A He(I) photoelectron spectroscopic study of the $\tilde{X}^2A''_2$ state of NH_3^+ and ND_3^+ . A reanalysis and evidence for the coriolis coupling between the bending υ_2 and υ_4 modes

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Abstract

In the high-resolution He(I) photoelectron spectrum of NH_3 and its isotopomer ND_3, the complete vibrational structure of the $\tilde{X}^2A''_2$ state of NH_3^+ and ND_3^+ is examined in detail. Three vibrational progressions are identified. The well-known strongest progression, already unambiguously assigned to the υ_2 out-of-plane bending mode, is observed from υ = 0-17 in NH_3^+ and from υ = 0-20 in ND_3^+. For NH_3^+ this vibration could be characterized not only by its energy $hc\omega_2 = 0.109 \pm 0.001$ eV (or $\omega_2 = 878 \pm 7$ cm^{-1}), but also by its first anharmonicity constant $hc\omega_{22}x_{22} = -(16.2 \pm 1.2) \times 10^{-4}$ eV (or $\omega_{22}x_{22} = -13.0 \pm 1.0$ cm^{-1}). The best fit of the experimental data required the introduction of a second anharmonicity constant, i.e. $hc\omega_{22}y_{22}= -(30.7 \pm 4.2) \times 10^{-6}$ eV (or $\omega_{22}y_{22}= -0.248 \pm 0.034$ cm^{-1}). The earlier reported weak progression, assigned to the vibrational combination $\upsilon_1 + n\upsilon_2$ transitions has been reexamined. Suitable handling of the data leads to two possible energies for the υ_1 degenerate NH stretching vibrational normal mode, i.e. $hc\omega_1 = 0.306 \pm 0.006$ or 0.422 ± 0.005 eV. Several arguments are brought to favour the value of $hc\omega_1 = 0.422$ eV (or $\omega_1 = 3404$ cm^{-1}). Finally a third weak progression, reported for the first time, is assigned to $\upsilon_4 + n\upsilon_2$ transitions where the υ_4 in-plane bending mode is optically forbidden. This vibrational normal mode is characterized by an energy $hc\omega_4 = 0.186 \pm 0.010$ eV ($\omega_4 = 1500 \pm 80$ cm^{-1}). In agreement with theoretical predictions, this transition becomes allowed through a strong Coriolis vibro-rotational coupling between the υ_4 and the υ_2 vibrational normal modes. The same measurements and the isotope effect on the molecular constants are investigated in ND_3^+ too.

1. Introduction

The dissociative ionization of NH_3 in its five dissociation channels has been investigated thoroughly by electron impact [1-3]. The photoionization of the NH_3^+ molecular ion, together with its three isotopomers NH_2D^+, NHD_2^+ and ND_3^+, has been studied carefully by photoionization mass spectrometry using synchrotron radiation [4]. The abundant autoionization fine structure has been disentangled and assigned. These phenomena were also observed and analyzed in the threshold photoelectron spectrum of NH_3 using synchrotron radiation [5].

Vibrational autoionization as well as the NH_3^+ ($\tilde{x}^2A''_2$) excitation up to the adiabatic ionization energy of the $\tilde{A}^2E$ state have been observed. Autoionizing state(s) converging to the e^{-1} (^2E) ionization continuum were also detected [5].

The most recent spectroscopic works dedicated to NH_3^+ were reported by Huet et al. [6] and Cramb and Wallace [7]. They investigated the REMPI spectrum of vibrationally autoionizing states and the vibrational structure in the NH_3^+ ($\tilde{X}^2A''_2$) ionization continuum, respectively. In the former work the $\upsilon_2 + \upsilon_3 - \upsilon_2$ hot band of NH_3^+ is extensively reported [6]. On the other hand, Habenicht et al. [8] measured the rotationally resolved zero kinetic energy (ZEKE) photoelectron spectrum of NH_3 by using a two-color 2 + 1 photon pump-probe technique. The rotational structure associated with $\upsilon_2 = 1$ and 2 has been investigated and the value of the two rotational constants have been obtained.

A few experimental and/or theoretical analysis of the $\tilde{x}^2A''_2$ state of NH_3^+ [9-11] have been reported. Carmichael [9] obtained the four vibrational frequencies of NH_3^+ from the potential energy surface of the ground state calculated using a Møller-Plesset perturbational approach. Botschwina [10,11] used the coupled electron-pair approximation level of calculations to determine vibrational energies, wavefunctions and intensities for the symmetric stretching (υ_1) and for the out-of-plane bending (υ_2) vibrations. For the $n\upsilon_2$ progression, the results of these calculations agree within 30 cm^{-1} with the experimental data of Rabalais et al. [12] and Ågren et al. [13] obtained by He(I) photoelectron spectroscopy.

The υ_3 normal mode has been observed and analyzed by Bawendi et al. [14] using a discharge cell and a difference frequency spectrometer combined with velocity modulation detection. This degenerate normal mode

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corresponds to the degenerate NH stretching and its wavenumber $\omega_3 = 3388.645$ cm^{-1}. Lee and Oka [15] measured the wavenumber ($\omega_2 = 867.008$ cm^{-1}) and the first anharmonicity constant ($\omega_{22}x_{22} = -18.191$ cm^{-1}) associated with the υ_2 normal mode. Vibration-rotation coupling and potential constants were also determined. Kraemer and Špirko [16] showed the important role played by the coupling between rotation and vibration in ionized ammonia. Particularly, a strong Coriolis interaction couples the out-of-plane (υ_2) and the in-plane (υ_4) bending vibrations.

Fig. 1. The most important parts of the experimental setup used in the present work and the 180° electrostatic tandem photoelectron spectrometer. For the easiness of the representation, all the elements are drawn in the same plane. The actual light path is parallel to the electron optical slits length.
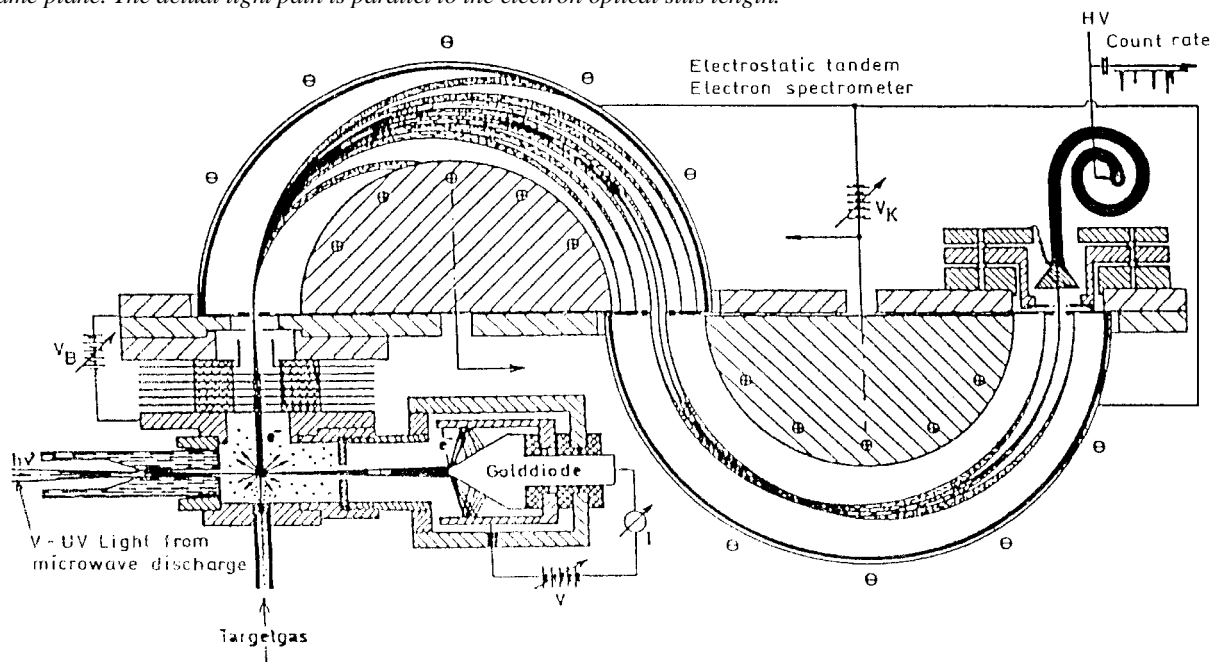
Though the vacuum UV photoelectron spectrum of NH$_3$ has been reported several times in the literature [12,13,17-19], we will report in this paper on an accurate high-resolution photoelectron spectrum of the $\tilde{X}^2A''_2$ state of NH$_3^+$. The accuracy achieved in the present experiment allowed us to deduce spectroscopic constants only known up to now by laser spectroscopy [15] and tentatively estimated earlier by photoionization [4]. The same measurements have been extended to the ND$_3$ molecule. The latest spectra of this species, reported in the literature by Weiss and Lawrence [18] and Potts and Price [19], were recorded under fairly low resolution (≈ 50 meV).

2. Experimental

The experimental setup and conditions used in this work have been outlined earlier [20] and will be described in detail in a forthcoming paper [21]. Only the most salient features will be laid out here.

A microwave discharge in He is used as a light source to generate the He(I) resonance line at 58.4 nm. The light beam is led into the ionization region through a glass capillary. At the opposite of the light entrance hole, the photoelectron current of a gold diode measures continuously the light intensity. At 90° with respect to the light beam, a high-resolution tandem electron spectrometer, made of two 180° electrostatic deflectors (see Fig. 1) working at constant but adjustable pass-energy (PE), is used to analyze the photoelectron energies [20]. The dispersion being 104, a theoretical resolution $\Delta E/E = 0.5\%$ is obtained with 0.5 mm slitwidth. The photoelectron spectra reported here are measured at a pass-energy PE =1.9 V. A resolution of 15 meV is achieved, as measured by the FWHM of the Xe$^+$ and Kr$^+$ $^2P_{3/2}$ peaks. The energy scale is calibrated with respect to the four peaks of the Xe$^+$ and Kr$^+$ $^2P_{3/2}$-$^2P_{1/2}$ spin-orbit doublets observed in a NH$_3$(ND$_3$)/Xe/Kr mixture. The accuracy is better than 2 meV for the first photoelectron band.

The ammonia-h$_3$ sample used in this work was of commercial grade (Linde A.G.) of 99.95% purity. The ammonia-d$_3$ purchased from Merck, Sharp and Dohme was of 99.7 at.%. Both gases were introduced without further purification. The sample gas pressure in the ionization region is of 5×10^{-6} mbar. When ND$_3$ is investigated the inlet system and electron analyzer are swept by the deuterated sample during several hours

before running the experiment.

Table 1 *Experimental (PES and PIS), least square fit (FIT) data and their deviations (Δ) (eV) for the υ_2 vibrational progression observed in the NH_3^+ ($\tilde{X}^2A''_2$) ground state band*

υ	PFS$_{OBS}$[a]	FIT$_{CALC.}$[b]	Δ[c] (X10^{-3})	PIS[d] [4]	PES[d] [12,13]	PES[d] [18]
0	10.069	10.0680	1.0	10.072	10.073	-
1	10.182	10.1800	2.0	10.191	10.182	10.175
2	10.293	10.2949	-1.9	10.309	10.294	10.292
3	10.411	10.4127	-1.7	10.422	10.409	10.409
4	10.531	10.5331	-2.1	10.530	10.531	10.535
5	10.657	10.6558	1.2	10.643	10.654	10.657
6	10.782	10.7808	1.2	10.767	10.780	10.779
7	10.910	10.9079	2.1	10.896	10.908	10.913
8	11.038	11.0368	1.2	11.036	11.038	11.032
9	11.170	11.1674	2.6	11.160	11.169	11.163
10	11.300	11.2995	0.5	11.289	11.302	11.294
11	11.433	11.4329	0.1	11.434	11.433	11.425
12	11.565	11.5674	-2.4	11.564	11.570	11.559
13	11.700	11.7028	-2.8	-	11.703	11.695
14	11.840	11.8390	0.9	-	11.839	11.826
15	11.975	11.9758	-0.8	-	11.979	11.976
16	12.115	12.1129	2.1	-	12.115	12.107
17	12.250	12.2503	-0.3	-	12.255	12.233

[a]This work: accuracy ± 0.002 eV.
[b]Least square fit data rounded to 4 decimal digits.
[c]Deviations between experimental (PES$_{0BS}$) and calculated (FIT$_{CALC}$) data.
[d]Accuracy on the data ± 0.010 eV, as mentioned by the authors.

3. Experimental results and discussion

3.1. The He(I) photoelectron spectrum of the $\tilde{X}^2A''_2$ state of NH_3^+ and ND_3^+

The He(I) photoelectron spectrum of NH_3 is displayed in Fig. 2 in the 9.9-12.3 eV energy range where Fig. 2a represents the overall spectrum of the first band whereas Fig. 2b shows an expanded intensity scale to enhance the weak vibrational structures.

The first photoelectron band is characterized by a strong and long vibrational progression starting at 10.069 ± 0.002 eV consisting of 18 well-resolved peaks, the positions of which are listed in Table 1. Their FWHM is equal to 30 meV, i.e. twice the FWHM measured on the $Ar^+(^2P_{3/2})$-peak.

Superimposed on this major structure at least one weak and displaced progression is more clearly resolved than in earlier reported spectra [12]. An enlarged view of these structures is shown in Fig. 2b and their positions are recorded in Table 2.

Table 2 *Experimental (PES), least square fit (FIT) data and their deviations (Δ) (eV) for the $n\upsilon_2 + \upsilon_1$ vibrational progression observed in the first NH_3^+ ($\tilde{X}^2A''_2$) band*

$n\upsilon_2 + \upsilon_1$	PES$_{0BS.}$[a]	FIT$_{CALC.}$[b]	Δ (x10^{-3})[c]
2,1	10.732	10.7331	-1.1
3,1	10.856	10.8560	0.0
4,1	10.982	10.9806	1.4
5,1	11.107	11.1070	0.0
6,1	11.237	11.2351	1.9
7,1	11.363	11.3648	-1.8
8,1	11.497	11.4963	0.7
9,1	11.628	11.6295	-1.5
10,1	11.763	11.7645	-1.4
11,1	11.903	11.9011	1.9

[a]This work: accuracy ±0.002 eV.
[b] Least square fit data rounded to 4 decimal digits.
[c] Deviations between experimental (PES$_{0BS}$) and calculated (FIT$_{CALC}$) data.

Fig. 2. *The He(I)-photoelectron spectrum of the $\tilde{X}^2A''_2$ state of $NH_3{}^+$: (a) the overall spectrum, (b) the intensity-enhanced spectrum showing the weak features.*
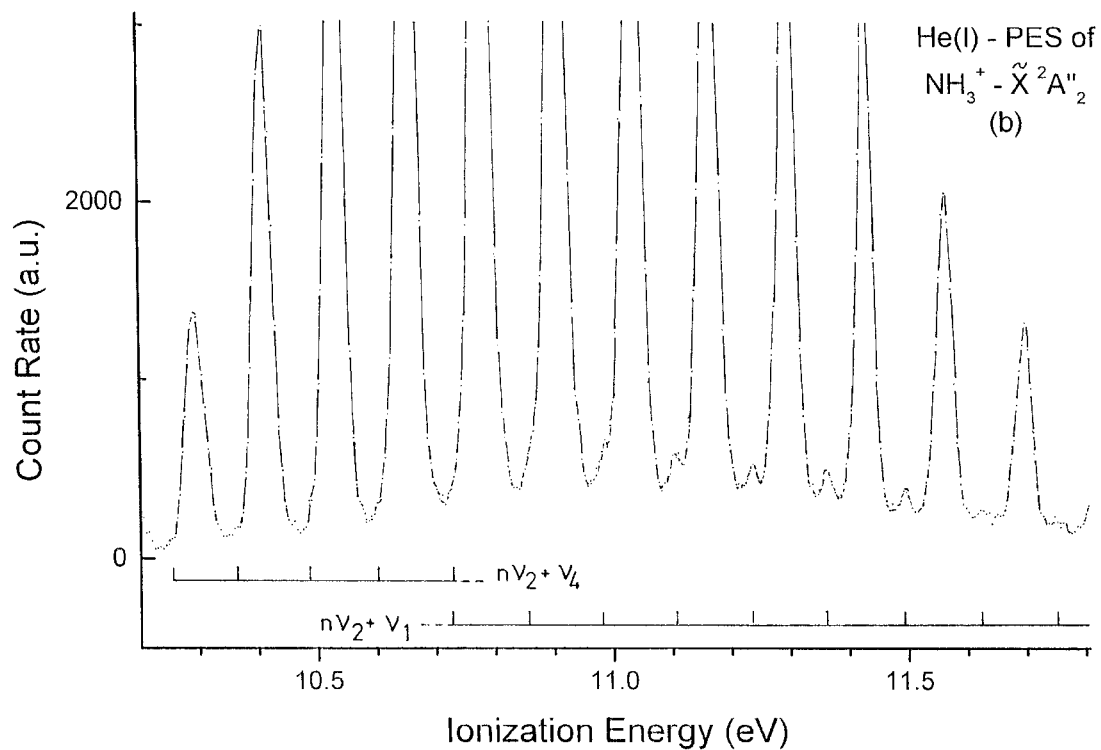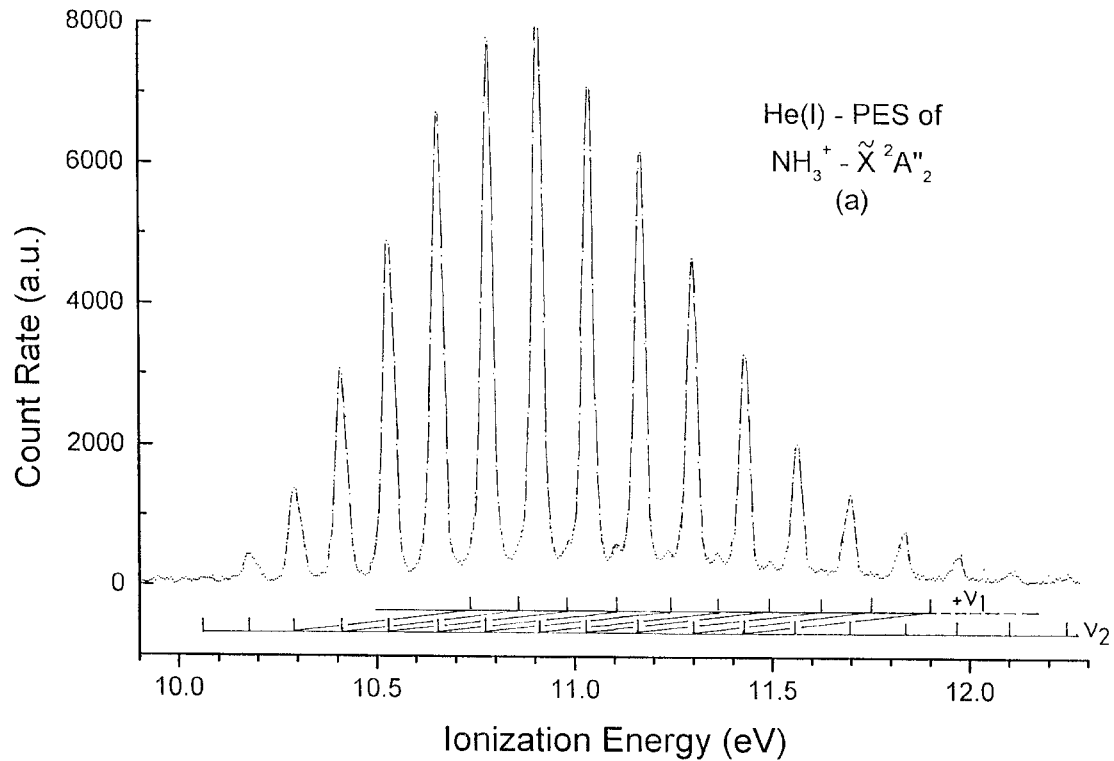
Table 3 Experimental (PES and PIS), least square fit (FIT) data and their deviations (Δ) (eV) related to the v_2 vibrational progression observed in the ND_3^+ ($\tilde{X}^2A''_2$) band

v	PFS$_{OBS}$[a]	FTT$_{CALC}$[b]	Δ (X10^{-3})[c]	PIS [4][d]	PES [19][d]	PES [18][d]
0	10.104	10.1054	-1.4	10.083	10.12	-
1	10.195	10.1939	1.1	10.185	10.23	10.180
2	10.278	10.2799	-1.9	10.277	10.32	10.290
3	10.369	10.3694	-0.4	10.363	10.41	10.380
4	10.460	10.4603	-0.3	10.460	10.50	10.473
5	10.554	10.5525	1.5	10.551	10.60	10.581
6	10.647	10.6459	1.1	10.643	10.69	10.664
7	10.740	10.7406	-0.6	10.740	10.78	10.752
8	10.835	10.8363	-1.3	10.831	10.88	10.832
9	10.933	10.9331	-0.1	10.934	10.98	10.932
10	11.030	11.0308	-0.8	11.041	11.07	11.029
11	11.130	11.1294	0.6	11.128	11.18	11.131
12	11.229	11.2288	0.2	11.240	11.27	11.236
13	11.329	11.3289	0.1	11.327	11.38	11.341
14	11.430	11.4297	0.3	11.461	11.48	11.426
15	11.530	11.5310	-1.0	-	11.58	11.538
16	11.633	11.6329	0.1	-	11.69	11.648
17	11.737	11.7351	1.9	-	11.79	11.736
18	11.837	11.8378	-0.8	-	11.89	11.831
19	11.940	11.9407	-0.7	-	-	-
20	12.044	12.0438	0.2	-	-	-

[a]This work: accuracy ±0.002 eV.
[b]Least square fit data rounded to 4 decimal digits.
[c]Deviations between experimental (PES$_{0BS}$) and calculated (FIT$_{CALC}$) data.
[d]Accuracy on the data ±0.010 eV, as mentioned by the authors.

Table 4 Experimental (PES), least square fit (FIT) and their deviations (Δ) (eV) for the $nv_2 + v_1$ vibrational progression observed in the first ND_3^+ ($\tilde{X}^2A''_2$) band

$nv_2 + v_1$	PFS$_{OBS}$[a]	FIT$_{CALC}$[b]	Δ(X10^{-3})[C]
0,1	10.435	10.4338	1.2
1,1	10.522	10.5232	-1.2
2,1	10.614	10.6137	0.3
3,1	10.701	10.7050	-4.0
4,1	10.800	10.7973	2.7
5,1	10.891	10.8906	0.4
6,1	10.987	10.9848	2.2
7,1	11.086	11.0799	6.1
8,1	11.165	11.1760	-11.0
9,1	11.274	11.2730	1.0
10,1	11.375	11.3710	4.0
11,1	11.467	11.4699	-2.9
12,1	11.571	11.5698	1.2

[a]This work: accuracy ±0.002 eV.
[b]Least square fit data rounded to 4 decimal digits.
[c]Deviations between experimental (PES$_{0BS}$) and calculated (FIT$_{CALC}$) data.

The He(I) photoelectron spectrum corresponding to the ionization of ND_3 in its ground electronic state is shown in Fig. 3 in the 10.0-12.2 eV energy range.

In Fig. 3a the overall spectrum is displayed and Fig. 3b clearly shows two additional weak vibrational progressions.

Similarly to NH_3, the first band unambiguously shows the main long vibrational progression starting at 10.104 ± 0.002 eV. It consists of 21 well-resolved peaks and their corresponding positions are listed in Table 3. The FWHM = 25 meV observed for these peaks significantly differs from the FWHM = 15 meV measured for $Ar^+(^2P_{3/2})$-peak and from FWHM = 30 meV for the peaks of the main progression in NH_3^+ ($\tilde{X}^2A''_2$) state.

To the authors' knowledge, the weak and displaced series superimposed on the major structure is observed for the first time. The peak positions for this progression are listed in Table 4.

Table 5 *Experimental (PES), least square fit (FIT) data and their deviations (Δ) (eV) for the $nv_2 + v_4$ vibrational progression observed in the $\tilde{X}^2A''_2$ band of NH_3^+ and ND_3^+*

$nv_2 + v_4$	NH_3^+			ND_3^+		
	PES[a]	FIT[b]	Δ(X10^-3)[c]	PES[a]	FIT[b]	Δ(X10^-3)[c]
0,1	10.259	10.2540	5.0	10.224	10.2209	3.1
1,1	10.365	10.3717	-6.7	10.307	10.3094	-2.4
2,1	10.495	10.4894	5.6	10.398	10.3991	-1.1
3,1	10.596	10.6071	-11.1	10.493	10.4902	2.8
4,1	(10.732)	10.7248	7.2	10.580	10.5825	-2.4
5,1	-	-	-	10.672	10.6761	-4.1
6,1	-	-	-	10.771	10.7710	0.0
7,1	-	-	-	10.867	10.8671	-0.1
8,1	-	-	-	10.966	10.9646	1.4
9,1	-	-	-	11.070	11.0633	6.7
10,1	-	-	-	11.165	11.1633	1.7
11,1	-	-	-	11.259	11.2582	0.8

[a]This work: accuracy ± 0.002 eV.
[b]Least square fit data rounded to 4 decimal digits.
[c]Deviations between experimental (PES) and calculated (FIT) data.

Moreover, and more clearly than in the NH_3 photoelectron spectrum, a third series of weak peaks is observed in ND_3 and their positions are listed in Table 5 together with the few corresponding structures observed in NH_3 (see Fig. lb).

4. Discussion

The NH_3 molecule has a pyramidal geometry and belongs to the C_{3v} symmetry group. It has the ground state configuration given by

$$(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2:\tilde{X}^1A_1$$

The removal of a $3a_1$ electron leads to a $^2A_1$ state in the C_{3v} symmetry group and corresponds to the removal of one of the two lone-pair electrons localized on the nitrogen atom [22]. This ionization process involves a dramatic change in geometry, leading to a planar $\tilde{X}^2A''_2$ NH_3^+ cation belonging to the D_{3h} symmetry group [9-11,14-16].

The four vibration normal modes of NH_3^+ in the D_{3h} symmetry group are represented in Fig. 4. This representation is derived from force-field calculations performed by using the GAUSSIAN 94 set of programs at the UHF/6-31G(d) level. From the symmetry view point, only two vibrational normal modes should show up in the photoelectron spectrum: the v_1 symmetric NH stretching mode (belonging to the A_1 representation in the C_{3v} and to the A_1 representation in the D_{3h} point group) and the v_2 out-of-plane bending mode (belonging to the A_1 representation in the C_{3v} group and to A''_2 in the D_{3h} group). As the photoionization process involves a change of equilibrium geometry from a pyramidal configuration in the neutral molecule to a planar geometry in the ground state of the ion, the problem of the activity of the different normal modes has to be solved in the common subgroup, i.e. the C_{3v} point group. The two normal modes mentioned above will be therefore optically active. Contrarily, the two degenerate normal modes, i.e. v_3 (the degenerate NH stretching mode) and v_4 (the in-plane bending motion), belonging to the E or E' representation in the C_{3v} and in the D_{3h} point groups respectively, will be optically unallowed. For the sake of clarity, in the following sections (4.1-4.3), the three different vibrational progressions observed in the present experiments will be discussed separately.

4.1. The prominant vibrational progression nv_2

The energies corresponding to the position of the $\tilde{X}^2A''_2$ NH_3^+ long series of peaks observed in the present work are listed in the second column of Table 1. These data were fit to the standard vibronic energy expression (1)

$$E_v = E_0 + \left(v + \tfrac{1}{2}\right)hc\,\omega_i - \left(v + \tfrac{1}{2}\right)^2 hc\,\omega_{ii}\,x_{ii}$$
$$+ \left(v + \tfrac{1}{2}\right)^3 hc\,\omega_{ii}\,y_{ii} + \ldots \qquad (1)$$

where higher-order anharmonic contributions are neglected [23]. In this relationship E_v, E_0, h, c, ω_i, ω_{ii}, x_{ii} and y_{ii} have the usual meaning. To obtain the best fit, the first four terms of Eq. (1) had to be used. Fitted energy values and their deviation from the experimental values are listed in columns 3 and 4 of Table 1, respectively.

Fig. 3. *The He(I)-photoelectron spectrum of the $\tilde{X}^2A''_2$ state of ND_3^+: (a) the overall spectrum, (b) the intensity-enhanced spectrum showing the weak features.*
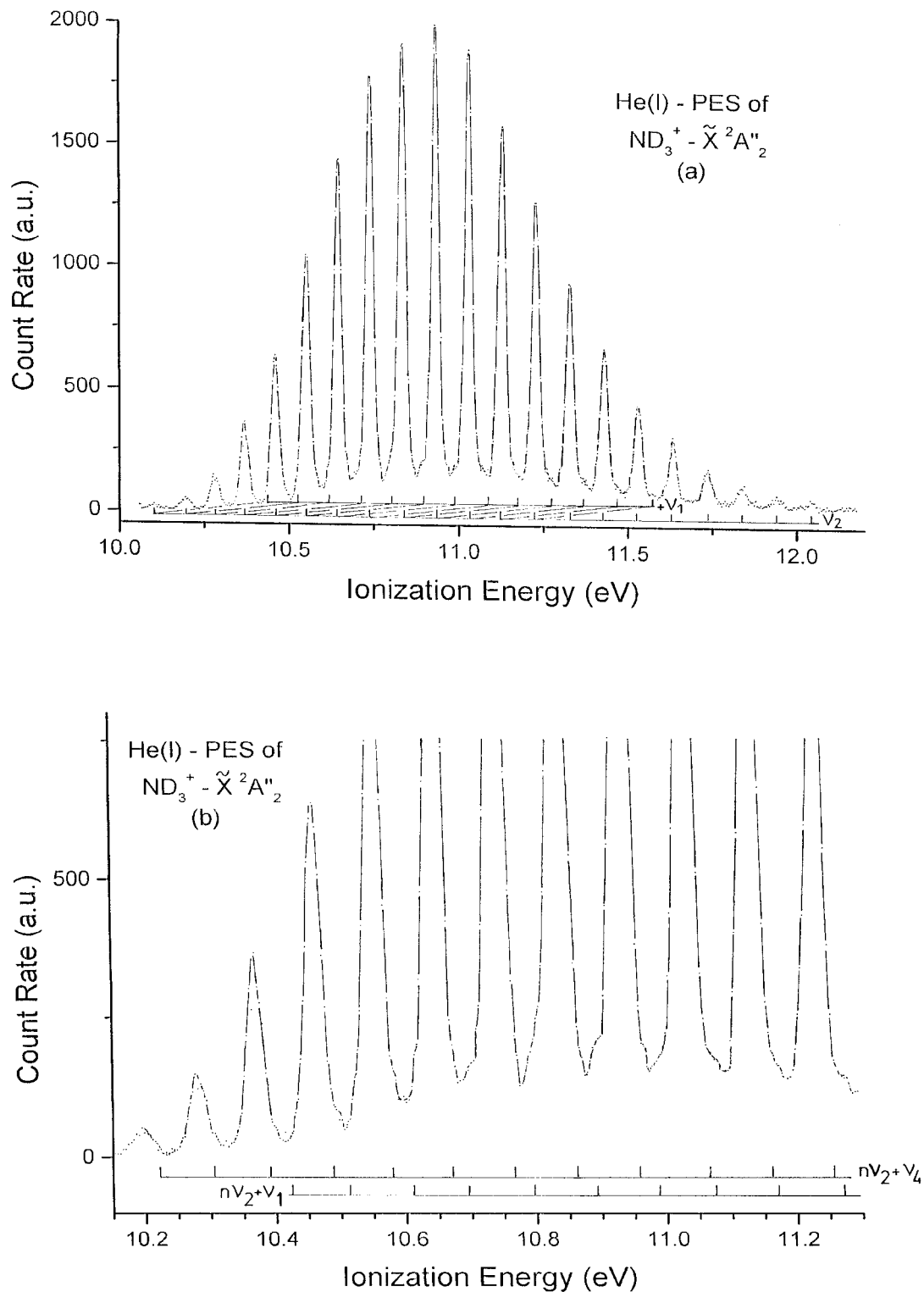
Fig. 4. *Schematic representation of the four vibrational normal modes of the planar NH$_3^+$ ($\tilde{X}^2A_2''$) molecular ion in the D$_{3h}$ symmetry point group.*
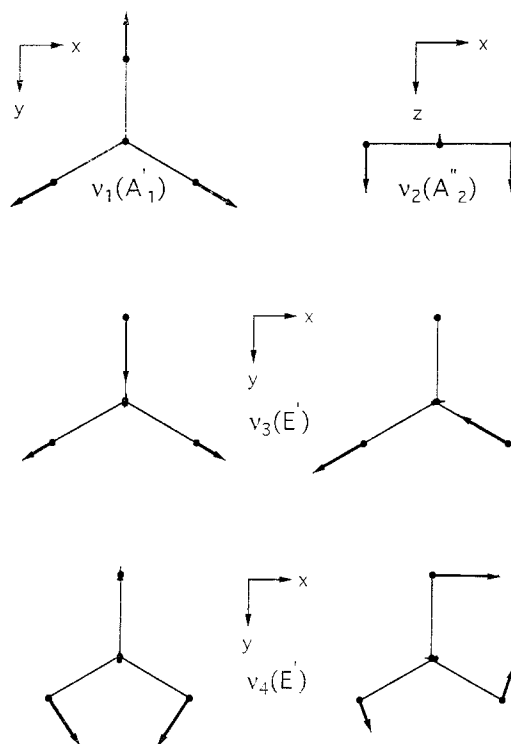
The values calculated for the four parameters E_0, $hc\omega_2$, $hc\omega_{22}x_{22}$ and $hc\omega_{22}y_{22}$ are listed in Table 6. From this least square fit the adiabatic ionization energy IE$_{ad}$ = 10.067 eV is in good agreement with the ionization energy determined experimentally at IE$_{ad}$ = 10.069 ± 0.002 eV. The value $hc\omega_2$ = 0.109 ± 0.001 eV (ω_2 = 878 ± 7 cm^{-1}) found by this data handling has to be compared with previous photoelectron spectroscopic determinations, i.e. 0.112 ± 0.005 eV (903 ± 40 cm^{-1}) [12] and 0.117 eV (943 cm^{-1}) [18]. This latter value looks significantly higher than that determined in this work. By photoionization mass spectrometry [4] a value of ω_2 = 890 cm^{-1} has been obtained by a least square fit applied to the 12 observed members of the v_2 vibrational progression. Truncating the present data to the first 10 levels and Eq. (1) to the first three terms ω_2 = 892 cm^{-1} is obtained. The wavenumber of ω_2 = 878 ± 7 cm^{-1} measured in NH$_3^+$ ($\tilde{X}^2$A''$_2$) has to be compared to its value in the neutral molecule where ω_2 = 931.58 cm^{-1} [23]. As observed, through the ionization of the 3a$_1$ orbital, the out-of-plane 'inversion' vibration is expected to involve less energy than in the neutral molecule.

The present result can also be compared to those obtained by optical spectroscopic methods and to theoretical predictions. Lee and Oka [15] reported ω_2 = 867 cm^{-1} in very good agreement with the present result. Ab initio calculations at different levels applied to NH$_3^+$ gave ω_2 values of 848 cm^{-1} [9], 898 cm^{-1} [11] or 904 cm^{-1} [16].

From the above mentioned data handling two other molecular parameters, i.e. the first and the second anharmonicity constants, were also determined. Their values are listed in Table 6.

The first anharmonicity constant is given by $hc\omega_{22}x_{22}$ = - (16.2 ± 1.2) × 10^{-4} eV ($\omega_{22}x_{22}$ = -13.0 ± 1.0 cm^{-1}). This value is in very good agreement with the only optical spectroscopic determination reported so far by Lee and Oka [15], i.e. $\omega_{22}x_{22}$ = - 18.2 cm^{-1}. In an earlier photoionization mass spectrometric determination [4] this quantity was determined as being $\omega_{22}x_{22}$ = - 8.0 cm^{-1}.

Table 6 also shows values of this constant as derived from the energy values reported by Weiss and Laurence [18] and Agren et al. [13] and applying Eq. (1) truncated to the first three terms.

The fourth parameter in Eq. (1), necessary to the best fit and interpreted as the second anharmonicity constant, has been determined to be $hc\omega_{22}y_{22}$ = -(30.7 ± 4.2) × 10^{-6} eV ($\omega_{22}y_{22}$ = -0.248 ± 0.034 cm^{-1}). In the literature no data related to this constant is available for comparison.

Table 6 *Experimental spectroscopic constants (eV) of* $NH_3^+(\tilde{X}^2A''_2)$ *and* $ND_3^+(\tilde{X}^2A''_2)$ *as determined from the* v_2, $nv_2 + v_1$ *and* $nv_2 + v_4$ *progressions observed by the He(I) photoelectron spectroscopy*

		This work	[12,13]	[18]
$NH_3^+(\tilde{X}^2A''_2)$:	T_e:	$10.013^2 \pm 0.001^7$	10.017	10.117
	ω_2:	$0.108^9 \pm 0.000^8$	[0.112]	[0.115]
	$(\omega x)_{22}$:	$-(16.2 \pm 1.2) \times 10^{-4}$	$-[10.0 \times 10^{-4}]^a$	$-[8.2 \times 10^{-4}]^a$
	$(\omega x)_{22}$:	$-(30.7 \pm 4.2) \times 10^{-6}$	-	-
	ω_1:	0.422 ± 0.006	-	-
	ω_4:	0.186 ± 0.010	-	-
$ND_3^+(\tilde{X}^2A''_2)$:	T_e:	10.063 ± 0.002^1	10.078	10.136
	ω_2:	$0.084^8 \pm 0.000^7$	[0.085]	[0.088]
	$(\omega x)_{22}$:	$-(8.3 \pm 0.5) \times 10^{-4}$	$-[8.0 \times 10^{-4}]^a$	$-[5 \times 10^{-4}]^a$
	$(\omega x)_{22}$:	$-(12.5 \pm 1.6) \times 10^{-6}$	-	-
	ω_1:	0.328 ± 0.006	-	-
	ω_4:	0.116 ± 0.004	-	-

[a]In brackets: values determined by linear regression on the values reported in Refs. [13] and [18].

The corresponding vibrational progression nv_2, just described for NH_3^+, has also been observed and measured for ND_3^+. The corresponding photoelectron band is made of 21 strong peaks for which the energy positions and the result of the fit to Eq. (1) are listed in columns 2 and 3 in Table 3. In the present case also, four parameters were introduced for the best fit. The fitted data and deviations with respect to the experimental energies are displayed in columns 3 and 4 in the same Table 3.

The first result of this least square fit is the adiabatic ionization energy of ND_3^+ given by $IE_{ad} = 10.105 \pm 0.003$ eV instead of 10.104 ± 0.002 eV determined experimentally.

The value $hc\omega_2 = 0.084^8 \pm 0.000^5$ eV ($\omega_2 = 684 \pm 4$ cm^{-1}) is determined in this work. Though the experiments devoted to ND_3^+ are scarce in the literature, a few photoelectron [13,17-19] and photoionization [4] experiments and theoretical calculations [11,13,16] are available for comparison. The present determination is in good agreement with the value of 0.085 eV [13] and 0.088 eV [18] measured by photoelectron spectroscopy and 0.087 eV by photoionization [4]. In the valence field-force approximation [24] a ratio of $\omega_2(NH_3^+)/\omega_2(ND_3^+) \simeq$ 1.304 is predicted and compares favourably with the ratio of 1.284 ± 0.018 determined in the present experiment.

By ab initio quantum mechanical calculations Botschwina [11] determined $\omega_2(ND_3^+)$ =683 cm^{-1} or 0.0847 eV, whereas Ågren et al. [13] and Kraemer and Špirko [16] calculated $\omega_2(ND_3^+) = 0.851$ eV. The isotopic ratio $\omega_2(NH_3^+)/\omega_2(ND_3^+)$ is found to be 1.315 [11], 1.305 [13] and 1.317 [16].

The first anharmonicity constant has been deduced from the present data, leading to $hc\omega_{22} x_{22} = -(8.3 \pm 0.5) \times 10^{-4}$ eV ($\omega_{22}x_{22} = -6.69 \pm 0.40$ cm^{-1}). Photoelectron spectroscopic data [12,13,18] allowed us to estimate this constant using Eq. (1), i.e. -8.0×10^{-4} eV [13] and -3.9×10^{-4} eV [16]. By photoionization $\omega_{22}x_{22} = -6.2 \times 10^{-4}$ eV. The second anharmonicity constant has also been determined, i.e. $hc\omega_{22}y_{22} = -(12.5 \pm 1.6) \times 10^{-6}$ eV ($\omega_{22}y_{22} = -0.101 \pm 0.013$ cm^{-1}). No other experimental data for either $\omega_{22} x_{22}$ or $\omega_{22} y_{22}$ are available for comparison in the literature. To the authors' knowledge no theoretical work reported about the value of these constants.

However, it is noteworthy to mention that for both anharmonicity constants the ratios defined by $[\omega_{22}x_{22}(NH_3^+)/\omega_{22}x_{22}(ND_3^+)]^{1/2}$ and $[\omega_{22}y_{22}(NH_3^+)/\omega_{22}y_{22}(ND_3^+)]^{1/3}$ have about the same value within experimental error, i.e. 1.40 + 0.07 and 1.35 ± 0.20 respectively, i.e. very close to $\sqrt{2} = 1.414$. This value is not very different from the ratio $\omega_2(NH_3^+)/\omega_2(ND_3^+)$ and within experimental error the relationship could be given by:

$$\frac{\omega_2}{\omega_2^i} \propto \sqrt{\frac{\omega_{22}\, x_{22}}{\omega_{22}^i\, x_{22}^i}} \propto \sqrt[3]{\frac{\omega_{22}\, y_{22}}{\omega_{22}^i\, y_{22}^i}}$$

For the first anharmonic constant this relationship holds in a diatomic molecule [24] using a Morse potential. In the case considered here, a more realistic potential is the modified Pöschl-Teller potential [25,26]. This potential takes anharmonicity into account for vibrational modes belonging to a non-degenerate and non-totally symmetric representation like the v_2 deformation in the D_{3h} point group. This potential is defined by the following expression

$$V(\phi) = -\frac{V_0}{\cosh^2\left(\dfrac{\phi}{a}\right)}$$

where φ is the bending angle coordinate and the parameter *'a'* governs the width of the potential well.

It turns out that the bound levels of this potential are given exactly by the same equation as for the Morse potential, corrected by a small additional constant. In the case of the υ_2 normal mode in planar NH_3^+ $\tilde{X}^2A''_2$ state (see Fig. 4), if the small-amplitude motion of the N atom is neglected in a first approximation and only the motion of the H atoms is considered, the vibrational wavenumber and anharmonicity are given by

$$\omega_2 = \frac{\hbar}{4\pi a^2 I_z c}\sqrt{\frac{8 I_z V_0 a^2}{\hbar^2} + 1} \simeq \frac{1}{2\pi ac}\sqrt{\frac{2V_0}{I_z}}$$

$$\text{with } I_z = 3m_H r_{NH}^2 \text{ and}$$

$$\omega_2 x_2 = \frac{\hbar}{4\pi a^2 I_z c}$$

On the basis of this model, we can predict the following isotope effect on the vibrational constants

$$\frac{\omega_2(NH_3^+)}{\omega_2(ND_3^+)} \simeq \sqrt{\frac{m_D}{m_H}} = \sqrt{2}$$

and

$$\sqrt{\frac{\omega_2 \cdot x_2(NH_3^+)}{\omega_2 \cdot x_2(ND_3^+)}} \simeq \sqrt{\frac{m_D}{m_H}} = \sqrt{2}$$

These results would account for the isotope effect observed on both the frequency υ_2 or wavenumber ω_2 and on the anharmonicity constants $\omega_{22}x_{22}$ and possibly $\omega_{22}y_{22}$. Note that these relations can also be deduced by expanding the potential $V(q)$ in even powers of the appropriate normal coordinate q, i.e.

$$V(q) = \tfrac{1}{2}k_2 q^2 + \tfrac{1}{4!}k_4 q^4 + \tfrac{1}{6!}k_6 q^6 + \ldots$$

with

$$k_2 \gg k_4 \gg k_6 \gg \ldots$$

4.2. The weak intensity progression $\upsilon_1 + n\upsilon_2$

A first weak and long progression has been observed in the He(I) photoelectron spectrum of NH_3 and it is displaced with respect to the main peaks. The energy positions of these structures are listed in the second column of Table 2. This progression has usually been assigned to the $\upsilon_1 + n\upsilon_2$ combination mode [12,13].

A least square fit has been applied to these data using Eq. (1) with the observed starting point of the progression at 10.732 eV being assigned to either $2\upsilon_1 + n\upsilon_2$ or $3\upsilon_1 + n\upsilon_2$. For these two possible assignments, two values of the ionization energy $IE_{ad} + _{\upsilon 1}$, corresponding to the ionization and excitation of one υ_1 quantum number, are obtained, i.e. $IE_{ad} + _{\upsilon 1} = 10.491$ eV and $IE_{ad} + _{\upsilon 1} = 10.374$ eV. In both cases the best fit is obtained when truncating Eq. (1) at the third term and by this way an anharmonicity constant $hc\omega_{22}x_{22} = -(8.6 \pm 0.7) \times 10^{-4}$ eV is calculated. This value is also obtained for when the least square fit is applied only to the first ten members of the main progression.

These two possible values of the ionization and υ_1 excitation energy would lead to two possible values of $hc\omega_1$, i.e. 0.422 ± 0.005 eV ($\omega_1 = 3404 \pm 40$ cm^{-1}) or 0.306 ± 0.006 eV ($\omega_1 = 2470 \pm 50$ cm^{-1}) respectively. To our knowledge only one experimental work [12] measured this progression leading to $hc\omega_1 = 0.340$ eV ($\omega_1 = 2742$ cm^{-1}).

By multiphoton (2 + 1) photoelectron spec-troscopy (MPI-PES) Miller et al. [27] interpreted their data by assigning them to $\upsilon_1 + n\upsilon_2$ transitions and determined $\omega_1(NH_3^+) = 3150 \pm 100$ cm^{-1}. These authors explicitly

stated that the interpretation of the progression observed in the He(I) photoelectron spectrum should be incorrect. The ω_1 value proposed by the latter authors is in good agreement with the most accurate ab initio quantum mechanical calculations [11,16]. Botschwina [11] reported $\omega_1 = 3212 \pm 30$ cm^{-1} and suggested to interpret the He(I) photoelectron spectroscopic observations by fitting them by the progression $nv_2 + 2v_4$. Kreamer and Špirko [16] obtained $\omega_1 = 3232$ cm^{-1} in very good agreement with Botschwina [11].

One argument favouring the assignment proposed by Botschwina [11] is that the excitation of the $nv_2 + 2v_4$ combination of vibrational normal modes is symmetry-allowed. However, as will be shown in Section 4.3, the value determined for $2\omega_4$ in this work is 0.372 eV (3000 cm^{-1}), which is significantly smaller than the energy of 0.422 ± 0.006 eV (3404 ± 40 cm^{-1}) observed in this work and assigned to the v_1 normal mode. On the basis of this first argument, the former assignment could very likely be discarded.

An other strong argument against the assignment presented by Rabalais et al. [12] is the comparison between the wavenumbers of the neutral molecule (ω_1=3336 cm^{-1} [23]) and the value $\omega_1 = 2742$ cm^{-1} assigned by Rabalais et al. [12] to the v_1 normal mode of the NH$_3^+$($\tilde{X}^2A''_2$) state. This would correspond to a large modification (about 20%) which should be induced by the ionization out of a NH *bonding* orbital. In fact, the a$_1$ orbital involved in the ionization of NH$_3$ has mainly a NH *non-bonding* character and is not compatible with a fairly dramatic lowering of the wavenumber ω_1 upon ionization.

Contrarily, if the other possible value compatible with our data, i.e. $\omega_1 = 3404 \pm 40$ cm^{-1} is accepted, it indicates a modification of about 2% of the wavenumber with respect to the neutral molecule. If this slight increase is significant, it would indicate a weak antibonding character of the ionized orbital. This would give rise to an increase of the force constant k_1 and a decrease of the NH bond length. Quantum mechanical calculations lead to the opposite conclusion [11,13,16].

The same progression has been observed in the He(I) photoelectron spectrum of ND$_3^+$. In this case a longer progression is observed and the experimental values of the peaks position are recorded in column 2 of Table 4.

These results were also fitted to Eq. (1), starting the progression at $1v_2 + 1v_1$ or $0v_2 + 1v_1$ for an energy measured at 10.435 eV. The results of the fit are listed in column 3 of Table 4 together with their deviation from the experimental values (see column 4). The corresponding ionization energies, including the excitation of one v_1 vibrational quantum number, are IE$_{ad}$ + $_{v1}$ = 10.345 ± 0.009 eV and IE$_{ad}$ + $_{v1}$ = 10.434 eV. The best fit is obtained by Eq. (1) truncated at the third term and the anharmonicity constant $hc\omega_{22}x_{22}$ = -(4.7 ± 1.0) $\times$ 10^{-4} eV. As mentioned earlier, the value of this parameter differs from -8.3 $\times$ 10 $^{-4}$ eV determined above because of the observation of a small portion of the progression only.

With the arguments presented earlier in this section, the ionization energy favoured in this work, and assigned to the v_1 excitation is IE = 10.434 eV and the wavenumber characterizing v_1 is $hc\omega_1 = 0.328 \pm 0.005$ eV ($\omega_1 = 2645 \pm 40$ cm^{-1}). This interpretation could only be compared with theoretical predictions. To the authors' knowledge no previous photoelectron spectroscopic result is available for comparison. Only a few theoretical predictions are reported in the literature, i.e. 2361 cm^{-1} [11] and 3031 cm^{-1} [16]. By (2 + 1) MPI Miller et al. [27] observed the $v_1 + nv_2$ transition in the C' Rydberg state of ND$_3$ and a value of ω_1(ND$_3$, C') = 2324 ± 2 cm^{-1} is reported and is indicative of the value for the ionized state.

On the other hand the present value has to be compared with $hc\omega_1$(NH$_3^+$) = 0.422 ± 0.005 eV ($\omega_1 = 3404 \pm 40$ cm^{-1}) as determined in this work. The isotope effect is measured by the ratio ω_1(NH$_3^+$)/ω_1(ND$_3^+$) = 1.287 ± 0.034. This is fairly close to the expected value of $\sqrt{2}$ predicted by the valence-force field approximation [23].

4.3. The new weak intensity progression $v_4 + nv_2$

In addition to the two progressions already reported in earlier and in the present spectroscopic work, one additional *weak* progression is observed in the low-energy region of the $\tilde{X}^2A''_2$ state of NH$_3^+$. A similar progression shows up more clearly in ND$_3^+$. The peak position corresponding to these weak structures are listed in Table 5 for both NH$_3^+$ and ND$_3$+.

As for the previous results obtained in this work, these experimental data are fitted to Eq. (1) and the result is recorded in Table 5 where the observed structures are assigned to a new $nv_2 + v$ progression with $n = 0$-4 in NH$_3^+$ and $n = 0$-11 in ND$_3^+$. By this least square fit ionization energies IE$_{ad}$ $_+$ $_v$(NH$_3$) = 10.254 ± 0.005 eV and IE$_{ad}$ $_+$ $_v$(ND$_3^+$) = 10.221 ± 0.004 eV are obtained. On the other hand, from the same least square fit the wavenumber assigned to this third vibrational normal mode is $hc\omega$(NH$_3^+$) = 0.186 ± 0.010 eV ($\omega = 1500 \pm 80$ cm^{-1}) and $hc\omega$(ND$_3^+$) = 0.116 ± 0.004 eV ($\omega = 945 \pm 32$ cm^{-1}).

For the assignment of this vibrational normal mode the comparison with the wavenumbers of the corresponding normal modes in the neutral molecule is helpful. Beside the two previously identified vibrations

only two normal modes are possible in NH_3, i.e. the degenerate NH stretching vibration v_3 characterized by $\omega_3 = 3443$ cm^{-1} [28] and the antisymmetric bending vibration v_4 with $\omega_4 = 1627$ cm^{-1}. Both vibrational modes are antisymmetric (E representation) in the C_{3v} point group. They belong to the E representation in the D_{3h} point group. Optical transitions from the NH_3 ground vibronic state $\tilde{X}^1A_1$ to one of these vibrational levels in the ionic state are forbidden under normal circumstances. However, the v_3 vibrational mode has been observed in NH_3^+ by Bawendi et al. [14] by a difference frequency spectrometer combined with a velocity modulation detection. These authors determined molecular constants very accurately and $\omega_3 = 3388.645$ cm^{-1}. This value fits well with the corresponding vibration in neutral NH_3 where $\omega_3 = 3443$ cm^{-1} [28].

The only possible vibrational mode to be assigned to the progression starting at 10.254 eV is the v_4 in-plane bending mode. The wavenumber observed in NH_3^+, i.e. $\omega_4 = 1500 + 80$ cm^{-1}, is fairly close to $\omega_4 = 1627$ cm^{-1} observed in neutral NH_3. The only slight modification upon ionization of this quantity is expected. In ND_3^+ the corresponding wavenumber is $\omega_4 = 945 \pm 32$ cm^{-1} which is related to the wavenumber $\omega_4 = 1191$ cm^{-1} in ND_3 [23]. The ratio measuring the isotope effect $\omega_4(NH_3^+)/\omega_4(ND_3^+)$ is equal to 1.366 in the neutral state, whereas it is 1.587 ± 0.016 in the ionized state. Possibly the discrepancy has to be ascribed partially to the change of symmetry but also to an overestimate of $\omega_4(NH_3^+)$ owing to lack of experimental data in the least square fit.

On the other hand, the present results may be compared with ab initio calculations performed by Kraemer and Špirko [16], who reported values of $\omega_4(NH_3^+) = 1517$ cm^{-1} and $\omega_4(ND_3^+) = 1118$ cm^{-1}. Comparisons made earlier in this discussion between the experimental results obtained in the present work and predictions inferred from these calculations provided quite good agreement. However, as mentioned earlier, the v_4 normal mode is symmetry-forbidden in both the C_{3v} and the D_{3h} symmetry point groups as the normal coordinate $\vec{q}_4$ belongs to the doubly degenerate E' representation. Kraemer and Špirko [16] calculated the ground state potential energy surface of NH_3^+ at various levels of theory (complete active space SCF, multi-reference CI, coupled-pair-function). They fitted their calculated points and some experimental data to an empirical analytical function. With this potential function they calculated vibrational energies taking into account

Table 7 *Comparison between the experimental vibrational energies (eV) obtained in this work and the calculated data of Kraemer an Špirko [16].*

NH_3^+			ND_3^+		
Experimental energies (this work)	Calculated energies [16]	Assignments $\ell v_1 + mv_2 + nv_4$	Experimental energies (this work)	Calculated energies [16]	Assignments $f v_\gamma + mv_2 + nv_4$
10.069	-	0 + 0 + 0	10.104	-	0 + 0 + 0
10.182	10.181	0 + 1 + 0	10.195	10.189	0 + 1 + 0
10.259	10.257	0 + 0 + 1	10.224	10.243	0 + 0 + 1
10.293	10.297	0 + 2 + 0	10.278	10.277	0 + 2 + 0
10.365	10.368	0 + 1 + 1	10.307	10.327	0 + 1 + 1
10.411	10.417	0 + 3 + 0	10.369	10.367	0 + 3 + 0
10.495	10.482	0 + 2 + 1	10.398	10.414	0 + 2 + 1
10.531	10.540	0 + 4 + 0	10.435	10.480	1 + 0 + 0
10.596	10.599	0 + 3 + 1	10.460	10.458	0 + 4 + 0
10.657	10.666	0 + 5 + 0	10.493	10.502	0 + 3 + 1
10.732		1 + 2 + 0	10.522		1 + 1 + 0
10.732		0 + 4 + 1	10.554	10.552	0 + 5 + 0
10.782	10.794	0 + 6 + 0	10.580		0 + 4 + 1
10.856		1 + 3 + 0	10.614		1 + 2 + 0
10.910	10.924	0 + 7 + 0	10.647	10.647	0 + 6 + 0
10.982		1 + 4 + 0	10.672		0 + 5 + 1
11.038	11.056	0 + 8 + 0	10.701		1 + 3 + 0
11.107		1 + 5 + 0	10.740	10.743	0 + 7 + 0
11.170	11.190	0 + 9 + 0	10.771		0 + 6 + 1
			10.800		1 + 4 + 0
			10.835	10.841	0 + 8 + 0
			10.867		0 + 7 + 1
			10.891		1 + 5 + 0
			10.933	10.940	0 + 9 + 0

The experimental energy of the vibrationless level measured in this work is taken as the reference.

vibro-rotational couplings within the non-rigid inverter Hamiltonian approximation. The most salient conclusion of their work is the occurrence of a *strong* (*x-y*) Coriolis interaction [16] between the υ_2 and the υ_4 bending vibrational states of the NH_3^+ ($\tilde{X}^2A''_2$) electronic state. The symmetry condition to be obeyed is now that the direct product between the three irreducible representations corresponding to, respectively, the υ_4 normal mode, the rotational motion about the *x* or *y* axis and the υ_2 mode contains the totally symmetric representation, i.e.

$$\Gamma\left(\vec{q}_4\right) \otimes \Gamma\left(R_x, R_y\right) \otimes \Gamma\left(\vec{q}_2\right) \supset A'_1$$

In the D_{3h} point group

$$\vec{q}_4 \in E', \left(R_x, R_y\right) \in E'', \vec{q}_2 \in A''_2$$

The direct product is then equal to $A_1' + A_2' + E'$, so that transitions giving rise to the $n\upsilon_2 + \upsilon_4$ progression become allowed. An additional argument favouring this assignment comes from the comparison of the experimental vibrational energies measured in this work and the corresponding data calculated by Kraemer and Špirko [16] and shown in Table 7. For the $n\upsilon_2$ and the $n\upsilon_2 + 1\upsilon_4$ progressions and in both NH_3^+ and in ND_3^+ the agreement is very satisfactory. The Coriolis coupling is expected to be large enough to bring about the small intensity features observed in the photoelectron spectrum. Our data give therefore a direct and quantitative experimental evidence of a coupling between two vibrational normal modes in an ionized molecule. Such couplings are of fundamental importance in molecular dynamics as they bring about the rapid intramolecular vibrational energy redistribution which is the basic condition for the statistical theories to be applied.

5. Conclusions

The careful examination of the high-resolution NH_3 and ND_3 He(I) photoelectron spectrum allowed us to perform accurate measurements and to interpret of the complete vibrational structure of the $\tilde{X}^2A''_2$ state of NH_3^+ and ND_3^+. Three vibrational progressions, involving the excitation of three different vibrational normal modes, were observed.

First, the well-known and strongest progression corresponding to the excitation of the υ_2 out-of-plane bending normal mode has been characterized not only by its energy $hc\omega_2 = 0.109 \pm 0.001$ eV ($\omega_2 = 878 \pm 7$ cm^{-1}), but also by the first anharmonicity constant $hc\omega_{22}x_{22} = -(16.2 \pm 1.2) \times 10^{-4}$ eV ($\omega_{22}x_{22} = -13.0 + 1.0$ cm^{-1}) in very good agreement with the most accurate spectroscopic determinations. The best fit of the experimental data required the introduction of a higher-order term interpreted as the second anharmonicity constant

$$hc\omega_{22}y_{22} = -(30.7 \pm 4.2) \times 10^{-6} \quad eV \quad (0.248 \pm 0.034 \text{ cm}^{-1}).$$

Secondly, a first weak progression has generally been assigned to the excitation of a combination of $\upsilon_1 + n\upsilon_2$ vibrations where υ_1 corresponds to the degenerate NH stretching vibrational mode. The appropriate data analysis performed in this work provided two different possibilities for the energy of υ_1, i.e. $hc\omega_1 = 0.306 \pm 0.006$ eV ($\omega_1 = 2470 \pm 50$ cm^{-1}) or 0.422 ± 0.005 cV($\omega_1 = 3404 \pm 40$ cm^{-1}). Together with several other arguments, the analysis of the present data favours the latter value to be ascribed to υ_1.

Finally, a second series of weak structures has been assigned to the excitation of a $\upsilon_4 + n\upsilon_2$ progression, reported for the first time. The energy associated with this vibrational motion is $hc\omega_4 = 0.186 \pm 0.010$ eV ($\omega_4 = 1\,500 \pm 80$ cm^{-1}). This doubly degenerate symmetry-forbidden in-plane bending vibrational mode becomes allowed through a strong vibro-rotational Coriolis coupling between the υ_4 and υ_2 vibrational motions, as discussed by Kraemer and Špirko [16].

These transitions have also been observed in ND_3^+ where the corresponding molecular constants have been derived and the isotope effect has been investigated.

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