ammonia in its electronic ground state is a non-planar molecule with a pyramidal conformation belonging to the C_{3v} symmetry, with its 10 electrons yielding an electronic configuration of $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2 : \tilde{X}^1A_1$. According to Furlan *et al.*,⁵³ the major contribution to the N–H bonding is from the pair of degenerate e orbitals resulting from the N atom $2p_{xy}$ combination with the H atom $1s$ orbitals. However, the electronic excited states of NH_3 have planar configurations¹⁹ belonging to the D_{3h} symmetry and the ground-state electronic configuration can alternatively be written as $(1a_1')^2(2a_1')^2(1e')^4(1a_2'')^2 : \tilde{X}^1A_1'$, where a_1 and e in C_{3v} correlate with a_1' , a_2'' and e' , e'' in D_{3h} , respectively. Electronic excitations discussed within the context of this work are solely due to promotion from the highest occupied molecular orbital (HOMO), nitrogen lone pair n_N ($2p_z$), $3a_1$ in C_{3v} , or $1a_2''$ in D_{3h} to Rydberg orbitals.^{11,25,26,28,63,70–73} These are optically allowed by selection rules if resulting from $\tilde{X}^1A_1'$ transitions to $^1A_2'$ and $^1E'$ states.⁷⁰ Relevant to the present study, the main fundamental vibrational energy (and wavenumber) of NH_3 in the ground state is 0.118 eV (950 cm^{-1}) for the umbrella mode, $\nu_2'(a_2'')$, where for the assignments of the vibronic structure, we will adopt the notation 2_m^n , with m and n the initial and final vibrational states.

The lowest ionization energy has been determined by different experimental techniques, although we still note a lack of agreement between the different vertical and adiabatic values.^{15,39,43–48} Nevertheless, the experimental adiabatic value which is needed to calculate the quantum defects associated with transitions to Rydberg orbitals results from the removal of an electron from the lone pair n_H and is here taken from Ref. 48 to be 10.186 eV $(1a_2'')^{-1}$.

The vibronic absorption bands (mainly for the umbrella mode) also show some contributions from the unresolved rotational structure (see Sec. V A) in ammonia's $\tilde{A} \leftarrow \tilde{X}$ transition. The vibrational-level dependent rotational energies F_v of a symmetric top molecule can be determined by the usual expression,⁷⁰

$$F_v(J, K) = B_v J(J+1) + (C_v - B_v)K^2, \quad (1)$$

where $B_v = \frac{\hbar}{4\pi c I_{xx}}$ and $C_v = \frac{\hbar}{4\pi c I_{zz}}$ are the rotational constants of the v th vibronic level, I_{zz} and I_{xx} ($=I_{yy}$) are the two different moments of inertia, and K is the component of the angular momentum about the principal rotational axis of the molecule. Thus, for each value of K , several transitions corresponding to different values of J can occur. Reiser *et al.*⁴⁸ observed that the photoelectron ionization of ammonia from the electronic ground state, $\tilde{X}(^1A_1')$, mainly involves $K = 0$ in both states, and $\Delta K = 0$, which means that the transition energy essentially reduces to that of a rigid

diatomic rotator, since the rotational constants are not very different in the neutral and ionic states.¹⁵ The rovibronic analysis of Ziegler's $\tilde{A} \leftarrow \tilde{X}$ transition⁶⁹ also shows that the rotational constants do not change appreciably from the neutral to the excited state (i.e., for $v'_2 \leq 3$), so the fine structure can be related to rotational branches which correspond, in a first approximation, to $\Delta J = -1, 0, +1$ and assigned to $P, Q,$ and R -branches, respectively. According to Ziegler,^{38,69} the two resolvable features (or branch heads) from the lowest vibronic bands, $v'_2 \leq 3$, are solely due to the R branch and overlapping P and Q branches. The comprehensive comparison of the room temperature and cold molecular jet NH_3 spectra revealed that the features observed in the latter occur around the Q -branch of the room temperature rotational envelope.²⁹ For a thorough discussion on state resolved rovibronic analysis, see Refs. 15, 38, and 69.

III. THEORETICAL METHODS

Ab initio calculations were carried out to obtain the geometry and excitation energies of the ammonia molecule (Table I) and the vertical ionization energies (IEs) (Table II), with the MOLPRO package.⁷⁴ Because MOLPRO cannot handle nonabelian symmetry groups, the calculations were performed using the smallest abelian subgroup of C_{3v} , i.e., C_s . The ground state geometry was optimized at the frozen coupled-cluster with single and double and perturbative triple excitations [CCSD(T)]⁷⁵ level using Dunning's aug-cc-pV6Z atomic basis sets.⁷⁶ However, in order to be able to visualize the orbitals using the Molden program,⁷⁷ h and i orbitals were removed from the basis set [aug-cc-pV6Z(g) basis set]. The electronic spectra were computed at the equation of motion coupled cluster method restricted to single and double excitation (EOM-CCSD) level⁷⁸ at the

TABLE I. Calculated vertical excitation energies [EOM-CCSD level with the aug-cc-pV6Z(g)+R basis set] and optical oscillator strengths (f_L) of NH_3 compared with experimental data and other works.

D_{3h}	C_{3v}	E (eV)	f_L	$\langle r^2 \rangle^a$	Assignment	E (eV) Expt.	E (eV) ^b	f_L^b
$\tilde{X}^1A'_1$	$\tilde{X}^1A_1$			16				
$1^1A''_2$	1^1A_1	6.672	0.0824	38	$3a_1 \rightarrow 3s(a_1)$	6.396	6.56	0.0775
$1^1E''$	1^1E	8.195	0.0052	61	$3a_1 \rightarrow 3p(e)$		7.89/8.01	0.0017
$1^1A'_1$	2^1A_1	8.640	<0.0001	83	$3a_1 \rightarrow 3p(a_1)$		8.46	0.0025
$2^1A''_2$	3^1A_1	9.187	0.0013	152	$3a_1 \rightarrow 4s(a_1)$		9.02	0.0074
$2^1E''$	2^1E	9.187	0.0145	96	$3a_1 \rightarrow 3d(e)$	8.682	9.07	0.0008
$1^1E'$	3^1E	9.405	0.0456	127	$3a_1 \rightarrow 3d(e)$	8.651	9.45/9.48	0.0621
$3^1A''_2$	4^1A_1	9.438	0.0368	140	$3a_1 \rightarrow 3d(a_1)$	8.682	8.87	0.0161
$3^1E''$	4^1E	9.663	0.0006	265	$3a_1 \rightarrow 4p(e)$		9.41/9.42	0.0033
$2^1A'_1$	5^1A_1	9.800	<0.0001	331	$3a_1 \rightarrow 4p(a_1)$		9.63	0.0077
$4^1E''$	5^1E	9.969	0.0064	367	$3a_1 \rightarrow 4d(e)$			
$4^1A''_2$	6^1A_1	9.994	<0.0001	516	$3a_1 \rightarrow 5s(a_1)$	9.394		
$2^1E'$	6^1E	10.081	0.0202	487	$3a_1 \rightarrow 4d(e)$	9.329		
$5^1A''_2$	7^1A_1	10.097	0.0173	522	$3a_1 \rightarrow 4d(a_1)$	9.329		
$5^1E''$	7^1E	10.200	0.0002	785	$3a_1 \rightarrow 5p(e)$			
$3^1A'_1$	8^1A_1	10.261	0.0001	931	$3a_1 \rightarrow 5p(a_1)$			
$6^1A''_2$	9^1A_1	10.353	<0.0001	1308	$3a_1 \rightarrow 6s(a_1)$			
$6^1E''$	8^1E	10.353	0.0044	822	$3a_1 \rightarrow 5d(e)$	9.643/9.680		
$7^1E''$	9^1E	10.443	0.0110	1135	$3a_1 \rightarrow 6p(e)$			
$7^1A''_2$	10^1A_1	10.453	0.0117	1091	$3a_1 \rightarrow 5d(a_1)$	9.65(3)		
$8^1E''$	10^1E	10.471	0.0056	1530	$3a_1 \rightarrow 7p(e)$			
$4^1A'_1$	11^1A_1	10.499	0.0030	1989	$3a_1 \rightarrow 6p(a_1)$			
$8^1A''_2$	12^1A_1	10.545	0.0015	2803	$3a_1 \rightarrow 7s(a_1)$	9.82(1)		
$9^1E''$	11^1E	10.602	<0.0001	3540	$3a_1 \rightarrow 8p(e)$			
$5^1A'_1$	13^1A_1	10.624	0.0001	3851	$3a_1 \rightarrow 7p(a_1)$			
$9^1A''_2$	14^1A_1	10.654	0.0003	5244	$3a_1 \rightarrow 8s(a_1)$			
$10^1E''$	12^1E	10.717	0.0014	3466	$3a_1 \rightarrow 9p(e)$			
$10^1A''_2$	15^1A_1	10.734	0.0001	6027	$3a_1 \rightarrow 9s(a_1)$			
$11^1A''_2$	16^1A_1	10.753	<0.0001	3640	$3a_1 \rightarrow 10s(a_1)$			
$3^1E'$	13^1E	10.782	0.0060	1194	$3a_1 \rightarrow 5d(e)$			
$11^1E''$	14^1E	10.930	0.0108	1471	$3a_1 \rightarrow 9p(e)$			

^aMean value of r^2 (electronic radial spatial extents).

^bFrom Ref. 57.

TABLE II. Calculated vertical ionization energies (CCSD(T) geometry, with the aug-cc-pV6Z(g) basis set) compared with experimental values for NH_3 (in eV).

	$^2A_1 (3a_1^{-1})$
Koopmans' theorem	11.704
ROHF	9.507
RMP2	11.060
UCCSD	10.867
UCCSD(T)	10.963
RCCSD	10.871
RCCSD(T)	10.967
Experiment	
Reference 15	10.93
Reference 45	10.87
Reference 43	10.896
Reference 88	10.911

obtained CCSD(T) geometry. For a better description of Rydberg excited states, a set of diffuse functions (8s, 8p, 6d), taken from Kaufmann *et al.*,⁷⁹ was added to the original basis set of the N atom [aug-cc-pV6Z(g)+R basis set]. The oscillator strengths of the electric dipole transitions were calculated using the length gauge. Finally, the lowest vertical ionization energies of NH_3 were also obtained at the restricted and unrestricted CCSD(T) levels,⁸⁰ while the adiabatic energy was obtained at the UCCSD(T)/aug-cc-pV6Z(g) level and after the harmonic zero point (vibrational) energy (ZPE) correction.

IV. EXPERIMENTAL METHODS

A high-resolution vacuum ultraviolet (VUV) photoabsorption spectrum of ammonia (Figs. 1–5 and Tables I and III–XIII for assignments) was recorded at the AU-UV beam line of the ASTRID2 synchrotron facility at Aarhus University, Denmark. The experimental setup used for the photoabsorption measurements has been

FIG. 1. High-resolution VUV photoabsorption spectrum of ammonia in the 5.4–10.8 eV photon energy range. See the text for details.

(a)

(b)

FIG. 2. VUV photoabsorption spectrum of ammonia in the: (a) 5.4–7.6 eV and (b) 5.4–6.0 eV photon energy ranges. See the text for details. **FIG. 3.** VUV photoabsorption spectrum of ammonia in the 7.3–8.9 eV photon energy range. See the text for details.

FIG. 4. VUV photoabsorption spectrum of ammonia in the 8.6–9.9 eV photon energy range. See the text for details.

described before,⁸¹ with some recent changes reported comprehensively in Ref. 82. Briefly, synchrotron radiation passes through a static gas sample and the transmitted light intensity is detected by using a photomultiplier tube (PMT). The incident wavelength is selected using a toroidal dispersion grating with 2000 lines/mm providing a resolution of 0.075 nm, corresponding to 3 meV at the midpoint of the energy range studied. For wavelengths below 210 nm (energies above 5.9 eV), the small gap between the PMT and the exit transmission window (MgF₂) of the gas cell is evacuated using a scroll pump to prevent any absorption by molecular oxygen in the air contributing to the spectrum. Measurements at higher wavelengths are carried out with this section at atmospheric pressure so that O₂ absorbs any higher order light produced by the monochromator. The ammonia sample absolute pressure in the absorption cell is measured by using a capacitance manometer (Chell CDG100D). In order to guarantee the absence of any

FIG. 5. VUV photoabsorption spectrum of ammonia in the 9.5–10.8 eV photon energy range. See the text for details.

saturation effects in the data recorded, the absorption cross sections were carefully measured over the pressure range 0.04–0.68 mbar, with typical attenuations of less than 50%. The synchrotron beam ring current was monitored throughout the collection of each spectrum and background scans were recorded with the cell evacuated. Absolute photoabsorption cross sections, σ , in units of Megabarn (1 Mb $\equiv 10^{-18}$ cm²) were obtained using the Beer-Lambert attenuation law, $I_t = I_0 e^{(-N\sigma l)}$, where I_t is the light intensity transmitted through the gas sample, I_0 is that through the evacuated cell, N is the molecular number density of the sample gas, and l is the absorption path length (15.5 cm). In order to accurately determine cross sections, the VUV spectrum was recorded in small (5 or 10 nm) sections, with at least 10 points overlapping the adjoining sections. The accuracy of the cross section is estimated to be better than $\pm 5\%$, and only when absorption by the sample is very weak ($I_0 \approx I_t$), does the error increase as a percentage of the measured cross section.

The gas sample used in the VUV photoabsorption measurements was purchased from Air Liquide, with a stated purity of $\geq 99.98\%$. The sample was used as delivered.

V. RESULTS AND DISCUSSION

The absolute high-resolution VUV photoabsorption cross section of ammonia is shown in Fig. 1 in the 5.4–10.8 eV photon energy range, with detailed sections of the measured cross section depicted in Figs. 2–5. The electronic excitation is extremely rich in fine structure with the umbrella mode (or out-of-plane bending mode), ν_2' , dominant for the entire energy range, and above 7.0 eV is due to the overlap of different electronic states. The absorption bands are classified as excitations from the ground to Rydberg (see Sec. V F) states of the types $(nsa_1' \leftarrow 1a_2'')(\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1')$, $(npe' \leftarrow 1a_2'')(\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1')$, $(npa_2'' \leftarrow 1a_2'')(\tilde{C}'^1A_1' \leftarrow \tilde{X}^1A_1')$, $(nde'' \leftarrow 1a_2'')(\tilde{D}^1E' \leftarrow \tilde{X}^1A_1')$, $(nda_1' \leftarrow 1a_2'')(\tilde{D}''^1A_2'' \leftarrow \tilde{X}^1A_1')$, $(nsa_1' \leftarrow 1a_2'')(\tilde{E}'^1A_2'' \leftarrow \tilde{X}^1A_1')$, $(nde'' \leftarrow 1a_2'')(\tilde{E}^1E' \leftarrow \tilde{X}^1A_1')$, $(nde'' \leftarrow 1a_2'')(\tilde{F}^1E' \leftarrow \tilde{X}^1A_1')$, and $(nsa_1' \leftarrow 1a_2'')(\tilde{G}^1A_2'' \leftarrow \tilde{X}^2A_1')$. Tables III–XIII show the energy values for the vibrational assignments in the different absorption bands of ammonia and these are compared whenever possible with previous data in the literature. In Fig. 6, we display the $\tilde{A}$ -, $\tilde{B}$ -, and $\tilde{D}$ -states' $\Delta\nu_2'$ as a function of the umbrella mode ν_2' quantum number to show the anharmonicity of this vibrational mode in the excited states of NH₃.

A. The $\tilde{A}$ -state of ammonia

The key features within this band have been studied by experimental methods,^{2,3,7,13,20–22,28–30,40,51,69} and also through different levels of theory.^{56,57,59,62,63} The photoabsorption spectrum in the 5.4–7.6 eV energy region is presented in Fig. 2(a), and the proposed assignments are summarized in Tables III and XIII. The lowest-lying excited state of ammonia with a maximum at 6.396 eV, with a local cross section value of 20 Mb, has been assigned to the $(3sa_1' \leftarrow 1a_2'')(\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1')$ transition and shows an extensive fine structure. The 0_0^0 origin band is at 5.719 eV with a 2_0^n ($n = 0$ –14) progression of the umbrella mode, ν_2' , with an average spacing of 0.116 eV (935.5 cm⁻¹) (Table III). The energy spacing

TABLE III. Proposed vibrational assignments in the ($\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1'$) absorption band of ammonia in the photon energy range 5.4–7.6 eV.^a Energies in eV.

Assignment	This work		EELS		Photoabsorption/multiphoton absorption				
	Energy	ΔE	Reference 53	Reference 2	Reference 3	Reference 18	Reference 22	Reference 28	Reference 29
2_3^0	...	...	...	...	...	...	...	5.426	...
?	5.48(5) (w, s, b)	...	...	...	...	...	...	...	...
?	5.51(1) (s)	...	...	...	...	...	...	...	...
2_2^0	5.522	...	...	5.523	5.565	...	...	5.522 ^b	...
*	5.534	...	...	...	...	...	...	...	...
?	5.59(3) (s)	...	...	...	...	...	...	...	...
2_1^0	5.603	...	...	5.605	5.623	...	...	5.607 ^b	...
*	5.616	...	...	...	...	...	...	...	...
2_1^1	5.707	...	...	...	5.718	...	...	5.708 ^b	...
0_0^0	5.719	...	5.728	5.721	5.720	5.719	5.721	5.726	5.732
*	5.734	...	...	...	5.732	...	...	5.732	...
2_1^2	5.817	...	...	...	...	...	...	5.825 ^b	...
2_0^1	5.828	0.109	5.838	...	5.829	5.829	5.829	5.835	5.835
*	5.840	...	...	...	...	...	...	5.840	...
2_1^3	5.924	...	...	...	...	...	...	...	...
2_0^2	5.940	0.112	5.948	...	5.940	5.941	5.942	5.945	5.948
*	5.951	...	...	...	5.950	...	...	5.950	...
2_0^3	6.053	0.113	6.060	...	6.053	6.052	6.054	6.056	6.060
2_0^4	6.167	0.114	6.173	...	6.169	6.164	6.169	6.167	6.173
2_0^5	6.283	0.116	6.287	...	6.281	6.282	6.284	6.282	6.291
2_0^6	6.396	0.113	6.402	...	6.395	6.393	6.398	6.392	6.405
2_0^7	6.510	0.114	6.517	...	6.509	6.510	6.512	6.510	6.515
2_0^8	6.627	0.117	6.634	...	6.626	6.627	6.629	6.625	6.633
2_0^9	6.744	0.117	6.751	...	6.743	6.747	6.746	6.744	6.752
2_0^{10}	6.859	0.115	6.869	...	6.861	6.862	6.864	6.860	6.867
2_0^{11}	6.980	0.121	6.989	...	6.980	6.980	6.982	6.981	6.986
2_0^{12}	7.099	0.119	7.106	...	7.102	7.102	7.102	7.098	7.105
2_0^{13}	7.219	0.120	7.224	...	7.224	7.224	7.223	7.213	7.227
2_0^{14}	7.34(3) (b)	0.124	7.347	...	...	7.342	7.345	7.340	7.354

^a(w) weak feature. (s) shoulder structure. (b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features); * see the text for details; ? unassigned feature.

^bReference 21.

$\Delta\nu_2'$ as a function of the ν_2' quantum number (see Fig. 6) varies from 0.109 up to 0.124 eV, which is certainly not related to the feature's positions given by an average experimental resolution of ~ 2.5 meV, therefore indicating a considerable anharmonic nature of the potential energy surface. Such behavior was also reported by Vaida *et al.*²⁹ in their cold molecular jet experiments. Another interesting aspect of this absorption band pertains to the possible role of another progression involving the totally symmetric N–H stretching mode, ν_1' , contributing to the underlying cross section signal as proposed by Duncan,¹⁸ Avouris *et al.*,⁵⁶ and Ziegler,³⁸ the latter suggesting that ν_1' could only be slightly bound due to the dissociative character along the N–H coordinate. Cheng and co-workers²² also considered such ν_1' contribution based on their complete active-space self-consistent field (CASSCF) calculations, but they were less confident on such an assumption based on the much smaller displacement from the ground to the excited

electronic state than that found for ν_2' . Robin pointed out that the ($n_N \rightarrow 3s$) character (see Sec. V F) in the electron impact energy loss data at different scattering angles ($0^\circ \leq \theta \leq 5^\circ$) and the constant Franck-Condon factors are reminiscent of a single vibronic transition.⁷¹ From the energy spacing between 0_0^0 and 2_0^3 that may correspond to one quantum of ν_1' (0.334 eV, 2693 cm^{-1}), we have carefully re-examined the energy spacing for other features in the band and did not find any vibrational patterns consistent with higher members of such a mode being excited. However, in order to further our investigations, we have also performed a comprehensive vibrational structure analysis by fitting the features with Lorentzian functions (not shown here), which show that the background enhancement is due to the superposition of longer tails of those $n\nu_2'$ quanta, lending support to a previous assessment in jet-cooled beam experiments of no symmetric stretching ν_1' progression in this energy region.^{29,69}

TABLE IV. Proposed vibrational assignments in the ($\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$) absorption band of ammonia in the photon energy range 7.3–8.9 eV.^a Energies in eV.

This work			EELS		Photoabsorption/multiphoton absorption						
Assignment	Energy	ΔE	Reference 53	Reference 7	Reference 12	Reference 18	Reference 22	Reference 23	Reference 28	Reference 39	Reference 40
0_0^0	7.34(3)(b)	...	...	7.344	...	...	...	...	...	...	7.344 ^b
2_0^1	7.456	0.113	7.460	7.460	...	7.457	7.345	7.344	7.448	...	7.455 ^b
2_0^2	7.570	0.114	7.575	7.576	...	7.573	7.456	7.455	7.566	...	7.571 ^b
2_0^3	7.689	0.119	7.692	7.695	...	7.691	7.572	7.571	7.687	...	7.690 ^b
2_0^4	7.811	0.122	7.813	7.816	...	7.815	7.690	7.690	7.808	...	7.812 ^b
2_0^5	7.935	0.124	7.936	7.941	...	7.938	7.812	7.812	7.933	...	7.936 ^b
2_0^6	8.059	0.124	8.062	8.067	...	8.063	7.936	7.936	8.058	8.061–8.074	8.062
2_0^7	8.187	0.128	8.189	8.193	...	8.189	8.062	8.062	8.184	8.198	8.190
2_0^8	8.312	0.125	8.317	8.322	...	8.319	8.189	8.189	8.314	...	8.318 ^b
2_0^9	8.445	0.133	8.447	8.448	8.448	8.449	8.317	8.318	8.442	...	8.447
2_0^{10}	8.576	0.131	8.577	8.582	8.579	8.580	8.446	...	8.574	...	8.575
2_0^{11}	8.709	0.133	8.708	8.716	8.711	8.711	8.577	...	8.708	...	8.703
2_0^{12}	8.842	0.133	...	8.851	8.843	8.843	8.709	...	...	...	...

^a(b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features).^bReference 20.

Features below the origin band have been assigned to hot bands 2_1^n ($n = 0-3$) with an average energy spacing of 0.107 eV [see Fig. 2(b) and Table III]. Such an assignment is in good accord with Walsh and Warsop.²⁸ Moreover, the relative intensities (weights) of the 2_1^0 and 2_2^0 hot bands to 0_0^0 are found to be 14% and 1.9%, in good agreement with the Franck-Condon factors calculated by Harshbarger⁵⁹ and the experimental data of Ziegler.⁶⁹ The feature at 5.48(5) eV remains unassigned, but may be part of the 2_3^0 transition which is only visible in the data of Ref. 28. Features at 5.734, 5.840, and 5.951 eV (see

Table III) are assigned to *R*-branch members of 2_0^0 , 2_0^1 , and 2_2^2 , in good agreement with previous data,^{3,28} while new features at 5.534 and 5.616 eV are tentatively assigned to be *R*-branch members from 2_2^0 and 2_1^0 . A close inspection of Fig. 2(b) also shows shoulder structures to lower energies of the *Q* ($\Delta J = 0$), *P* ($\Delta J = -1$)-branches, i.e., 2_0^0 , 2_0^1 , and 2_2^2 . It is interesting to note that the energy splitting between the maximum values of the *Q*-, *P*-, and *R*-branches, $\Delta_{Q,P,R}$, for 2_0^0 , 2_0^1 , 2_0^2 , 2_0^3 , and 2_2^2 are 0.012, 0.013, 0.016, 0.011, and 0.011 eV. Features at 5.51(1) and 5.59(3) remain unassigned; however, they

TABLE V. Proposed vibrational assignments for progressions in the ($\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$) transition in the photon energy range 7.3–8.9 eV.^a Energies in eV.

This work								
Assignment	Energy	ΔE	Assignment	Energy	ΔE	Assignment	Energy	ΔE
2^n	7.44(5)(s,b)	...	...	...	...	...	...	...
2^{n+1}	7.56(4)(s)	0.119	2^n	7.67(2)(s,b)	...	...	...	...
2^{n+2}	7.68(2)(s,w)	0.118	2^{n+1}	7.79(7)(s,b)	0.125	2^n	7.906	...
2^{n+3}	7.80(4)(s,w)	0.122	2^{n+2}	7.91(7)(s,b)	0.120	2^{n+1}	8.030	0.124
2^{n+4}	7.92(6)(s,w)	0.122	2^{n+3}	8.04(2)(s,b)	0.125	2^{n+2}	8.146	0.116
2^{n+5}	8.04(9)(s)	0.123	2^{n+4}	8.16(1)(s,b)	0.119	2^{n+3}	8.265	0.119
2^{n+6}	8.17(2)(s)	0.123	2^{n+5}	8.28(3)(s)	0.122	2^{n+4}	8.386	0.121
2^{n+7}	8.303	0.131	2^{n+6}	8.40(3)(w)	0.120	2^{n+5}	8.50(8)(s,w)	0.122
2^{n+8}	8.43(4)(s)	0.131	...	...	...	...	...	...
2^{n+9}	8.56(5)(s)	0.131	...	...	...	...	...	...
2^{n+10}	8.69(7)(s)	0.132	...	...	...	...	...	...
2^{n+11}	8.82(3)(s)	0.126	...	...	...	...	...	...

^a(s) shoulder structure. (b) broad structure. (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features).

TABLE VI. Proposed vibrational assignments in the ($\tilde{C}'^1A'_1 \leftarrow \tilde{X}^1A'_1$) absorption band of ammonia in the photon energy range 7.7–8.9 eV.^a Energies in eV.

This work			EELS	Photoabsorption/multiphoton absorption					References 41 and 42
Assignment	Energy	ΔE	Reference 53	Reference 7	Reference 14	Reference 20	Reference 39	Reference 40	
(n – 2) ^b	...	...	...		...	...	...	7.688	...
(n – 1) ^b	7.78(1)(w, s)	...	...		...	...	...	7.795	...
0 ₀ ⁰	7.905	0.124	...	7.924	...	7.908	...	7.908	7.920
2 ₀ ¹	8.02(0)(b)	0.115	8.028	8.042	...	8.023	8.025	...	8.025
2 ₀ ²	8.137	0.117	8.137	8.153	...	8.141	8.134	...	8.136
2 ₀ ³	8.256	0.119	8.250	8.270	...	8.261	8.234	...	8.250
2 ₀ ⁴	8.381	0.125	8.369	8.392	8.367	8.383	...	...	8.368
2 ₀ ⁵	8.50(8)(s, w)	0.127	8.489	8.510	8.490	...	...	...	8.490
2 ₀ ⁶	...	...	8.611	8.629	8.613	...	...	...	8.613
2 ₀ ⁷	...	...	8.733	8.746	8.738	...	...	...	8.739
2 ₀ ⁸	...	...	...	8.870	...	...	...	...	8.867

^a(w) weak feature. (s) shoulder structure. (b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features).

^bReference 40.

may belong to the unresolved rotational contribution or even to a triplet state in the case of the former. Although such optically forbidden transition may not be discernible in the VUV spectrum, the very weak feature at 5.51(1) eV with a local cross section value of 6×10^{-3} Mb [Fig. 2(b)] may also be related to Furlan *et al.*'s (0–0) transition at 5.480 eV accompanied by vibrational excitation of two ν'_2 quanta, although these authors do not discard the possibility of a quantum lower at 5.340 eV.⁸³ We also note that the comprehensive

data of Cvejanovic *et al.*⁸⁴ on the triplet states of ammonia excited by low-energy electrons reports vibrational progressions of ν'_2 in the lowest triplet $\tilde{a}^3A'_2$ state, with a feature at 5.49 eV. Moreover, these authors suggest the vertical and the adiabatic values at 5.72 and 5.14 eV. We have performed calculations on the first triplet state of NH₃ at the CCSD(T) and UCCSD(T) levels with the aug-cc-pV6Z(g) basis set, where the geometry remains D_{3h} with the NH bond length of 1.0617 Å (the calculated ground state distance at the same level

TABLE VII. Proposed vibrational assignments in the ($\tilde{D}^1E' \leftarrow \tilde{X}^1A'_1$) absorption band of ammonia in the photon energy range 8.6–10.5 eV.^a Energies in eV.

This work			EELS		Photoabsorption/multiphoton absorption			
Assignment	Energy	ΔE	Reference 53	Reference 7	Reference 11	Reference 18	Reference 26	Reference 40
0 ₀ ⁰	8.651	...	8.650	8.655	8.657	8.651	8.651	8.682
2 ₀ ¹	8.760	0.109	8.762	8.766	...	8.763	8.759	8.793
2 ₀ ²	8.875	0.115	8.874	8.881	8.827	8.878	8.874	8.907
2 ₀ ³	8.992	0.117	8.994	8.999	...	8.997	8.992	9.023
2 ₀ ⁴	9.113	0.121	9.115	9.120	9.007	9.119	9.114	9.143
2 ₀ ⁵	9.237	0.124	9.239	9.241	...	9.242	9.239	9.266
2 ₀ ⁶	9.363	0.126	9.365	9.369	...	9.370	9.364	9.392
2 ₀ ⁷	9.492	0.129	9.493	9.498	...	9.496	9.492	9.521
2 ₀ ⁸	9.622	0.130	9.625	9.626	...	9.626	9.621	...
2 ₀ ⁹	9.753	0.131	9.759	9.754	...	9.755	9.752	...
2 ₀ ¹⁰	9.889	0.136	9.888	9.889	...	9.891	9.884	...
2 ₀ ¹¹	10.018	0.129	10.018	10.021	...	10.023	10.018	...
2 ₀ ¹²	10.15(3)(w, b)	0.135	10.150	10.156	...	10.154	10.151	...
2 ₀ ¹³	10.29(1)(s)	0.138	...	...	...	...	...	...
2 ₀ ¹⁴	10.42(4)(w, b)	0.133	...	...	...	...	...	...

^a(w) weak feature. (b) broad structure. (s) shoulder structure (the last decimal of the energy value is given in brackets for these less-resolved features).

TABLE VIII. Proposed vibrational assignments in the ($\tilde{D}''^1A_2'' \leftarrow \tilde{X}^1A_1'$) absorption band of ammonia in the photon energy range 8.6–10.5 eV.^a Energies in eV.

This work			EELS	Photoabsorption/Multiphoton absorption			
Assignment	Energy	ΔE	Reference 53	Reference 7	Reference 18	Reference 26	Reference 40
0_0^0	8.682	...	...	8.677	8.682	8.687	8.688
2_0^1	8.792	0.110	8.802	8.794	8.803	8.798	8.798
2_0^2	8.907	0.115	8.913	8.901	8.916	8.917	8.913
2_0^3	9.024	0.117	9.034	9.023	9.034	9.036	9.035
2_0^4	9.145	0.121	9.155	9.138	9.158	9.157	9.157
2_0^5	9.268	0.123	9.277	9.261	9.281	9.279	9.280
2_0^6	9.394	0.126	9.400	9.386	9.401	9.403	9.407
2_0^7	9.52(3)(s)	0.129	9.527	9.521	9.531	9.530	9.537
2_0^8	9.65(3)(w, s)	0.130	9.652	9.662	9.659	...	...
2_0^9	9.78(7)(w, s)	0.134	...	...	9.787	...	...
2_0^{10}	...	...	...	...	9.931	...	...
2_0^{11}	...	...	...	...	10.058	...	...
2_0^{12}	...	...	...	...	10.186	...	...

^a(s) shoulder structure. (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features).

being 1.0122 Å). The UCCSD(T) vertical energy was obtained at 6.365 eV (the EOM-CCSD value for the singlet state is at 6.672 eV; see Table I) and after harmonic ZPE correction yields an adiabatic energy value of 5.275 eV which corresponds to the 3s excitation.

B. The $\tilde{B}$ - and $\tilde{C}'$ -states of ammonia

The second absorption band of ammonia (Fig. 3), which has the lowest overall intensity in the VUV spectrum (Fig. 1), is comprised of at least two optically forbidden transitions

that have been assigned to $(npe' \leftarrow 1a_2'')(\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1')$ and $(npa_2'' \leftarrow 1a_2'')(\tilde{C}'^1A_1' \leftarrow \tilde{X}^1A_1')$, the former allowed by magnetic dipole selection rules and the latter by electric quadrupole selection rules.⁵³ Although the characters of the two bands result in low intensity features when compared with optically allowed transitions (0.5 for $\tilde{B}$ and 0.04 for $\tilde{C}'$ relative to the most intense $\tilde{A}$ feature), the nature of $(\tilde{C}'^1A_1' \leftarrow \tilde{X}^1A_1')$ results in a considerably lower yield when compared to the $(\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1')$ transition (~0.08 of the most intense transition of $\tilde{B}$). Moreover, the $(\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1')$ transition borrows intensity through a close-lying allowed transition via

TABLE IX. Proposed vibrational assignments for progressions in the ($\tilde{D}^1E' \leftarrow \tilde{X}^1A_1'$) transition in the photon energy range 8.6–9.8 eV.^a Energies in eV. These features have not been plotted to avoid congestion. See the text for details.

This work			Reference 18	This work			Reference 18
Assignment	Energy	ΔE	Energy	Assignment	Energy	ΔE	Energy
2^n	8.929	...	8.929	2^n	9.325	...	...
2^{n+1}	9.04(7)(s)	0.118	...	2^{n+1}	9.463	0.138	...
2^{n+2}	9.17(5)(w, b)	0.128	...	2^{n+2}	9.58(9)(w)	0.126	...
2^{n+3}	9.30(0)(w, b)	0.125	...	...	...	...	...
...	...	...	9.423	2^n	9.433	...	9.433
...	...	...	9.544	2^{n+1}	9.559	0.126	9.559
...	...	...	9.681	2^{n+2}	9.68(9)(s)	0.130	9.687
...	...	...	9.806	2^{n+3}	9.81(8)(s)	0.129	...
...	...	...	...	...	...	...	...
...	...	...	...	2^n	9.437	...	9.442
...	...	...	...	2^{n+1}	9.570	0.133	9.571
...	...	...	...	2^{n+2}	9.69(5)(s)	0.125	...

^a(s) shoulder structure. (w) weak feature. (b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features).

TABLE X. Proposed vibrational assignments in the ($\tilde{E}'^1A_2'' \leftarrow \tilde{X}^1A_1'$) and ($\tilde{E}^1E' \leftarrow \tilde{X}^1A_1'$) absorption bands of ammonia in the photon energy range 8.8–10.8 eV.^a Energies in eV.

This work			EELS		Photoabsorption/multiphoton absorption					
Assignment	Energy	ΔE	Reference 53	Reference 7	Reference 14	Reference 15	Reference 18	Reference 26	Reference 28	Reference 40
$\tilde{E}'$ state of NH_3										
0_0^0	8.80(7)(s)	...	...	9.150	9.051	...	...	...	...	9.040
2_0^1	8.91(8)(s)	0.111	...	9.272	9.161	...	...	...	...	9.155
2_0^2	9.03(7)(s)	0.119	...	9.397	9.275	...	...	...	...	9.277
2_0^3	9.15(2)(s)	0.115	...	9.526	9.393	...	...	...	...	...
2_0^4	9.28(0)(s)	0.128	...	9.658	9.515	...	...	...	...	...
2_0^5	9.39(8)(s)	0.118	...	9.794	9.639	...	...	...	...	...
2_0^6	9.523	0.125	...	9.934	9.764	...	...	...	...	...
2_0^7	9.643	0.120	...	10.077	9.899	...	...	...	...	...
2_0^8	9.766	0.123	...	10.224	10.028	...	...	...	...	...
2_0^9	...	...	...	10.374	...	...	...	...	...	...
2_0^{10}	...	...	...	10.528	...	...	...	...	...	...
$\tilde{E}$ state of NH_3										
0_0^0	9.329	...	...	9.334	...	...	...	9.326	9.326	9.326
2_0^1	9.434	0.105	9.446	9.438	...	...	...	9.442	9.440	9.440
2_0^2	9.542	0.108	9.552	9.551	...	...	...	9.559	9.556	9.557
2_0^3	9.680	0.138	9.678	9.684	...	...	...	9.678	9.678	9.678
2_0^4	9.803	0.123	9.804	9.806	...	...	...	9.802	9.800	9.800
2_0^5	9.928	0.125	9.928	9.928	...	...	...	9.928	9.925	9.925
2_0^6	10.056	0.128	10.055	10.060	...	10.051	...	10.054	10.053	...
2_0^7	10.186	0.130	10.186	10.188	...	10.180	...	10.183	10.180	...
2_0^8	10.317	0.131	10.320	10.315	...	10.311	10.322	10.313	...	...
2_0^9	10.452	0.135	10.450	10.445	...	10.443	10.450	10.448	...	...
2_0^{10}	10.580	0.128	10.581	10.575	...	10.573	10.574	10.575	...	...
2_0^{11}	10.705	0.125	10.714	10.704	...	10.696	...	...	...	...
2_0^{12}	...	...	10.845	10.835	...	10.823	...	...	...	...
2_0^{13}	...	...	10.974	...	...	10.955	...	...	...	...

^a(s) shoulder structure (the last decimal of the energy value is given in brackets for these less-resolved features).

a relevant vibronic coupling character, yielding a Jahn-Teller effect due to the doubly degenerate nature of the $^1E''$ states.^{19,40}

The band spectral assignments are given in Tables IV–VI, with progressions assigned to the umbrella ν_2' vibrational mode. The average excited state frequency of the ν_2' -mode in the $\tilde{B}$ state appears to increase from 0.116 eV in the $\tilde{A}$ state to 0.125 eV in this band (see Fig. 6) as a result of the 2_0^n ($n = 0$ –12) progression, whereas in the case of the $\tilde{C}'$ state, we obtain an average value of 0.121 eV. This enhancement is reminiscent of the anharmonic character of the potential energy surface. As in the case of the $\tilde{A}$ state, Douglas and Hollas¹⁹ performed a comprehensive analysis of the rotational fine structure of the $\tilde{B}$ state and concluded that this is due to the geometric planarity of the molecule. Additionally, these authors have located the 0_0^0 transition of the $\tilde{B}$ state at 7.343 eV, Furlan *et al.*⁵³ electron energy loss spectroscopy data at 7.460 eV, Walsh and Warsop²⁸ ultraviolet absorption data report its origin at 7.447 eV, while the configuration interaction (CI) calculation of Runau *et al.*⁶³

place it at 6.97 eV. Our assignment at 7.34(3) eV (see Table IV) is in accord with Douglas and Hollas¹⁹ and also Glowonia and co-workers⁴⁰ value at 7.344 eV obtained in multiphoton ionization of expansion-cooled ammonia experiments. Table V presents the proposed vibrational assignments for the $\tilde{B}$ state involving the ν_2' -mode, where at least three different progressions have been identified. However, due to the considerable congested fine structure, we tentatively place the first members $2''$ at 7.44(5), 7.67(2), and 7.906 eV. Another interesting aspect of the $\tilde{B}$ state concerns the enhancement of the background signal for $9 \leq n \leq 12$ which has been identified by Li and Vidal¹² as a homogeneous predissociation, i.e., coupling to one or more states of the same vibronic symmetry¹⁴ with no strong rotational dependence. For further details, refer to Refs. 12 and 14. Finally, Glowonia *et al.*⁴⁰ and Langford *et al.*¹⁴ commented on the extent of the Jahn-Teller distortion affecting the degenerate $\tilde{B}^1E''$ state. Vibronic interaction within ammonia plays a role in dictating the nature of the

TABLE XI. Proposed vibrational assignments in the ($\tilde{F}^1E' \leftarrow \tilde{X}^1A'_1$) and ($\tilde{G}^1A''_2 \leftarrow \tilde{X}^1A'_1$) absorption bands of ammonia in the photon energy range 9.5–10.8 eV.^a Energies in eV.

This work			EELS		Photoabsorption/multiphoton absorption				
Assignment	Energy	ΔE	Reference 53	Reference 7	Reference 14	Reference 15	Reference 18	Reference 26	Reference 28
$\tilde{F}$ state of NH_3									
0_0^0	9.643 ^b	...	9.759	9.647	9.508 ^c	...	9.786	9.636	9.640
2_0^1	9.760	0.117	9.888	9.754	9.622 ^c	...	...	9.753	9.763
2_0^2	9.890 ^d	0.130	10.018	9.878	9.737 ^c	...	10.022	9.869	9.889
2_0^3	10.018 ^d	0.128	10.150	9.978	9.855 ^c	9.988	10.152	9.990	10.016
2_0^4	10.15(3)(s) ^d	0.135	10.274	10.119	9.978 ^c	10.113	10.273	10.116	10.143
2_0^5	10.276	0.123	10.400	10.245	10.102 ^c	10.239	10.395	10.243	...
2_0^6	10.401	0.125	10.528	10.376	...	10.375	10.523	10.371	...
2_0^7	10.527	0.126	10.657	10.506	...	10.500	10.654	10.501	...
2_0^8	10.657	0.130	10.786	10.632	...	10.629	...	10.635	...
2_0^9	10.789	0.132	10.914	10.762	...	10.760	...	10.764	...
2_0^{10}	...	...	...	10.895	...	10.888	...	10.893	...
2_0^{11}	...	...	...	11.031	...	11.023	...	11.024	...
$\tilde{G}$ state of NH_3									
0_0^0	9.778	...	...	9.778	9.733 ^c	...	...	9.778	...
2_0^1	9.89(8)(s)	0.120	...	9.895	9.844 ^c	...	...	9.896	...
2_0^2	10.034	0.136	...	10.018	9.961 ^c	10.012	...	10.016	...
2_0^3	10.154	0.120	...	10.146	10.080 ^c	10.144	...	10.142	...
2_0^4	10.28(4)(s)	0.130	10.274	10.274	...	10.269	...	10.272	...
2_0^5	10.41(9)(s)	0.135	10.400	10.399	...	10.394	...	10.397	...
2_0^6	10.54(5)(w)	0.126	10.528	10.524	...	10.521	...	10.524	...
2_0^7	10.67(4)(s)	0.129	10.657	10.654	...	10.650	...	10.651	...
2_0^8	10.78(9)(w)	0.115	10.786	10.786	...	10.788	...	...	...
2_0^9	...	...	10.914	...	...	10.909	...	...	...

^a(s) shoulder structure. (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features).

^bOverlap with $\tilde{E}'$.

^c A'_1 component.

^dOverlap with $\tilde{D}$.

excited states, and according to Nieman and Colson,⁴² E'' and A''_2 states can be connected with e' vibrations. As such, doubly degenerate vibrations ν'_3 (degenerate stretching mode) and ν'_4 (degenerate deformation mode) may be built on a progression in ν'_2 . Weak shoulder features observed in the $\tilde{B}$ state that remain unassigned could be connected to this effect, although we are cautious enough not to attempt a definitive assignment.

We now turn our attention to the $\tilde{C}'$ band which is weakly excited by photon absorption⁵³ and has deserved comprehensive investigation from different experimental techniques.^{14,15,18,28,39–42,59} According to Glowonia *et al.*,⁴⁰ this band borrows intensity through vibronic mixing with close A''_2 symmetry states, viz., $\tilde{D}''$ (see Figs. 3 and 4). The weak vibrational structure involving excitation of the umbrella mode is presented in Table VI where only six terms have been identified. Generally speaking, the umbrella mode vibrational frequency increases with increasing quantum number, which is in agreement with Nieman and Colson's finding.⁴²

The 0_0^0 origin band is at 7.905 eV in good agreement with the data of Douglas²⁰ and Nieman and Colson,^{41,42} where

the latter reported for the first time well-resolved rotational structure. Harshbarger⁵⁹ reported an optical oscillator strength of the ($\tilde{C}'^1A'_1 \leftarrow \tilde{X}^1A'_1$) relative to the ($\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$) transition of about 30 times smaller which is in reasonable agreement with the present value of 25.

C. The $\tilde{D}$ -, $\tilde{D}''$ -, $\tilde{E}'$ -, and $\tilde{E}$ -states of ammonia

The photoabsorption spectrum containing the $\tilde{D}$ -, $\tilde{D}''$ -, $\tilde{E}'$ -, and $\tilde{E}$ -states of ammonia extends from 8.6 up to 10.8 eV and can be seen in Figs. 4 and 5, with the present spectral assignments being given in Tables VII–X and XIII. The bands have been assigned to ($\tilde{n}de'' \leftarrow 1a''_2$)($\tilde{D}^1E' \leftarrow \tilde{X}^1A'_1$), ($\tilde{n}da'_1 \leftarrow 1a''_2$)($\tilde{D}''^1A''_2 \leftarrow \tilde{X}^1A'_1$), ($\tilde{n}sa'_1 \leftarrow 1a''_2$)($\tilde{E}'^1A''_2 \leftarrow \tilde{X}^1A'_1$), and ($\tilde{n}de'' \leftarrow 1a''_2$)($\tilde{E}^1E' \leftarrow \tilde{X}^1A'_1$) transitions, respectively. Glowonia and co-workers⁴⁰ performed a comprehensive analysis of the jet-cooled multiphoton ionization spectrum comprising a total of seven $\tilde{D}$ - and $\tilde{E}$ -states together with their rotational band contours.

TABLE XII. Proposed vibrational assignments for progressions in the photon energy range 9.8–10.8 eV.^a Energies in eV. See the text for details.

This work			Reference 18	This work		
Assignment	Energy	ΔE	Energy	Assignment	Energy	ΔE
2^n	9.85(7)(w)	...	...	2^n	9.86(5)(s, b)	...
2^{n+1}	9.98(4)(s)	0.127	9.993	2^{n+1}	9.992	0.127
2^{n+2}	10.11(3)(s)	0.129	10.117	2^{n+2}	10.120	0.128
2^{n+3}	10.23(8)(s)	0.125	10.243	2^{n+3}	10.245	0.125
2^{n+4}	10.36(5)(s)	0.127	10.374	2^{n+4}	10.384	0.139
2^{n+5}	10.49(5)(w)	0.130	10.505	2^{n+5}	10.509	0.125
2^{n+6}	10.62(4)(s)	0.129	10.634	2^{n+6}	10.637	0.128
2^{n+7}	10.764	0.140	10.765	2^{n+7}	10.766	0.129
...	...	...	...	...	...	...
...	...	...	...	2^n	10.33(9)(s)	...
...	...	...	...	2^{n+1}	10.45(9)(w)	0.120
...	...	...	...	2^{n+2}	10.59(2)(s)	0.133
...	...	...	...	2^{n+3}	10.716	0.124

^a(w) weak feature. (s) shoulder structure. (b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features).

The 0_0^0 transitions of the $\tilde{D}$ -, $\tilde{D}''$ -, $\tilde{E}'$ - and $\tilde{E}$ -states are in good agreement with the data available in the literature (see references in Tables VII–X). The photon energy region where these states are discernible is also dominated by extended vibrational progressions involving the ν_2' -mode, where the average excitation energy is 0.126 eV. We have plotted in Fig. 6 the $\tilde{D}$ -state $\Delta\nu_2'$ as a function of the umbrella mode ν_2' quantum number where the energy spacing between adjacent quanta is identical to the $\tilde{B}$ -state. Here, again, we observe an anharmonic behavior of the potential energy surface of this vibrational mode.

The most intense features have been assigned to the transition from the ground electronic state to the $\tilde{D}$ -state for which we observe 14 vibrational levels (Table VII), and above 7 quanta of mode ν_2' , these are superimposed with other features belonging to other closely-lying electronic states, $\tilde{F}$ and $\tilde{G}$ (see Sec. V D). The band maximum is placed at 9.113 eV with a local cross section value of 53.21 Mb and assigned to 2_0^4 . In addition to the previous reported data on this absorption band, two new features are discernible at 10.29(1) and 10.42(4) eV and tentatively assigned to 2_0^{13} and 2_0^{14} . Additional progressions related to the $\tilde{D}$ -state are listed in Table IX, therefore contributing to the considerably congested absorption features in this energy region.

The $\tilde{D}''$ -state shows a progression of 9 quanta of the ν_2' -mode with the last two members barely visible (Table VIII). The average energy spacing is 0.120 eV, and it is interesting to note that the old data of Duncan¹⁸ report up to 12 quanta being excited. The maximum intensity at 9.268 eV is reached for 2_0^5 with a cross section of 14.81 Mb.

Above 8.8 eV, two other states have been identified, $\tilde{E}'$ and $\tilde{E}$, and their vibrational assignments are listed in Table X. For the first state, we could identify only a progression of the umbrella mode up to 8, while for the second state up to 11 eleven quanta, with

average excitation energies of 0.125 and 0.12 eV, respectively, were identified.

D. The $\tilde{F}$ - and $\tilde{G}$ -states of ammonia

Above 9.6 eV and below the first ionization energy (10.186 eV¹⁵), two transitions ($nde'' \leftarrow 1a_2''$)($\tilde{F}^1E' \leftarrow \tilde{X}^1A_1'$) and ($nsa_1' \leftarrow 1a_2''$)($\tilde{G}^1A_2'' \leftarrow \tilde{X}^1A_1'$) (Fig. 5) have been identified together with their 2_0^n progressions (Tables XI and XIII), where for the latter state the progressions are marked as dashed lines in Fig. 5. The average energy spacing of the ν_2' -mode is 0.126 eV in both states. Note that this energy region is also very rich in weak and/or shoulder structures that remain unassigned, although features at (i) 9.544, (ii) 9.658, (iii) 10.036, (iv) 10.147, and (v) 10.260 eV, with a difference of about 0.111–0.114 eV [except (ii) and (iii)], may belong to another 2_0^n progression. The lower-lying members of the $\tilde{F}$ -state overlap with $\tilde{E}'$ - and $\tilde{D}$ -states. Between 9.85 and 10.77 eV, we observe at least three progressions with their assignments summarized in Table XII, one of which in reasonable agreement with those reported by Duncan¹⁸ and Furlan *et al.*⁵³ Finally, Langford *et al.*¹⁴ investigated the spectroscopy of these states by presenting detailed measurements of the (2+1) resonance enhanced multiphoton ionization (REMPI) spectrum of NH₃ together with state rotational constants.

E. Ionization energies of ammonia

Table II presents the calculated vertical ionization energies (IEs) for ammonia at different levels of theory compared with the experimental values available in the literature, where the geometry was kept at D_{3h} symmetry with the NH bond length fixed at 1.0122 Å. A general overview of the tabulated values reveals that all

TABLE XIII. Energy value (eV), quantum defect (δ), and assignment of the Rydberg series converging to the ionic electronic ground state of ammonia, NH_3 .^a

This work			Reference 25	Reference 26	Reference 28
E_n	δ	Assignment			
$\text{IE}_1 = 10.186 \text{ eV}^{\text{b}} \left(1a_2''\right)^{-1}$					
$(nsa_1' \leftarrow 1a_1'')(\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1')$					
5.719/6.396	1.25/1.10	$3sa_1'$	5.726	...	5.719
8.682	0.99	$4sa_1'$	8.681	...	8.649
9.394	0.85	$5sa_1'$	9.296	...	9.325
9.65(3) (s)	0.95	$6sa_1'$	...	...	...
$(nde'' \leftarrow 1a_2'')(\tilde{D}^1E' \leftarrow \tilde{X}^1A_1')$					
8.651	0.02	$3de''$	...	8.649	...
9.329	0.02	$4de''$	...	9.325	...
9.680	−0.19	$5de''$	...	9.635	...
9.803	0.04	$6de''$	...	9.776	...
$(nda_1' \leftarrow 1a_2'')(\tilde{D}'^1A_2'' \leftarrow \tilde{X}^1A_1')$					
8.682	−0.01	$3da_1'$	...	8.681	...
9.329	0.02	$4da_1'$	...	...	...
9.65(3) (s)	−0.05	$5da_1'$	...	...	...
9.803	0.04	$6da_1'$	...	...	...
$(nde'' \leftarrow 1a_2'')(\tilde{F}^1E' \leftarrow \tilde{X}^1A_1')$					
9.643	−0.01	$5de''$	...	...	...
$(nsa_1' \leftarrow 1a_2'')(\tilde{G}^1A_2'' \leftarrow \tilde{X}^1A_1')$					
9.82(1) (s)	0.89	$7sa_1'$	...	...	...
9.91(2) (s)	0.95	$8sa_1'$	...	...	...

^a(s) shoulder structure (the last decimal of the energy value is given in brackets for these less-resolved features).
^bAdiabatic value from Ref. 15.

FIG. 6. Ammonia $\tilde{A}$, $\tilde{B}$, and $\tilde{D}$ states $\Delta v'_2$ as a function of the umbrella mode v'_2 quantum number together with standard error bars. The linear fittings are used as guiding lines only.

the theoretical methods agree reasonably well with each other with the exception of Koopmans' theorem,⁸⁵ the ROHF (Restricted open-shell Hartree-Fock),⁸⁶ and the RMP2 (restricted Møller-Plesset)⁸⁷ methods. Such discrepancy is not surprising in view of the improper electron correlation (and relaxation) treatment in Koopmans' theorem, as well as ROHF and RPM2 methods. In order to assign the ammonia lowest lying Rydberg members converging to the ionic electronic ground states only, we have used the experimental adiabatic IE value of 10.186 eV (Table XIII), which is in very good agreement with the calculated adiabatic value of 10.167 eV obtained at the UCCSD(T)/aug-cc-pV6Z(g) level and after the harmonic ZPE correction (corresponding to a planar geometry with a NH bond length of 1.0208 Å).

F. Rydberg transitions

Ammonia electronic excitation in the photon energy range studied in this work displays a prominent Rydberg character; a summary of the experimental energies, assignments, and quantum defects can be found in Tables I and XIII. The peak positions have been tested using the Rydberg formula:

$E_n = E_I - \frac{R}{(n-\delta)^2}$, where E_I is the ionization energy, n is the principal quantum number of the Rydberg orbital of energy E_n , R is the Rydberg constant (13.61 eV), and δ is the quantum defect resulting from the penetration of the Rydberg orbital into the core. The Rydberg structures of ammonia have been analyzed on several occasions,^{2,8,9,11,13,14,27–29,34,40–42,46,53,55,59,60,69,72,73,78,83,88–92} and we note a reasonable agreement among the different authors. However, a comprehensive reinvestigation of the Rydberg character of ammonia electronic excitations, such as that we report here, is hence desirable.

The lowest-lying Rydberg transition is assigned to $(nsa'_1 \leftarrow 1a''_2)$ ($\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$), with the first member $n = 3$ at 5.719 eV and a quantum defect $\delta = 1.25$ (Table XIII), in good agreement with 5.81 eV from the calculated adiabatic Rydberg transition of Chantranupong *et al.*⁵⁷ and 5.726 eV (46 181 cm^{−1}) from the experimental data of Ashfold and co-workers.²⁵ These authors have attributed this rather large value of the quantum defect to a mixed Rydberg/valence character of the electronic transition. Robin⁷¹ reported on the possibility that the lowest-lying optically allowed state ($\tilde{A}$) would lie on a valence continuum (i.e., NH₂ + H), which was further explored by Herzberg and Longuet-Higgins,⁹¹ having concluded that a small electronic overlap yields a weakly predissociated Rydberg state (see Sec. V F). Twelve vibrational components of the $(3sa'_1)(\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1)$ transition have been identified due to excitation of the ν'_2 umbrella mode. Transitions to $n = 4$ –6 members of the nsa'_1 series lie within the $\tilde{D}''$ state, whereas $n = 7, 8$ in the $\tilde{G}$ state.

The first members of the nd series are associated with peaks at 8.651 eV ($\delta = 0.02$) and 8.682 eV ($\delta = -0.01$), have been assigned to transitions $(nde'' \leftarrow 1a''_2)(\tilde{D}^1E' \leftarrow \tilde{X}^1A'_1)$ and $(nda'_1 \leftarrow 1a''_2)(\tilde{D}''^1A''_2 \leftarrow \tilde{X}^1A'_1)$, and are accompanied by 14 and 9 quanta of the ν'_2 -mode, respectively. Transitions to the $4de''\tilde{E}$, $4da'_1\tilde{E}$, and $5de''\tilde{F}$ states are allowed and appear in the absorption spectrum of Fig. 4. For higher members of the Rydberg series, we have not made any attempt to identify features due to their low intensity in the absorption spectrum.

Regarding the Rydberg series of forbidden transitions, a comprehensive discussion can be found in Leach *et al.*³⁴ and references therein. However, we report only on the $(3pe' \leftarrow 1a''_2)$ ($\tilde{B}^1E'' \leftarrow \tilde{X}^1A'_1$) and $(3pa'_2 \leftarrow 1a''_2)(\tilde{C}'^1E'' \leftarrow \tilde{X}^1A'_1)$ umbrella mode progressions in Fig. 3 (see Tables IV and VI, respectively).

G. Predissociative and dissociative characters of ammonia absorption bands

The role of predissociation and dissociation channels of excited electronic states has deserved the attention of different research groups in several occasions.^{8,10,12,28,33,34,36–39,69,92,93} Although we will not comprehensively investigate the direct role of those bond breaking channels here, extensive studies on the absorption spectrum of ammonia together with fluorescence spectroscopy have allowed the relevant contributions and related yields to be established.^{8,10,33–38} Thus, this section aims to link those investigations with the electronic state spectroscopy of the relevant absorption bands, lending support to those former studies.

The predissociation character of the $(\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1)$ band has been reported by Walsh and Warsop²⁸ and Ziegler,⁶⁹ where the

former authors attributed a relevant mechanism for 2_0^n ($n \geq 3$) due to the interaction with the lowest excited intravalency shell state, while the latter to the unity quantum yield NH₃ → NH₂ + H photodissociation from the ultraviolet absorption studies of Tannenbaum *et al.*⁹³ and Groth *et al.*⁹² The ammonia electronic excitation to $3sa'_1$ resembles the $(\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1)C_{2v} \leftrightarrow (\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1)D_{3h}$ transition in water at 7.4 eV. Yet, the absorption band in H₂O is highly predissociative,^{71,89,94} which is not the case for NH₃. It is relevant to note that Ziegler's rovibronic absorption analysis suggests no direct evidence of a low-lying repulsive valence state but rather a strong dependency of the photodissociation rates with the excited $1 \leq \nu'_2 \leq 3$ quantum numbers.³⁸

The dynamical predissociation behavior of the rotational levels associated with the $\tilde{B}(\nu'_2)$ and $\tilde{C}'(\nu'_2)$ Rydberg states has been explored for the first time by Dobber *et al.*³⁹ through (2+1) and (2+1') REMPI spectroscopy, where the H atom from the dissociation product was detected in a two-colour pump-probe nanosecond excitation experiment. Finally, Li and Vidal¹² found that the predissociation of the $\tilde{B}$ state is nearly independent of the rotational quantum numbers within one vibrational band (see Sec. V B).

The fluorescence studies of Okabe and Lenzi³⁶ report on the photodissociation processes NH₃ → NH₂($\tilde{A}^2A_1$) + H and NH₃ → NH($c^1\Pi$) + H₂ yielding electronic excited radicals, where the first reaction may correlate with $\tilde{B}^1E''$, $\tilde{D}''^1A''_2$, $\tilde{E}'^1A''_2$, and the electronic excited states above 9.64 eV and the continuum, while the second reaction with the continua above 7.75 eV. We note that the VUV spectrum (see Fig. 1) above 8.5 eV has an underlying contribution which shifts the absorption features upward.

Suto and Lee's³⁷ photodissociation cross sections and quantum yields of emission from photofragments of ammonia in the wavelength region 106–200 nm (6.2–11.7 eV) yield the channels NH₂($\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$), NH($c^1\Pi \rightarrow a^1\Delta, b^1\Sigma^+$), and NH($b^1\Sigma^+ \rightarrow X^3\Sigma^-$). From the fluorescence data, threshold energies have been found for the different photodissociation products. Additionally, these authors have shown that all vibronic levels of ammonia's $\tilde{B}$ and $\tilde{C}'$ states yield NH₂($\tilde{A}^2A_1$) emission. The complete active space self-consistent field (CASSCF) method of McCarthy and co-workers³⁵ calculated the potential landscape of the photodissociation process NH₃($\tilde{A}$) → NH₂($\tilde{X}^2B_1$) + H(2S) confirming the planar structure of the $\tilde{A}$ -state where the barrier (~ 3000 cm^{−1})¹⁰ for NH₂...H dissociation increases for bent structures. Another relevant aspect pertains to the predissociation of the $\tilde{A}$ -state with 2_0^n ($n \geq 2$) where an important anharmonic coupling between bending (or umbrella mode) and stretching modes may be present.¹⁰ This is due to both centrifugal and Coriolis forces, which are dependent on the $\tilde{A}$ -state rotational angular momentum, dictating the dissociation rate and influencing the excess energy being available.

Through state selective photodissociation dynamics of the two lowest umbrella vibrational states (0 and 1) of the $\tilde{A}$ -state, Biesner *et al.*³³ used H atom photofragment translational spectroscopy to show that the majority of the accompanying NH₂($\tilde{X}^2B_1$) fragments are formed vibrationally cold, but with high levels of rotational angular momentum. Resonance Raman scattering spectra probing the photodissociative levels of the ($\tilde{X} \rightarrow \tilde{A}$) Rydberg transitions of NH₃ and ND₃ have been reported by Ziegler,³⁸ showing that rates of

photodissociation have a strong dependence on the excited ν_2' -mode level quantum number.

Finally, we note a comprehensive fluorescence excitation (FEX) study in the spectral energy range 6–15 eV, evidencing novel analysis of the NH_2 ($\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$) spectra, new information on photodissociation processes leading to formation of NH_2 ($\tilde{A}^2A_1$) and of NH in different excited states, as well as relevant information on the heat of formation of the NH radical ($\Delta_f H_0(\text{NH}) = 3.70 \pm 0.01$ eV), and the thermochemical limits of the dissociation reactions of NH_3 . For further details, see Ref. 34 and references therein.

H. Absolute photoabsorption cross sections and atmospheric photolysis

Previous absolute VUV photoabsorption cross sections of ammonia are available in the wavelength ranges 240–120 nm (5.17–10.33 eV),³¹ 235–185 nm (5.28–6.70 eV),³⁰ 225–210 nm (5.51–5.90 eV),² 225–175 nm (5.51–7.08 eV),³ 220–140 nm (5.64–8.86 eV),²² 220–105 nm (5.64–11.81 eV),²⁷ 144–110 nm (8.61–11.27 eV),²⁶ and 122–106 nm (10.16–11.70 eV).¹⁷ From the data of Syage *et al.*,³¹ the vertical excitation of the $\tilde{A}$ -state yields 9.3 Mb compared to our cross section value of 20 Mb; Thompson *et al.*,³⁰ Watanabe,²⁷ and Dick and Ziko² report at 215 nm (5.767 eV) cross section values of 0.054 Mb and 0.06 Mb in good agreement with our value of 0.057 Mb. The cross section values of Chen *et al.*³ in the spectral region 225 nm (5.510 eV) to 208 nm (5.961 eV) vary from 0.001 to 10 Mb while the present VUV data vary from 0.012 to 1.37 Mb. Excellent agreement is found with the data of Cheng and co-workers²² for the cross section values of the $\tilde{A}$ - and $\tilde{B}$ -states. Regarding the data of Wu *et al.*,²⁶ the 0_0^0 value of the $\tilde{D}$ -state at 8.651 eV with a cross section of 5.53 Mb is in general good agreement with the present value of 5.07 Mb. As far as the data of Xia *et al.*¹⁷ at 115 nm (10.781 eV) are concerned, their local cross section is 20 Mb in good accord with 19.9 Mb from the data in Fig. 1.

High-resolution VUV absolute photoabsorption cross sections in combination with solar actinic flux measurements from the literature⁹⁵ can be used to determine the photolysis rates of ammonia in the Earth's atmosphere (0–50 km altitude). Since 2002, we have employed a simple methodology to calculate the photolysis lifetime which is the reciprocal of the photolysis rate at a given altitude.⁹⁰ The quantum yield for dissociation is assumed to be unity, where such an assumption seems reasonable given the fluorescence data of Suto and Lee.³⁷ Photolysis lifetimes of less than one sunlit day were calculated at altitudes above 30 km. This indicates that ammonia molecules are efficiently broken up by VUV absorption at these altitudes. At lower altitudes, the photolysis lifetimes increase to tens and hundreds of sunlit days. Reche *et al.*⁹⁶ report a comprehensive study of urban NH_3 levels produced by vehicle emissions as well as from biological sources, such as humans, sewage systems, and garbage containers, with an urgent need to control and reduce such emissions. Additionally, the recent work of Warner *et al.*⁹⁷ provides evidence that in the last 14 years, there has been a considerable increase in atmospheric ammonia concentrations due to farming and animal husbandry involving reactive nitrogen mainly from fertilizer use. According to these authors, the ammonia's main sink mechanism involves dry deposition and wet removal by precipitation, as well as conversion to particulate ammonium by reaction with

acids. These arise mainly from the oxidation of SO_2 and NO_x pollutants produced in fossil fuel combustion. Therefore, compared with these reactions, UV photolysis is not expected to play a significant role in the tropospheric removal of NH_3 molecules.

VI. CONCLUSIONS

We have presented a comprehensive revisited study of the VUV electronic spectroscopy of ammonia in the 5.4–10.8 eV, with the most reliable complete set of absolute photoabsorption cross sections in this region. The main absorption features are due to electronic excitations from the ground state to Rydberg states, with novel assignments in the photon energy covered in this work, which have not been previously reported in the literature. Theoretical calculations on the vertical excitation energies and oscillator strengths were performed using the equation-of-motion coupled cluster method restricted to the single and double excitation level. These have been used in the assignment of the Rydberg transitions. The analysis of the observed vibronic structure in the photoabsorption spectra is generally consistent with earlier data, although the higher resolution of the present experiments has enabled us to propose for the first time assignments of the ($\tilde{D}^1E' \leftarrow \tilde{X}^1A_1'$), the ($\tilde{F}^1E' \leftarrow \tilde{X}^1A_1'$), and the ($\tilde{G}^1A_2'' \leftarrow \tilde{X}^1A_1'$) absorption bands; these in the Rydberg excitations, i.e., where $n > 3$, have not been reported before in ($nda_1' \leftarrow 1a_2''$)($\tilde{D}''^1A_2'' \leftarrow \tilde{X}^1A_1'$), in ($nde'' \leftarrow 1a_2''$)($\tilde{F}^1E' \leftarrow \tilde{X}^1A_1'$), and in ($nsa_1' \leftarrow 1a_2''$)($\tilde{G}^1A_2'' \leftarrow \tilde{X}^1A_1'$). The umbrella mode, ν_2' , is the dominant excited vibrational mode, and the comprehensive analyses of the different absorption bands have revealed the considerable anharmonic nature of the potential energy surfaces. The possible role of another progression involving the totally symmetric N–H stretching mode, ν_1' , contributing to the underlying cross section signal was not observed in the present measurements. The photolysis lifetimes of ammonia have also been carefully derived for the Earth's troposphere and stratosphere and show that solar photolysis is expected to be a weak sink in the terrestrial atmosphere.

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