Double Differential Cross Sections and Generalized Oscillator Strength Distributions of Ammonia

Karin Yamamoto, Keisuke Nogami, Yuta Hino, and Yasuhiro Sakai
Department of Physics, Toho University, Miyama 2-2-1, Funabashi, Chiba, 2748510 Japan
E-mail: karin@ph.sci.toho-u.ac.jp

Abstract. The absolute double differential cross section (DDCS), the generalized oscillator strength distribution (GOSD), and the ionization efficiency of ammonia (NH₃) were investigated from the threshold to 40 eV under the condition of 200 and 400 eV incident electron energies and 6 and 8 degree scattering angles using electron energy-loss spectroscopy and electron-ion coincidence techniques. To determine the absolute values, we used a mixture of helium (He) and NH₃ and normalized the measured relative DDCS spectrum by the differential cross section for 2¹P excitation of He. Our results are in close agreement with previous dipole (e, e) spectroscopy, although the incident electron energy is lower. The ionization efficiency curve obtained from coincidence measurements indicated the existence of doubly excited states that cause neutral dissociation.

1. Introduction
Differential cross sections (DCSs) and generalized oscillator strengths (GOSs) are fundamental quantities obtained from electron energy-loss spectra. They provide information on the electronic structure of matter and its interaction with electromagnetic radiation. The concept of GOS was introduced by Bethe [1, 2] in 1930 based on the first Born approximation. Essentially the GOS is a function of the magnitude of momentum transfer only. When the first Born approximation is not valid, a similar calculated quantity depends on both the magnitude of momentum transfer and the incident electron energy. This is sometimes known as the apparent GOS. Here, we use the term GOS regardless of whether the first Born approximation was valid. Much theoretical and experimental work on optically forbidden transitions and excited states in continuum regions remains to be done, but a wealth of DCS and GOS data exist for various excited states lying in discrete region in atoms and molecules. Determination of the absolute DCS is difficult in the region where the first Born approximation is not valid. In general, when the incident electron energy is high, we can use the TRK sum rule [3] to normalize the GOS from the electron energy-loss spectrum. If the incident electron energy is not high enough, the difference between the summation of total scattered signal and the TRK sum rule [3] cannot be ignored. Therefore, the energy regions and potentials of these states are not well understood.

We have developed a new normalization method for the determination of absolute DCS under the condition that the incident energy is not high enough, and we have studied the excitation and ionization processes of ammonia (NH₃). NH₃ plays an important role in the physics and chemistry of the upper atmosphere of the Earth and other planets. The study of doubly excited states in NH₃ has mainly entailed photo-ionization experiments [4]. In these studies, the
ionization efficiency (ratio of photo-ionization to photo-absorption cross section) was obtained as a function of impact photon energy. The doubly excited states and their decay processes were discussed using ionization efficiency curves. In electron-impact experiments, oscillator strengths for the photo-absorption, photo-ionization and photo-dissociation of NH$_3$ were determined by Wight et al. using much higher electron energies [5]. However, in these studies, information on optically forbidden doubly excited states was not obtained because of the high-energy electron impact. Additionally, the cross sections for the emission of fluorescence by neutral fragments in the photo-excitation of NH$_3$ were measured as a function of impact photon energy by Kato et al. [6] Most recently, the electron energy-loss spectrum of NH$_3$ tagged by Lyman-α photons was demonstrated for 100 eV incident electron energy and at 8 deg scattering angle by Ishikawa et al. [7] These measurements are also tools for obtaining information on doubly excited states in molecules. Two optically forbidden doubly excited states of NH$_3$ were predicted by Ishikawa et al. [7].

In electron-impact experiments, smaller incident energies (larger momentum transfer $K^2$) reveal information on optically forbidden states. We have demonstrated the measurement of the DCSs and GOSs of NH$_3$ for 200 and 400 eV incident electron energies and 6 degree scattering angle. Furthermore, to obtain information on the optically forbidden doubly excited states of NH$_3$, we obtained the ionization efficiency curve by scattered electron- ion coincidence measurements for 200 eV incident electron energy and 8 degree scattering angle.

2. Experimental setup

The experimental apparatus used was an (e, e+ ion) spectrometer, which could measure the intensity of the formed ions at the same time as the scattered electrons, as a function of excitation energy.

The apparatus consisted of a pulsed electron gun, an electron-energy analyzer, and a time-of-flight (TOF) mass analyzer, as shown in Fig.1. The components were enclosed in a vacuum chamber, which was evacuated by a 520 L/s turbo molecular pump (TMP). We furnished the chamber with a 230 L/s TMP for the TOF mass analyzer as a differential pumping system. The ultimate vacuum pressure was lower than several $10^{-7}$ Pa, and the pressure was kept to $3 \times 10^{-4}$ Pa or less during the measurements.

![Figure 1. Schematic of the experimental apparatus.](image-url)
An electron beam emitted from a hairpin-type tungsten filament was accelerated and collimated by an electrostatic lens system, and was pulsed before emerging into the collision region. A target molecular beam was continuously generated from an effusive nozzle. The pulsed electron beam and the molecular beam crossed each other at the center of the 20 mm wide collision region. Hence, the pulsed electrons collided at right angles with the target molecules (crossed-beam geometry). The collision energies of the incident electrons were from 100 to 400 eV. The primary (continuous) electron current was about 1 nA, on average. After colliding with the target molecules, scattered electrons were analyzed with the electron-energy analyzer, and the formed ions were extracted from the collision region by application of a pulsed electric field. They were then analyzed using a Willy-McLaren type [8] TOF mass analyzer. The electron-energy analyzer was a simulated hemispheric electrostatic type [9] with a mean trajectory radius of 52 mm. The typical energy resolution was about 0.5 eV (full width at half-maximum: FWHM) for the present experiments. After acceleration along a 10 mm long second acceleration region, the extracted ions passed through a 480 mm field-free region. They were detected using a microchannel plate (MCP). We used a mixture of helium (He) and ammonia (NH$_3$) as the sample, to normalize the differential cross sections (DCSs) of NH$_3$ in the electron energy-loss spectra. A quadrupole mass spectrometer (QMS) installed in our apparatus next to the original TOF mass analyzer was used to confirm the mixing ratio $M$ of NH$_3$ to He. The mixing ratio $M$ is

$$M = \frac{I_{\text{NH}_3}}{I_{\text{He}}} \times \frac{\sigma_{\text{He}^+}}{\sigma_{\text{NH}_3^+}},$$

where $I$ is the observed signal intensity in the mass spectrum, $\sigma$ is the partial ionization cross section, and the subscripts denote the species.

Using the mixing ratio $M$, we estimated the DCSs of the molecules of interest. Some peaks and structures corresponding to the mixing ratio appeared in the electron energy-loss spectrum, which originated from NH$_3$ and He. Because the DCS for excitation of the $2^1P$ state in He is well known, the DCSs for the NH$_3$ excitations of interest could be estimated from

$$\left(\frac{d\sigma}{d\Omega}\right)_{2^1P} = \frac{I_{\text{NH}_3}}{I_{\text{He}}} \left(\frac{d\sigma}{d\Omega}\right)_{2^1P} / M,$$

where $I$ is the relative intensity of the electron energy-loss spectrum, and $d\sigma/d\Omega$ indicates the DCS. Therefore, the generalized oscillator strength (GOS) $F$ was determined using this absolute DCS value: [10]

$$F\left(K^2, E_i\right) = \frac{W}{2} \frac{k_i}{k_s} K^2 \left(\frac{d\sigma}{d\Omega}\right),$$

where $W$ is the excitation energy and $k_i$ and $k_s$ are the momentum of incident and scattered electrons, respectively. $K^2$ is the magnitude of momentum transfer

$$K^2 = k_i^2 + k_s^2 - 2k_i k_s \cos \theta,$$

where $\theta$ is the scattering angle. All quantities are in atomic units. For excitation energies greater than the first ionizing energy, the relationship between the DCS and GOS is

$$\frac{dF\left(K^2, E_i\right)}{dE} = \frac{W}{2} \frac{k_i}{k_s} K^2 \left(\frac{d^2\sigma}{dEd\Omega}\right),$$

where $dF/dE$ is the generalized oscillator strength distribution (GOSD) and $d^2\sigma/(dEd\Omega)$ is the double differential cross section (DDCS).
3. Results and discussion
3.1. Absolute double differential cross sections and generalized oscillator strength distributions of ammonia

The electric configuration of the ground state in C$_{3v}$ symmetry of NH$_3$ is (1a$_1$)$^2$ (2a$_1$)$^2$ (1e)$^4$ (3a$_1$)$^2$. The ionization thresholds for the (3a$_1$), (1e), and (2a$_1$) states are 10.85, 16.4, and 27.3 eV, respectively [11, 12].

Figure 2 shows typical electron energy-loss spectra of the He-NH$_3$ mixture gas and the pure NH$_3$ gas under the condition of 200 eV incident electron energy and 6 degree scattering angle. We found two peaks around 20 eV that are not seen in pure NH$_3$ gas in the spectrum of the mixture gas. These were the $^2$P and $^3$P excitation peaks of He. The mixing ratio $M$ was obtained from (1) as 0.75. The intensities $I_{\text{NH}_3^+}$ and $I_{\text{He}^+}$ were measured with QMS for 70 eV impact energy, and each of the partial cross sections was substituted as $\sigma_{\text{NH}_3^+}$ and $\sigma_{\text{He}^+}$. As $\sigma_{\text{NH}_3^+}$ and $\sigma_{\text{He}^+}$, we used an experimental value measured by Rejoub et al. [13] and a theoretical one calculated by Kim et al. [14] respectively. Using the mixing ratio $M$, the intensity, and the DCS for the $^2$P excitation peak of He, we determined the absolute DCSs of NH$_3$ from energy-loss spectra under the condition of 200 and 400 eV incident electron energies and 6 degree scattering angle.

![Typical electron energy-loss spectra of the He-NH$_3$ mixture gas and the pure NH$_3$ gas.](image)

**Figure 2.** Typical electron energy-loss spectra of the He-NH$_3$ mixture gas and the pure NH$_3$ gas: for 200 eV incident electron energy at 6 degree scattering angle. In the spectrum of the He-NH$_3$ mixture, the mixing ratio $M$ was 0.75. The peaks at 21 and 23 eV are $^1$P peaks of He, which were the main optically allowed transitions. The optically forbidden transitions contributed little to peak formation under the present experimental conditions.

The absolute GOSDs of NH$_3$ are shown in Figs. 3 (a) and (b), which were determined at 6 degrees for 200 eV and 400 eV incident electron energies, respectively. Figure 3 (c) shows the absolute optical oscillator strength determined by dipole (e, e) spectroscopy [15]. The magnitude of momentum transfer $K^2$ calculated by the energy loss and the scattering angle is given on the u-axis (upper horizontal axis). In these experiments, the values of $K^2$ ranged from about 0.15 to 0.3 a.u. for 200 eV, and from about 0.3 to 0.4 a.u. for 400 eV. The shape structures observed around 6.5 and 9.5 eV corresponded to excitations of valence (3a$_1$) and (1e) electrons to a
Rydberg state, respectively [15]. Although both peaks around 12 and 16 eV corresponded to the excitation of (1e) electrons, the ionization of (3a₁) electrons contribute to form these structures, because they appeared over the first ionization threshold. These features are common to these two results and the optical oscillator strengths from dipole (e, e) spectroscopy [15]. We were not able to detect any non-dipole transitions.

![Figure 3](image.png)

**Figure 3.** Absolute generalized oscillator strength distributions of NH₃: (a) our results for 200 eV incident electron energy at 6 degree scattering angle, (b) our results for 400 eV incident electron energy at 6 degree scattering angle, and (c) the dipole (e, e) results of Burton et al. [15]

### 3.2. Ionization efficiency curve of ammonia

To obtain the relative ionization efficiency, we divided the total ionic GOSD determined by the electron-ion coincidence by the total GOSD determined from the electron energy-loss spectrum. The ionization efficiency should be 1 when all processes are associated with ionization at a given excitation energy. As it is known that there are no doubly excited states in the 19-21 eV electron energy-loss region [7], we normalized the relative ionization efficiency to 1 in that region.

The ionization efficiency curve of NH₃ for 200 eV incident electron energy at 8 degree scattering angle is shown in Fig. 4. Both the photo-ionization results by Samson et al. [4] and the dipole (e, e+ ion) experiment results by Wight et al. [5] are shown in Fig. 4 for comparison. Clearly, the present efficiencies are in close agreement with the previous ones over the 10-20 eV energy range. However, our efficiency curve is slightly lower from 22 to 28 eV and from 30 to 36 eV than previous results [4, 5]. This means that optically forbidden doubly excited states exist in the range of 22-28 eV and 30-36 eV that decay by neutral dissociation.
Figure 4. Ionization efficiency curves of NH$_3$: our results for 200 eV incident energy at 8 degree scattering angle (■); the dipole (e, e+ion) results of Wight et al. (□) [5]; the photo-ionization results of Samson et al. (□) [4].

The existence of doubly excited states that cause neutral dissociation in this region has already been proposed by Ishikawa et al. [7], and is confirmed by our experiments.

4. Summary
We have investigated the DDCSs, GOSDs and ionization efficiency of NH$_3$. We used a mixture of He and NH$_3$ as the sample to determine the absolute DDCSs and GOSDs of NH$_3$. With this method, we could determine the absolute values without using the TRK sum rule. This means that we could discuss the GOS and GOSD even though the first Born approximation was not valid. Both GOSDs determined with 200 and 400 eV incident electron energies and 6 degree scattering angle have shown similar behavior to the optical oscillator strength obtained in previous dipole (e, e) spectroscopy. The ionization efficiency curve obtained by the coincidence measurements was slightly lower from 22 to 28 eV and 30 to 36 eV than the photo-ionization and dipole (e, e+ ion) results. Therefore, the existence of doubly excited states that cause neutral dissociation was confirmed by our experiments in these ranges. We will study a wider range of incident electron energies, scattering angles, and molecules in near future.

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