Photoabsorption cross sections of N H 3 , N H 2 D , N H D 2 , and N D 3 in the spectral range 110 – 144 nm

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Photoabsorption cross sections of NH_3, NH_2D, NHD_2, and ND_3 in the spectral range 110–144 nm

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Cross sections for photoabsorption of NH_3, NH_2D, NHD_2, and ND_3 near 298 K were measured in the spectral range of 110–144 nm using radiation from a synchrotron. Absorption cross sections and oscillator strengths of NH_3 agree satisfactorily with previous reports; those of ND_3 are improved over those in a previous report, whereas those of NH_2D and NHD_2 are new. The oscillator strengths of transitions to D, D', D'', F, and G states are nearly the same among all four isotopic variants, but those to D''' and E states vary substantially. Observed absorption bands are arranged into vibrational progressions in accord with known Rydberg transitions. All progressions show a common trend of vibrational intervals increasing with vibrational quantum numbers. The Rydberg orbitals for states $D(3de'')$, $D'(4sa_1')$, $D''(3da_1')$, $D'''(4pe')$, and $E(4de'')$ are readily assigned with quantum defects determined in these experiments, but assignments for $F(5de'')$ and $G(6de'')$ are uncertain. Absorption cross sections of dissociative continua underneath discrete structures are larger for NH_2D and NHD_2 than for NH_3 and ND_3, indicating that the rate of dissociation of ammonia might increase when its symmetry is broken. © *2007 American Institute of Physics.*
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I. INTRODUCTION

Ammonia (NH_3) has been observed in planetary atmospheres,[1,2] comets,[3] and interstellar media.[4] For application in modeling the photoinduced fractionation of isotopic variants in planetary atmospheres,[5,6] the absorption cross sections associated with transitions $A \leftarrow X$ and $B \leftarrow X$ of NH_3, NH_2D, NHD_2, and ND_3 were determined in the range of 140–220 nm.[7] We have extended, and report here, measurements to the shorter wavelength range of 110–144 nm.

The spectrum of NH_3 in the region of 110–144 nm shows complicated structure. Duncan[8] and Walsh and Warsop[9] assigned vibrational progressions for various electronic states, and Herzberg[10] labeled the associated electronically excited states as D, E, F, and G. The electronic excitation of these Rydberg transitions results in a structure altered from a pyramidal (C_{3v}) ground state to planar (D_{3h}) Rydberg states, causing the inversion (v_2) vibrational mode of the upper state to become active. The molecular symmetries and Rydberg notations of these electronic states are subject to some debate.[9,11–14] Leach *et al.*[15] summarized the current assignments; these authors recorded fluorescence excitation spectra between 82.6 and 206.6 nm (6–15 eV) by probing at

seven specific emission wavelengths of NH and NH_2 and assigned the observed features to various Rydberg states of NH_3. States D, E, and F are assigned to have symmetry $^1E'$ with excitation to $3de''$, $4de''$, and $5de''$ orbitals, respectively. Edvardsson *et al.*[14] and Watanabe and Sood[13] assigned the G state to be $^1A_2''(7sa_1')$, but Leach *et al.*[15] suggested that it be reassigned to $^1E'(6de'')$. More to these intense transitions, weak transitions to electronic states D' $^1A_2''(4sa_1')$ and D'' $^1A_2''(3da_1')$ were reported.[8,11,16,17] Several additional states, such as D''', E', E'', E''', F', F'', and G', have been observed with multiphoton excitations.[11,18,19]

Several authors have reported absorption cross sections of NH_3 in the range of 110–144 nm.[13,14,20–23] In contrast, only Edvardsson *et al.* reported absorption cross sections of ND_3 in the region of 108–125 nm,[14] and those of NH_2D and NHD_2 have not been reported previously.

Compared with NH_3, spectra of the three deuterium variants, especially NH_2D and NHD_2, are little studied. Duncan[24] photographed absorption spectra of NH_2D, NHD_2, and ND_3 in the range of 124.8–143.3 nm and arranged the observed bands into vibrational progressions of the D $^1E'(3de'')$ state. Li and Vidal[12] analyzed the rotational structure of the transition to the D state of ND_3. Edvardsson *et al.*[14] assigned observed bands in the region of 108–125 nm to vibrational progressions in states E, F, and G of ND_3. Grownia *et al.*[11] reported bands of states D''' and E; the latter was also investigated by Langford *et al.*[19] Locht

et al.[25] measured autoionization spectra of all four isotopic variants at wavelengths smaller than the ionization thresholds near 121.7 nm and found different spectral shapes and intensities; vibrational progressions were observed in transitions to states F and G of NH_2D, NHD_2, and ND_3.

We have measured absorption cross sections of NH_3, NH_2D, NHD_2, and ND_3 in the region of 110–144 nm with improved resolution and present here the spectral analysis and discussion of isotopic effects.

II. EXPERIMENTS

The experimental setup is described elsewhere.[5–7] Briefly, vacuum ultraviolet (VUV) light produced in the National Synchrotron Radiation Research Center (NSRRC) in Taiwan was dispersed with a high-flux 6 m monochromator. With a cylindrical grating having 600 grooves mm^{-1} and slits of width of 0.050 mm, a resolution of 0.02 nm was achieved. The wavelength was calibrated with absorption lines of Xe,[26] CO,[27,28] O_2,[29] and NO.[30–33] The accuracy of wavelength is limited by the scan step, 0.02 nm (~ 10 cm^{-1}) in this work.

The absorption cross section was measured with a double-beam apparatus with a LiF window placed at an angle of 45° to one beam to reflect partially the incident VUV beam for intensity monitoring. The transmitted beam passed through the sample cell. The VUV light of both beams was converted to visible light upon irradiation of a glass window coated with sodium salicylate and detected with a photomultiplier tube in a photon-counting mode. The absorption cross section σ was evaluated according to the equation $\ln(I_o/I) = n\sigma l + \alpha$, in which I_o and I are the intensities of reflected and transmitted light, respectively, n is the gas density, and $l = 89$ mm is the length of sample cell. The constant α was determined when the sample cell was evacuated under 10^{-7} Torr. At each wavelength, the σ value was obtained from a linear least-square fit of 4–11 measurements with sample gases at varied pressures. To avoid saturation effects, the maximum absorbance was limited to 1.5. To maintain a constant pressure of gas during data acquisition, a reservoir of volume of about 0.6 l was connected to the gas cell. The gas densities were derived from pressures measured with three capacitance manometers (MKS-Baratron) covering from 0.003 to 10 Torr. The temperature was monitored with a calibrated thermocouple.

NH_3 (99.99%, Matheson) and ND_3 (isotopic purity 99%, Cambridge Isotope Laboratories) were purified with a freeze-pump-thaw procedure at 77 K, followed by vacuum distillation from 206 to 77 K. NH_2D and NHD_2 were obtained from mixtures of NH_3 and ND_3. We measured the midinfrared absorption spectra of NH_3, ND_3, and two mixtures of initial concentration ratios $[NH_3]/[ND_3] = 2/1$ and 5/7 and found that the partition of isotopic variants conforms to a statistical distribution within experimental uncertainty. For the two mixtures, $[NH_3]:[NH_2D]:[NHD_2]:[ND_3]$ $= 0.2963:0.4444:0.2222:0.0370$ and $0.0723:0.3038:0.4253:0.1985$, respectively. This resulting statistical distribution is consistent with observations of Reid *et al.*,[34] and Akagi *et al.*,[35] who determined the compositions of equilibrated isotopic variants with NH_3 and ND_3 at varied
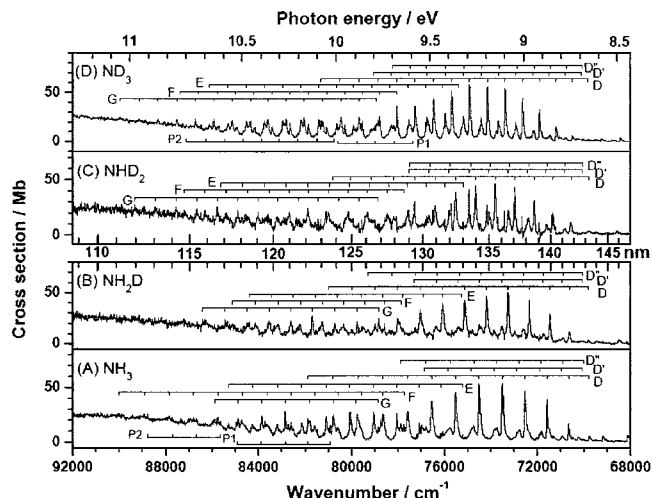

FIG. 1. Absorption cross sections (in units of Mb, 1 Mb=10^{-18} cm²) of NH_3 (A), NH_2D (B), NHD_2 (C), and ND_3 (D) in the spectral range of 68 000–92 000 cm^{-1} (108.7–147 nm and 8.43–11.4 eV). For convenience, the abscissas are plotted in three coordinates: cm^{-1}, nm, and eV.

initial concentrations. We found that the mixture near 295 K requires a few days to attain the final statistical distribution.

III. RESULTS AND DISCUSSION

A. Absorption cross sections

The absorption cross sections of NH_3, NH_2D, NHD_2, and ND_3 in the spectral range of 68 000–92 000 cm^{-1} (108.7–147 nm or 8.43–11.41 eV) are shown in Fig. 1. Considering all possible systematic errors, the experimental uncertainties are estimated to be within 10% of given values for NH_3 and ND_3 and 16% for NH_2D and NHD_2. The vibrational progressions (to be discussed later) are also assigned in these figures. Spectra of NH_3 and ND_3 exhibit similar patterns of features, whereas those of NH_2D and NHD_2 have disparate patterns, attributed to the breaking of molecular symmetry. For vibrational progressions, wavenumbers and cross sections of NH_3, NH_2D, NHD_2, and ND_3 are listed in Table I. Tabulated numerical values of cross sections at intervals of 0.02 nm are accessible at Ref. 49.

As shown in Fig. 1(A), NH_3 has a sharp structure in the range of 120–144 nm. The absorption cross section of peak depends on spectral resolution. Our values of these peaks are generally as much as twice those of Suto and Lee,[21] presumably because our resolution is about ten times theirs. Although the resolution of 0.02 nm used by Watanabe and Sood[13] is similar to ours, their absorption cross sections differ from ours in both absolute values and relative strength. For instance, our cross sections for lines $D(6)$, $D(5)$, and $D(4)$ at 75 517, 74 505, and 73 497 cm^{-1} (132.42, 134.22, and 136.06 nm) are 46.1, 52.9, and 53.6 Mb (Table I, 1 Mb=10^{-18} cm²), in contrast with their values of 49.5, 68.3, and 45.6 Mb, respectively.[13] According to our notation $D(v')$ specifies the upper electronic state D and its vibrational quantum number v'. This difference might be caused by light sources; our experiment used synchrotron from which radiation has a continuous and stable distribution, but the hydrogen discharge lamp used by Watanabe and Sood[9] emits dis-

TABLE I. Wavenumbers and cross sections σ (in Mb; 1 Mb$=10^{-18}$ cm^2) at vibrational progressions of NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$.

Vibronic states	NH$_3$ Position (cm^{-1})	σ (Mb)	NH$_2$D Position (cm^{-1})	σ (Mb)	NHD$_2$ Position (cm^{-1})	σ (Mb)	ND$_3$ Position (cm^{-1})	σ (Mb)
$D(v')$ state								
$D(0)$	69 764	5.53	69 793	4.13	69 764	4.01	69 832	1.87
$D(1)$	70 641	17.24	70 611	11.88	70 544	11.66	70 502	6.34
$D(2)$	71 561	38.80	71 459	28.95	71 332	20.09	71 185	15.45
$D(3)$	72 513	46.36	72 338	42.38	72 140	31.35	71 901	32.87
$D(4)$	73 497	53.64	73 249	50.39	72 950	42.70	72 632	43.92
$D(5)$	74 505	52.86	74 173	46.82	73 790	46.58	73 378	54.88
$D(6)$	75 517	46.09	75 109	42.98	74 644	44.72	74 129	55.74
$D(7)$	76 546	37.47	76 065	39.84	75 506	38.59	74 895	57.42
$D(8)$	77 585	28.40	77 032	33.25	76 382	27.30	75 677	51.10
$D(9)$	78 644[a]	25.51	78 015	24.21	77 268	30.46	76 464	43.58
$D(10)$	79 711	22.23	78 989	19.04	78 198	16.53	77 250	35.57
$D(11)$	80 793[a]	24.48	79 987	13.91	79 139	14.43	78 043[b]	36.91
$D(12)$	81 867[a]	21.79	80 972	12.15	80 055	15.43	78 845	22.21
$D(13)$							79 672[b]	24.73
$D(14)$							80 511	16.58
$D(15)$							81 294[a]	21.48
$D'(v')$ state								
$D'(0)$	70 057[a]	2.65	70 077[a]	3.00	70 077[a]	2.13	70 097[a]	2.08
$D'(1)$	70 949[a]	4.75	70 922	5.75	70 842[a]	5.18	70 785[a]	3.70
$D'(2)$	71 908	7.04	71 757	9.08	71 613	9.81	71 479	5.73
$D'(3)$	72 872	9.12	72 622	14.86	72 422	14.67	72 181	10.56
$D'(4)$	73 844	12.43	73 508	17.25	73 239	21.88	72 918	19.38
$D'(5)$	74 827	12.96	74 482	19.34	74 074	21.51	73 663	21.00
$D'(6)$	75 831	12.01	75 392	16.68	74 918	41.07	74 407	24.59
$D'(7)$	76 853[a]	11.42	76 336	17.09	75 792	22.44	75 173	25.30
$D'(8)$			77 304	12.99	76 664	18.12	75 951	28.45
$D'(9)$					77 543	22.53	76 732	24.54
$D'(10)$							77 519	22.31
$D'(11)$							78 299[a]	17.33
$D'(12)$							79 050[a]	14.04
$D''(v')$ state								
$D''(0)$	70 018	3.09	70 048	2.99	70 038[a]	2.64	70 067[a]	1.94
$D''(1)$	70 905	5.59	70 872	5.50	70 801[a]	6.06	70 741[a]	3.78
$D''(2)$	71 826	10.49	71 715	9.85	71 561	9.26	71 439	6.89
$D''(3)$	72 774	11.62	72 579	14.26	72 359	15.04	72 136	11.76
$D''(4)$	73 740	13.18	73 465[b]	14.72	73 185	16.18	72 857	13.22
$D''(5)$	74 725	15.23	74 404	16.03	74 022	16.01	73 605	16.21
$D''(6)$	75 754	13.79	75 347	16.51	74 847	11.27	74 368[a]	18.39
$D''(7)$	76 804	14.25	76 301[b]	14.86	75 731[c]	17.48	75 144[a]	18.87
$D''(8)$	77 882	16.95	77 244	15.69	76 617	14.51	75 922[a]	20.74
$D''(9)$			78 272[a]	12.91	77 483	12.73	76 750[a]	19.33
$D''(10)$			79 277[a]	13.75			77 476[a]	16.20
$D''(11)$							78 240[a]	14.45
$D'''(v')$ state								
$D'''(0)$	72 015	4.10	72 119	9.74	71 922	11.29	71 572	4.59
$D'''(1)$	72 960	4.64	72 975	11.82	72 653	16.44	72 265[b]	5.26
$D'''(2)$	73 931	5.96	73 850	13.05	73 400	22.30	72 994	7.32
$D'''(3)$	74 929	7.85	74 772	14.08	74 151	26.78	73 735	11.31
$D'''(4)$	75 942	9.04	75 666	13.25	74 918[b]	41.07	74 493[a]	13.00
$D'''(5)$	76 980[a]	15.70			75 700	28.61	75 223[b]	14.81
$D'''(6)$					76 488	22.91		
$D'''(7)$					77 274[b]	30.41		
$D'''(8)$					78 064	16.77		

TABLE I. (*Continued.*)

Vibronic states	NH$_3$ Position (cm^{-1})	σ (Mb)	NH$_2$D Position (cm^{-1})	σ (Mb)	NHD$_2$ Position (cm^{-1})	σ (Mb)	ND$_3$ Position (cm^{-1})	σ (Mb)
$E(v')$ state								
$E(0)$	75 211	7.03	75 247[a]	14.62	75 188	11.69	75 366[a]	4.68
$E(1)$	76 145	7.84	76 060[a]	39.76	75 976	14.63	76 081	7.33
$E(2)$	77 089	17.43	76 911[a]	18.28	76 758	16.99	76 781	19.10
$E(3)$	78 052	26.49	77 776	16.27	77 591	18.45	77 567	14.77
$E(4)$	79 049	27.86	78 669	14.25	78 400	17.85	78 358[b]	12.44
$E(5)$	80 063	27.59	79 628	12.65	79 216	14.81	79 114[b]	13.20
$E(6)$	81 082	23.38	80 599	13.29	80 064	15.45	79 911	16.88
$E(7)$	82 118	17.92	81 540	13.61	80 943[b]	18.34	80 632	18.32
$E(8)$	83 169	16.24	82 483	13.18	81 860	24.02	81 393	22.27
$E(9)$	84 260	16.38	83 425[c]	13.29	82 808	15.67	82 156	22.40
$E(10)$	85 284[a]	17.79	84 374[a]	20.73	83 710	15.79	82 946	21.38
$E(11)$					84 674	15.54	83 724	21.17
$E(12)$					85 631	17.13	84 517	21.17
$E(13)$							85 307	18.45
$E(14)$							86 118	17.60
$F(v')$ state								
$F(0)$	77 712[a]	10.38	77 852	15.00	77 724	12.00	78 045[c]	36.91
$F(1)$	78 656[a]	11.56	78 579	18.88	78 463[b]	19.57	78 777	25.80
$F(2)$	79 592	13.71	79 433	16.40	79 305[b]	21.11	79 529	20.75
$F(3)$	80 567	13.32	80 347	19.15	80 141	21.82	80 283	16.91
$F(4)$	81 583	14.86	81 248	21.57	80 985	21.06	81 050	13.80
$F(5)$	82 604	18.44	82 169	18.36	81 833[b]	20.93	81 846	17.82
$F(6)$	83 640	16.46	83 139	19.45	82 658	21.02	82 631	19.26
$F(7)$	84 688	18.02	84 133	20.75	83 528[b]	15.27	83 403	15.19
$F(8)$	85 763	22.71	85 121	20.00	84 463	17.26	84 175	14.18
$F(9)$	86 806	22.48			85 397	19.84	84 970	13.87
$F(10)$	87 843	23.89			86 296	22.86	85 748	16.57
$F(11)$	88 905[a]	25.56			87 199[b]	22.89	86 563	16.67
$F(12)$							87 260	18.90
$G(v')$ state								
$G(0)$	78 852[a]	14.10	78 827	24.32	78 864	10.09	78 927[a]	18.98
$G(1)$	79 806[a]	11.22	79 758	21.72	79 694	10.80	79 669[a]	24.73
$G(2)$	80 777[a]	24.48	80 704	20.27	80 528[a]	9.73	80 451	24.74
$G(3)$	81 793	20.16	81 668	27.78	81 433[a]	14.66	81 235	21.24
$G(4)$	82 837	28.13	82 590[b]	23.13	82 280[a]	14.67	82 023	23.97
$G(5)$	83 850	23.80	83 528[b]	22.26	83 125[a]	15.43	82 784	23.00
$G(6)$	84 875	21.66	84 474[b]	21.07	83 991	20.67	83 556	22.21
$G(7)$	85 896	20.99	85 441	23.66	84 875	22.65	84 331	20.61
$G(8)$			86 401	24.03	85 763	25.93	85 121	21.60
$G(9)$					86 655	23.83	85 911	23.71
$G(10)$					87 535	25.57	86 715	22.92
$G(11)$					88 449	25.90	87 520	22.69
$G(12)$					89 318[a]	27.74	88 324	22.56
$G(13)$							89 142[a]	23.01
$G(14)$							89 944[a]	25.16
P1 (unassigned)								
1	80 919	15.87					77 363	12.53
2	81 860	21.79					78 174	16.56
3	82 837[c]	28.13					78 989	16.60
4	83 892	17.52					79 758	14.60
5	84 927	18.89					80 567	14.76
P2 (unassigned)								
1	85 646	19.57					80 736	9.54
2	86 670	22.22					81 486	8.81

TABLE I.   (*Continued.*)

Vibronic states	NH$_3$		NH$_2$D		NHD$_2$		ND$_3$	
	Position (cm^{-1})	σ (Mb)	Position (cm^{-1})	σ (Mb)	Position (cm^{-1})	σ (Mb)	Position (cm^{-1})	σ (Mb)
3	87 719	22.66					82 291	8.31
4	88 763	25.39					83 084	8.32
5							83 850	9.26
6							84 660	11.08
7							85 441	12.64
8							86 252	14.30
9							87 108	17.03

[a]Wavenumbers of weak peaks are less accurate.
[b]Overlapped features could be deconvoluted.
[c]Overlapped peaks could not be deconvoluted.

crete lines. As at wavelengths smaller than 115 nm the absorption is dominated by a continuum, the cross section in this region is less affected by spectral resolution. In this range, our data are generally greater than those of Watanabe and Sood by 11%–15% (Ref. [13]) and those of Suto and Lee by 30%–40%.[21] Our data agree satisfactorily with those of Xia *et al.*[23] measured in the range of 110−122 nm at a resolution 0.8 nm, those of Samson *et al.*[22] at a few wavelengths near 110 nm, and those of Edvardsson *et al.*[14] in the range of 108−125 nm. Xia *et al.*[23] suggested that the previously reported smaller values[21] might be caused by scattered light in the monochromator and fluorescence from excited photofragments of NH$_3$.

Using synchrotron radiation, only Edvardsson *et al.*[14] measured absorption cross sections of ND$_3$ in the range of 108−125 nm. Their cross sections for peaks are generally smaller than our values because of their limited resolution of 0.08 nm. Their values near 110 nm in the absorption continuum agree satisfactorily with ours. In the range of 110−124 nm at a spectral resolution of 0.2 nm, Locht *et al.*[25] observed similar vibrational structures in the autoionization spectrum of ND$_3$ but reported no cross section.

The absorption cross sections of NH$_2$D and NHD$_2$ are unreported. The absorption spectra of NH$_2$D and NHD$_2$ shown in Figs. 1(B) and 1(C) differ significantly from those of NH$_3$ and ND$_3$. Locht *et al.*[25] observed similar vibrational

structures in autoionization spectra of NH$_2$D and NHD$_2$ with lower spectral resolution. The maximal absorption strengths of the transition $D \leftarrow X$ are similar for all four isotopic variants, except for that of ND$_3$ being ∼20% greater than that of NHD$_2$. In contrast, the maximal absorption strengths of transitions to the D' state of NH$_2$D, NHD$_2$, and ND$_3$ are 1.5, 3.1, and 2.1 times greater than that of NH$_3$.

B. Oscillator strengths

An integration of absorption cross section over a spectral range yields an oscillator strength (f-value), calculated with[36]

$$f = 1.13 \times 10^{-6} \int \sigma d\nu, \qquad (1)$$

in which σ is the absorption cross section in megabarns and ν is the wavenumber in cm^{-1}. As such a calculated oscillator strength is typically unaffected by spectral resolution, it serves as comparison among various experiments.

The f-values of NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$, calculated for the ranges of 110–118, 118–128, and 128−144 nm from our absorption spectra shown in Fig. 1, are listed in Table II with our previous results[7] for ranges of 144−165 and 165−218 nm. Additional results[37,38] with other integration ranges (112–122 and 122−144 nm) are included in Table II

TABLE II. Oscillator strengths of NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$.

Wavelengths range (nm)	NH$_3$	NH$_2$D	NHD$_2$	ND$_3$	Reference
110–118	0.1398	0.1441	0.1313	0.1261	This work
118–128	0.0850	0.0993	0.0857	0.0864	This work
128–144	0.0904	0.1081	0.0910	0.0964	This work
144–165	0.0123	0.0095	0.0112	0.0090	7
165–218	0.0800	0.0883	0.0811	0.0818	7
112–122	0.1352	0.1432	0.1277	0.1228	This work
	0.1359				37
	0.1460				38
122–144	0.1359	0.1632	0.1388	0.1445	This work
	0.1201				37
	0.1267				38

for comparison. For NH_3, our value of $f=0.1352$ for the range of 112–122 nm agrees with values of 0.1359 by Burton *et al.*[37] and 0.1460 by Zeiss *et al.*;[38] our value of 0.1359 for the range of 122–144 nm is 13% and 7% greater than values of 0.1201 and 0.1267 reported by these authors, respectively.

Chantranupong *et al.*[39] calculated the oscillator strengths of NH_3 for Rydberg transitions to states D, D', D'', and D''', which occur mainly in the wavelength range of 128–144 nm. The intense Rydberg transition $D(3de'')\leftarrow X$ of NH_3 has a theoretical oscillator strength of 0.0621,[39] which agrees with the value of 0.0582 determined from the sum of oscillator strengths for levels $v'=0-10$; because the levels with $v'>10$ are mixed with other states, their f-values are unavailable, but their contribution to the total oscillator strengths are expected to be less than 10% of the total. The calculated value[39] $f=0.0235$ for the combined Rydberg transitions to states $D'(4sa_1')$ and $D''(3da_1')$ of NH_3 agrees with our measured value of 0.0250 for the combined states D' and D'' measured for levels $v'=0-8$. Because the high-energy members of states D' and D'' are overlapped with transitions to other states, the experimental uncertainty of an f-value is expected to be ~15% of the given value. The total oscillator strength calculated for all transitions listed above by Chantranupong *et al.*[39] is 0.0974, in agreement with our experimental value of 0.0904 for NH_3 in the range of 128–144 nm listed in Table II.

For NH_3, NH_2D, NHD_2, and ND_3 measured in the spectral range of 110–144 nm, $f=0.3152$, 0.3515, 0.3080, and 0.3089, respectively. Although features of ND_3 have greater absorption maxima than those of NH_3, their f-values are similar because their widths are smaller. NH_2D has an f-value 12%–14% greater than for other variants, but the discrepancy might still lie within experimental uncertainties. As shown in Fig. 1, the onset of absorption continua beneath the discrete structures of NH_2D and NHD_2 occur at wavelengths much greater than those of NH_3 and ND_3, indicating that the dissociation of the former species might occur at smaller excitation energy.

C. Comparison of wavenumbers at absorption maxima

The wavenumbers at the absorption peaks of NH_3, NH_2D, NHD_2, and ND_3 and the corresponding cross sections are contained in Table I. The wavenumbers are arranged into vibrational progressions in accord with transitions from the ground electronic state to Rydberg states D, D', D'', D''', E, F, and G.[11,15] Transitions $D'\leftarrow X$ and $D''\leftarrow X$ are barely separated with our resolution, as shown in Fig. 1 and Table I. A detailed comparison among our and previous results appears in EPAPS.[40] Except the transition $D'''\leftarrow X$, our results agree satisfactorily with those reported previously.[8,9,11,13,14,16,25] The latter weak transition $D'''\leftarrow X$ was discussed only briefly by Glownia *et al.*[11] but we are unable to derive definitive assignments of bands associated with this transition because of its small intensity. Of two

progressions that remain unassigned, designated P1 and P2 in Table I and Fig. 1, one was observed also by Edvardsson *et al.*[14]

The spectra of NH_2D and NHD_2 in this region are little investigated. Our data for the transition $D\leftarrow X$ agree satisfactorily with those of Duncan,[24] but significant differences exist between our data for transitions $F\leftarrow X$ and $G\leftarrow X$ and those from autoionization spectra of Locht *et al.*[25] for some bands. According to Leach *et al.*,[15] the vibrational quantum numbers given by Locht *et al.*[25] should be decreased by one unit. Level $E(0)$ of NH_2D coincides with $D(6)$.

Except smaller vibrational spacings due to mass effects and more intense maxima correlating with smaller linewidths, the spectrum of ND_3 generally resembles that of NH_3. The measured wavelengths of transition $D\leftarrow X$ of ND_3 agree reasonably well with those of Duncan[24] and Glownia *et al.*,[11] but those of transition $D'''\leftarrow X$ differ by more than 200 cm^{-1} from those of Glownia *et al.*[11] Wavelengths of maxima for transitions D' and $D''\leftarrow X$ are unreported. For transition $E\leftarrow X$, our data agree satisfactorily with those of Edvardsson *et al.*[14] and Locht *et al.*[25] for the high vibrational levels, but are smaller by ~200 cm^{-1} than those of Glownia *et al.*[11] and Langford *et al.*[19] for the low levels. Considering the resolution and observed spacings of these bands, our measurements for the low levels are expected to be more reliable. For transitions $F\leftarrow X$ and $G\leftarrow X$, our data agree better with those of Edvardsson *et al.*[14] than with those of Locht *et al.*[25] Similar to NH_3, two progressions (designated P1 and P2) of ND_3 are unassigned; one of them was also observed by Edvardsson *et al.*[14]

As shown in Fig. 1, the intensity distributions of transitions of all four isotopic species have broad bell shapes, indicating that geometries are substantially altered between the lower and upper states. The adiabatic excitation energies of NH_3 for transitions to states are 8.650(D), 8.686(D'), 8.681(D''), 8.929(D'''), 9.325(E), 9.635(F), and 9.776(G) eV, respectively, and the vertical excitation energies of these states, with estimated vibrational quantum numbers $v'=5$ at maxima, are 9.24(D), 9.28(D'), 9.26(D''), 9.54(D'''), 9.93(E), 10.2(F), and 10.4(G) eV; the associated states are listed in parentheses. The uncertainties of these estimates on vertical excitation might be as large as ±0.12 eV because of uncertainties in identifying the band with the maximal intensity.

D. Vibrational intervals

As the first few bands of each progression are either weak or overlapped with another transition, the values of $\Delta G_{1/2}$ (energy between $v=0$ and $v=1$) are difficult to determine accurately. The vibrational wavenumbers ω_e and anharmonicities $\omega_e x_e$ of each progression, listed in Table III, are obtained by fitting observed wavenumbers to a standard equation taking into account anharmonicity $\omega_e x_e$; the previously reported data of states A and B are also fitted.[7] A common property of all progressions is that their vibrational intervals increase with vibrational quantum numbers. These observed vibrational intervals are well correlated among all isotopic variants and all states, indicating our assignments of

TABLE III. Vibrational wavenumbers ω_e and anharmonicities $\omega_e x_e$ (both in cm^{-1}) for various states of NH$_3$, NH$_2$D, NHD$_2$, and ND$_3$.

State	NH$_3$	NH$_2$D	NHD$_2$	ND$_3$
$A(3sa_1')^a$	884±5	810±10	731±8	655±6
	6.9±0.5	6.7±1.1	5.9±0.9	4.6±0.5
$B,C(3pe')^a$	906±9	850±11	796±14	709±6
	15.7±1.3	13.0±1.5	8.1±1.7	7.2±0.7
$D(3de'')$	890±11	827±13	762±8	675±6
	18.8±1.6	17.3±1.9	14.8±1.0	11.7±0.7
$D'(4sa_1')$	927±8	811±9	753±7	675±8
	12.7±1.6	18.6±1.8	15.3±1.2	11.6±1.2
$D''(3da_1')$	863±5	801±15	746±14	660±6
	26.7±1.0	22.5±2.6	16.4±2.4	16.0±1.2
$D'''(4pe')$	924±4	847±29	729±5	679±10
	22.9±1.1	16.1±10.4	8.6±1.1	20.7±3.6
$E(4de'')$	913±6	827±30	756±14	697±10
	18.3±1.0	18.1±5.6	17.5±1.9	2.8±1.0
$F(5de'')$	917±10	822±18	777±22	741±9
	19.8±1.9	22.5±3.4	14.1±3.2	5.5±1.1
$G(6de'')$	949±8	913±1	818±7	741±5
	11.1±1.4	17.0±0.6	8.0±0.9	5.6±0.6
Ion^b	948	899	825	738

^{a}Calculated from data of Cheng et al. (Ref. 7).
^{b}For NH$_3$ calculated from data of Edvardsson et al. (Ref. 14) for other species from Locht et al. (Ref. 25).

vibrational bands into various progressions to be consistent. The vibrational intervals correlate well with those of the first ionic state, also listed in Table III for comparison.[14,25]

For transitions to the nde'' series, the vibrational wavenumbers increase with quantum number n; that is, ω_e increases from 890 cm^{-1} for the D state to 913, 917, and 949 cm^{-1} for states E, F, and G, respectively.

E. Intensity variations of states D''' and E

The intensity of the transition to state D''' varies greatly among all four species, in contrast to the transition to states D, D', and D'' that varies little. The intensity of that transition to state D''' is small for NH$_3$ (unidentified in this work) and ND$_3$ but increases for NH$_2$D and becomes comparable with that in NHD$_2$, as shown in Fig. 1. The transition to state D''' of NHD$_2$ has an origin at 139.04 nm (71 922 cm^{-1}) and maximum intensity at 133.48 nm (75 700 cm^{-1}), hence an adiabatic energy of 8.93 eV and a vertical energy of 9.39 eV (corresponding to $v'=5$). This state likely corresponds to the $4p\pi/4p\sigma$ Rydberg states, of which the adiabatic energies of NH$_3$ are calculated to be 8.64/8.89 eV and the vertical energies to be 9.41/9.63 eV, respectively.[39] If this assignment is accepted, state D''' has a character similar to states B/C that are assigned[39] to the $3p\pi/3p\sigma$ Rydberg states, respectively. The oscillator strength for transition $B(3p\pi)\leftarrow X$ of NH$_3$ is calculated[39] to be only 0.0010, which is consistent with the $n \rightarrow 3p\pi/3p\sigma$ Rydberg transitions being optically forbidden and which is a tenth of the experimental value of 0.0123.[7] The $np\pi/np\sigma$ Rydberg states might acquire intensity through a mechanism involving vibronic spin-orbit coupling between singlet and triplet states.[41,42] With this borrowing effect included, the oscillator strength for the transition $B \leftarrow X$ of NH$_3$ was recalculated to be 0.0088, which is near

the experimental value.[7] The transition to state D''' might acquire intensity through a mechanism similar to that of the B state.

The intensity of the transition to state E also varies among all four isotopic species, but in a way the reverse of that to state D'''. The transitions to state E of NH$_3$, NHD$_2$, and ND$_3$ are more intense than that of NH$_2$D. This transition might lose strength through vibronic spin-orbit coupling between singlet and triplet states, in contrast with the intensity-borrowing mechanism.[41,42] The coupling strength clearly depends on molecular symmetry and vibronic states.

F. Quantum defects and assignments of Rydberg states

The effective quantum number of n^* is a primary parameter applicable for the assignment of a progression in a Rydberg transition. This value of n^* is calculated with[36]

$$n^* = n - \delta = [R/(IE - E)]^{0.5}, \tag{2}$$

in which n is the principal quantum number, δ is the quantum defect, IE is the ionization energy and E is the energy of an observed state, both expressed in wavenumber units, cm^{-1}, and R is the Rydberg constant, which is determined by[43]

$$R = R_\infty/[1 + m_e/(p + n)M_p], \tag{3}$$

in which $R_\infty = 109\,737.315\,686\,393$ cm^{-1} is adopted from Udem et al.,[44] $M_p/m_e = 1836.152\,666\,5$ is the ratio of masses of proton and electron given by Farnham et al.,[45] and p and n are the numbers of protons and neutrons in the nuclei, respectively. The Rydberg constants for NH$_3$, NH$_2$D, ND$_2$H, and ND$_3$ are calculated to be 109 733.80, 109 734.00, 109 734.17, and 109 734.33 cm^{-1}, respectively.

We adopted IE=10.1861 eV for NH$_3$, that is, the mean of 10.1856 eV (82 152.36 cm^{-1}) given by Edvardsson et al.,[14] 10.1865 eV (82 159 cm^{-1}) from Reiser et al.,[46] and 10.186 46 eV (82 158.751 cm^{-1}) from Seiler et al.[47] We adopted IE values of 10.191 and 10.191 eV to calculate the n^* values for NH$_2$D and NHD$_2$, respectively, from Locht et al.[25] and IE=10.193 eV for ND$_3$ from the mean of 10.201 eV by Langford et al.[19] and 10.185 eV by Locht et al.[25] The effective quantum numbers for all states of four isotopic variants are calculated from the band origins listed in Table I; the results appear in Table IV.

The Rydberg states of ammonia relevant to the current work are $D\,^1E'(3de'')$, $D'\,^1A_2''(4sa_1')$, $D''\,^1A_2''(3da_1')$, $D'''\,^1E''(4pe')$, $E\,^1E'(4de'')$, $F\,^1E'(5de'')$, and $G\,^1E'(6de'')$.[15] As shown in Table IV, the Rydberg assignments of states D, D', D''', and E are consistent with their quantum defects; that is, the δ values fit well with typical ranges ~1 for an s orbital, ~0 for a d orbital, and 0.2–0.8 for a p orbital. The assignments of states D, D', and D'' are also supported by the agreement of their oscillator strengths between experimental measurements and theoretical calculations, as discussed in the previous section. The value of $\delta=0.988$ for the D' state of NH$_3$ is greater than the mean value[48] of 0.897 for the $n=12-18$ Rydberg series of this state. The δ values listed

TABLE IV. Energies, effective quantum numbers n^*, and quantum defects δ for various Rydberg states of NH_3, NH_2D, NHD_2, and NH_3.

State	NH₃			NH₂D			NHD₂			ND₃		
	E (cm⁻¹)	n^*	δ	E (cm⁻¹)	n^*	δ	E (cm⁻¹)	n^*	δ	E (cm⁻¹)	n^*	δ
$D(3de'')$	69 764	2.976	0.024	69 793	2.975	0.025	69 764	2.971	0.029	69 832	2.977	0.023
$D'(4sa_1')$	70 057	3.012	0.988	70 077	3.009	0.991	70 077	3.009	0.991	70 097	3.009	0.991
$D''(3da_1')$	70 018	3.007	−0.007	70 048	3.005	−0.005	70 038	3.004	−0.004	70 067	3.006	−0.006
$D'''(4pe')$	72 015	3.289	0.711	72 119	3.300	0.700	71 922	3.268	0.732	71 572	3.321	0.679
$E(4de'')$	75 211	3.975	0.025	75 109	3.935	0.065	75 188	3.957	0.043	75 256	3.971	0.029
$F(5de'')$	77 712	4.969	0.031	77 785	4.988	0.012	77 724	4.954	0.046	78 040	5.127	−0.127
$G(6de'')$	78 852	5.762	0.238	78 827	5.707	0.293	78 864	5.739	0.261	78 927	5.778	0.222
$D''(4)$	73 725	2.997	0.003	73 465	2.983	0.017	73 185	2.986	0.014	72 865	2.966	0.034
$F(4)$	81 593	5.021	−0.021	81 248	4.914	0.086	80 985	4.933	0.067	81 050	5.057	−0.057
$G(4)$	82 850	5.954	0.046	82 590	5.853	0.147	82 250	5.816	0.184	82 034	5.760	0.240

in Table IV for states D'', F, and G are somewhat inconsistent with the expected values from their assignments; they are discussed further below.

The n^* values for the origins of state D'' for four isotopic variants are all slightly greater than 3, resulting in small negative values of δ. For all four species, as the origins of the transition to state D'' are weak and poorly separated from that to state D', their positions are difficult to determine accurately. In contrast, the transition to level $v'=4$ is strong and its position is well defined for every species; hence its quantum defect might be more reliable for a Rydberg assignment. For this reason, the δ values for level $v'=4$ of state D'' are calculated, with results listed in Table IV; the ionization energies for level $v'=4$ are 10.6559, 10.637, 10.600, and 10.551 eV (Ref. 25) for NH_3, NH_2D, NHD_2, and ND_3, respectively. Because the δ values for level $D''(4)$ are positive, the assignment of D'' to $3da_1'$ is acceptable.

As shown in Table IV, as the δ values of the F state are small for NH_3, NH_2D, and NHD_2, this state is appropriate for the $5de''$ Rydberg state, but for ND_3 the effective quantum number of this state is 5.127, so that this state seems to involve a $6p$ orbital instead of $5d$. An explanation might invoke mixing of the $F(0)$ level with $D(11)$, as shown in Fig. 1(D) for ND_3. To test this possibility, we calculated the n^* values for the well defined $F(4)$ levels of all four species; the results are listed in Table IV. The n^* values of the $F(4)$ level vary greatly among these four isotopic variants such that a correlation of the F state with the $5d$ orbital is unclear. The value $n^*=5.057$ for the $F(4)$ level of ND_3 still shows that the F state involves a $6p$ orbital; this state might hence not be a pure d orbital. Such a deviation cannot be rationalized according to an uncertainty of the ionization energy of ND_3. If IE=82 280 cm⁻¹ (10.201 eV) as estimated by Langford *et al.*,[19] the n^* value for the $F(0)$ level of ND_3 becomes 5.087, still in disagreement with the $5d$ assignment. Hence, the assignment of the F state to $5de''$ is uncertain; it might be mixed with p orbital.

The effective quantum numbers for the band origins of the transition to state G for NH_3 in four isotopic variants lie in a range of 5.707–5.778, which indicates that state G involves a $6p$ orbital instead of the assigned $6d$ orbital. State G was originally assigned as $^1A_2''(7sa_1')$ by Edvardsson *et al.*,[14] but Leach *et al.*[15] assigned this series as $^1E'(6de'')$

based on its large absorption strength and small width; they attributed the large quantum defect of the $G(0)$ level of NH_3 to a perturbation. To test the validity of that argument, we calculated the δ values of the $G(4)$ levels of four species, which are separate from other bands, with the same ionization energies used in the calculation of $D''(4)$. As listed in Table IV, the quantum defect of the $G(4)$ level is 0.046 for NH_3, but those are 0.147, 0.184, and 0.240 for NH_2D, NHD_2, and ND_3, respectively. The G state hence might be mixed with a p orbital. Unexpectedly large intensities were observed at the $G(4)$ level of NH_3, $G(3)$ of NH_2D, $G(8)$ of NHD_2, and $G(9)$ of ND_3, which might result from such mixing.

IV. CONCLUSION

The absorption cross sections of NH_3, NH_2D, NHD_2, and ND_3 near 298 K are measured in the spectral range of 110–144 nm. The precisions of these cross sections and the oscillator strengths of ND_3 are improved over those previously reported, whereas measurements on NH_2D and NHD_2 are new. For most transitions the oscillator strengths do not vary with isotopic substitution, except for transitions $D''' \leftarrow X$ of NH_2D and NHD_2 that are much greater than those of NH_3 and ND_3.

The wavelengths of NH_3 features agree satisfactorily with those previously reported. The spectrum of ND_3 resembles that of NH_3, except for smaller vibrational intervals, greater cross sections at maxima, and smaller widths. Our wavelengths for transitions $D''' \leftarrow X$ and $E \leftarrow X$ of ND_3 also are at variance with those of previous reports. The wavelengths of absorption maxima are arranged into vibrational progressions in accordance with Rydberg transitions. All progressions show a common characteristic that vibrational intervals increase with vibrational energies; vibrational anharmonicities for many states are determined for the first time.

The effective quantum numbers and quantum defects are consistent with Rydberg assignments to states $D\ ^1E'(3de'')$, $D'\ ^1A_2''(4sa_1')$, $D''\ ^1A_2''(3da_1')$, $D'''\ ^1E''(4pe')$, and $E\ ^1E'(4de'')$, but not for $F\ ^1E'(5de'')$ and $G\ ^1E'(6de'')$; these states might not be a pure d orbital, but mixed with p orbital.

ACKNOWLEDGMENTS

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