# Total electron scattering cross sections of $PH_3$ and $SiH_4$ molecules in the energy range 90–3500 eV

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(Received 21 February 2003; published 12 September 2003)

Total electron scattering cross sections of $PH_3$ and $SiH_4$ molecules have been obtained for 90–3500-eV electrons by measuring the attenuation of the electron beam through a gas cell. The present cross sections are compared to existing experimental cross sections as well as to theoretical predictions. No previous experimental electron scattering cross sections of $PH_3$ are reported in the literature.

DOI: 10.1103/PhysRevA.68.032708 PACS number(s): 32.80.Cy, 34.80.Bm, 34.80.−i

## I. INTRODUCTION

Total cross sections of electron scattering from atoms and molecules have been a subject of continuing investigation for many decades. Accurate experimental cross sections, required in applications in astrophysics, atmospheric physics, chemical physics, plasma physics, and semiconductor physics, are essential in developing theoretical models to understand the electron-atom interaction process. In recent years, the interest of this area of research has been focused at intermediate electron energies (400–5000 eV) [1–10] because the total electron cross-section measurements at these energies are sparsely available or not available for many atoms and molecules. For example, the experimental electron scattering cross section of the phosphine ($PH_3$) molecule is not reported in the literature. $PH_3$ gas is an important doping agent in the semiconductor industry; it is contained in some planetary atmospheres and interstellar atmospheres. Knowledge of the electron scattering cross section of $PH_3$ should be useful in these applications. About ten years ago, Zecca, Karwasz, and Brusa [11] measured the scattering cross section of three hydride molecules ($NH_3$, $H_2S$, and $SiH_4$) for 75–4000-eV energy electrons, developed a two-parameter formula to predict the cross section of hydrides at 200 eV or higher energies, and indicated the interest of the cross section of $PH_3$ and other hydrides for comparison with this formula. At the same time, Jain and Baluja [12] reported the theoretical cross sections of several molecules including $PH_3$ and stated the need for experimental cross sections of $PH_3$ in the keV energy range for comparison.

The present experiment was undertaken to measure the total electron scattering cross section of $PH_3$ and $SiH_4$ for 90–3500-eV electron energies. Though the cross sections of $SiH_4$ have been measured previously [11,13] for this energy range, these measurements are repeated in this experiment for comparison purposes. The present cross sections are compared with the existing theoretical predictions including the model proposed in Ref. [11].

## II. EXPERIMENT

The experimental arrangement, designed to measure the cross section based on linear transmission technique, is described in details in Refs. [14] and [15]. Briefly, a 90–3500-eV energy electron beam obtained from a Kimball Phys EGG 3101 electron gun was passed through a 24.5-cm-long gas cell with 0.76-mm-diam entrance and exit apertures. Electrons emerging from the gas cell pass through a double focusing electrostatic analyzer (ESA) whose entrance is 4.5 cm away from the exit of the gas cell. The ESA was operated in the constant 50-eV energy transmission mode with 1-mm-diam entrance and exit apertures. At these settings, the ESA resolution is 0.75 eV (full width at half maximum) or better and the accuracy of the energy scale is 0.1 eV or better. Electrons transmitted through the analyzer were collected on a Faraday cup and the intensity, typically about $10^{-10}$–$10^{-13}$ A, was measured by an electrometer (Keithley Model 6517-A). The Faraday cup, ESA, gas cell, and electron gun were shielded from Earth's magnetic field and other stray magnetic fields and maintained in a vacuum in the low $10^{-7}$ Torr region. When the gas was present in the gas cell, the pressure in the regions where the Faraday cup, ESA, and the electron gun are located was $1\times10^{-5}$ Torr or better.

## III. PROCEDURE AND ERRORS

The experimental procedure is based on the measurement of the electron-beam intensity attenuation through a gas. If the intensities of the attenuated beam and primary beam, respectively, are $I$ and $I_0$,

$$I = I_0 e^{-\sigma n P L}, \tag{1}$$

where $n$ is the number density of the molecules at 1 mTorr pressure, $P$ is the pressure in units of mTorr, $L$ is the gas-electron interaction length in m, and $\sigma$ is the total scattering cross section in $m^2$. According to this relationship, the variation of $\ln(I/I_0)$ with $P$ is a straight line whose slope is a measure of $\sigma$. An accurate determination of $\sigma$ requires an accurate measurement of $L$, $P$, $I$, and $I_0$.

In the present experiment, the geometrical length of the gas cell, 24.5 cm, was used as the gas-electron interaction length. It has been proven in the past [14,16–18] that the geometrical length of the type of gas cells use in the present experiment is essentially the interaction length. After measuring the geometrical length of the gas cell along with the thickness of the exit and entrance aperture plates, the error in the estimation of $L$ is determined to be 2% or less.

 

The gas pressure in the gas cell was measured by an MKS Baratron 126 A capacitance manometer. Possible errors in the pressure measurement by this device are mainly due to the zero drift in the scale and the temperature difference between the capacitance manometer head and the gas chamber. According to the manufacturer's specifications, the combined error due to zero drift and temperature differences is estimated to be 2% or less.

The intensity of the primary beam ($I_0$) and attenuated beam ($I$) were measured accurately by the ESA, Faraday cup, and electrometer combination after deflecting away the inelastically scattered electrons. However, the elastically scattered electrons in the forward direction are not distinguished in this method. In linear transmission-type cross-section measurements, the contribution from the elastically scattered electrons in the forward direction can be minimized by reducing the angular acceptance of the ESA. In the present experimental setup, the solid angle subtended by the entrance of the ESA and the center of the gas cell (angular acceptance) is about $1.2\times10^{-5}$ sr. Garcia and Manero [19] have studied the contributions from zero degree elastically scattered electrons in transmission-type experiments with the angular acceptance of about $10^{-5}$ sr using carbon dioxide ($CO_2$). As can be seen from their analysis, the error due to this contribution is less than 0.3% up to 5000-eV electron energy for $CO_2$. Since the number of electrons in $PH_3$ and $SiH_4$ is less than those of $CO_2$, it is reasonable to assume that this contribution in the present experiment is also 0.3% or lower. On the other hand, the contribution from the zero degree elastic scattering in the present experiment was estimated by extrapolating the experimental elastic scattering differential cross sections of Tanaka *et al.* [20] for $SiH_4$. It was found that the error due to the zero degree elastic scattering is about 0.1% or less for $SiH_4$.

Research grade target gases of $PH_3$, from Liquid Air Corp., Denver, CO, and $SiH_4$, from Matheson Co., Laporte, TX, both within minimum purity 99.9% or better, were used. An on-site residual gas analyzer (RGA), attached to the vacuum chamber where the ESA was housed, was used to make sure there was no air leak or other gas contaminant in the gas transport system. The cross-section measurements were performed using 0.5–10 mTorr gas pressure and $10^{-10}$–$10^{-13}$ A electron currents. For these pressures and currents no dependence of the cross section was found on the pressure or current.

Errors in the cross sections reported in this work arise from essentially five sources: (i) gas-electron interaction length determination (2% or less), (ii) pressure measurement (2% or less), (iii) contribution from the zero degree elastic scattering (1% or less), (iv) current measurement including possible current fluctuations during the experiment (2% or less), and (v) statistical error in determination of the slope (1% or less). These random errors combined quadratically to give a random error assignment of 4% or less for energies 300–3500 eV. At 200 eV and lower energies, the current was not as stable as at higher energies. As a result, there is an additional 4% error, giving the total error 6% or less in the cross sections at these energies.

TABLE I. Total cross section for electron scattering from $SiH_4$ and $PH_3$ in units of $10^{-20}$ $m^2$.

| Energy (eV) | $SiH_4$ | | | $PH_3$ |
|---|---|---|---|---|
| | This experiment | Ref. [11] | Ref. [13] | This experiment |
| 90 | 15.0±1.01 | 15.7 | 15.0 | 13.6±0.9 |
| 100 | 14.2±1.01 | 14.7 | 14.4 | 12.3±0.9 |
| 150 | 11.8±0.7 | 12.3 | 12.2 | 10.4±0.6 |
| 200 | 10.0±0.60 | 10.7 | 10.6 | 9.17±0.5 |
| 300 | 7.63±0.40 | 7.92 | 8.3 | 7.33±0.4 |
| 400 | 6.37±0.25 | 6.55 | 7.0 | 6.13±0.25 |
| 500 | 5.31±0.21 | 5.52 | | 5.15±0.20 |
| 600 | 4.49±0.18 | 4.67 | | 4.36±0.17 |
| 700 | 4.00±0.16 | 4.14 | | 3.93±0.16 |
| 800 | 3.69±0.15 | 3.67 | | 3.55±0.14 |
| 900 | 3.46±0.14 | 3.30 | | 3.33±0.13 |
| 1000 | 3.11±0.12 | 3.01 | | 2.96±0.11 |
| 1100 | 2.86±0.11 | 2.79 | | 2.75±0.11 |
| 1200 | 2.65±0.10 | | | 2.55±0.10 |
| 1250 | | 2.55 | | |
| 1400 | 2.41±0.10 | | | 2.32±0.10 |
| 1500 | | 2.17 | | |
| 1600 | 2.10±0.09 | | | 2.10±0.09 |
| 1750 | | 1.85 | | |
| 1800 | 1.94±0.08 | | | 1.94±0.08 |
| 2000 | 1.77±0.07 | 1.63 | | 1.76±0.07 |
| 2250 | 1.66±0.06 | 1.45 | | 1.65±0.06 |
| 2500 | 1.56±0.06 | 1.32 | | 1.54±0.06 |
| 3000 | 1.34±0.06 | 1.09 | | 1.30±0.06 |
| 3500 | 1.19±0.05 | 0.937 | | 1.18±0.05 |

## IV. RESULTS

Given in Table I are the measured total electron scattering cross sections of $PH_3$ and $SiH_4$ in the energy range 90–3500 eV. These cross sections are mean values of four to eight individual measurements. Each individual measurement was obtained by measuring the attenuated electron beam current for eight to ten different gas pressures, plotting the $\ln(I/I_0)$ against the pressure graph and obtaining the slope of it. In the same table the cross sections produced in other laboratories are also given for comparison.

## V. DISCUSSION

As can be seen from the table, the cross sections produced in the present experiment are in agreement with those produced by Zecca, Karwasz, and Brusa [11] for energies up to 1100 eV. At energies 2000 eV and above, the present cross sections are systematically higher that those of Zecca, Karwasz, and Brusa [11] reaching the highest percentage difference about 25% at 3500 eV. Though there are no common energy values to compare the cross sections produced in two laboratories directly between the energies 1100 and 2000 eV, it is apparent that the present cross sections are higher than those reported in Ref. [11] for these energies. In the comparison of $SiH_4$ cross sections produced in the present experi-

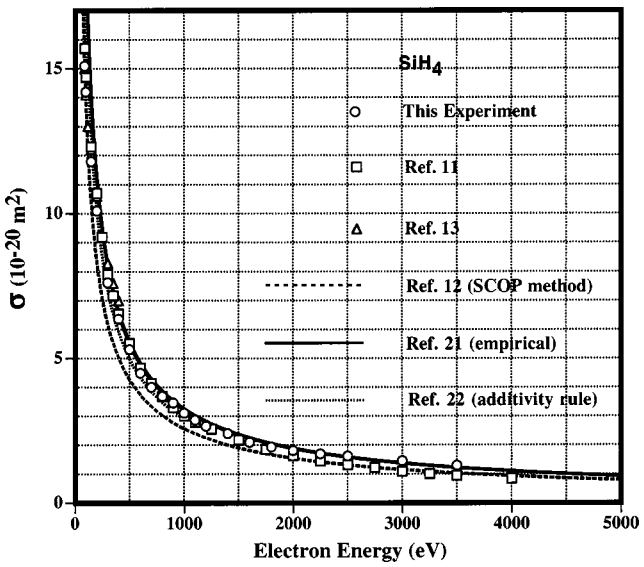


FIG. 1. Total electron scattering cross sections of $SiH_4$ in $10^{-20}$ $m^2$. The circles are the present measurements. The squares and the triangles are, respectively, the experimental cross sections of Zecca, Karwasz, and Brusa [11] and Sueoka, Mori, and Hamada [13]. The dashed and dotted lines are, respectively, the theoretical predictions by Jain and Baluja [12] and Jiang, Sun, and Wan [22] while the solid line is the predictions by an empirical model of Garcia and Manero [21].

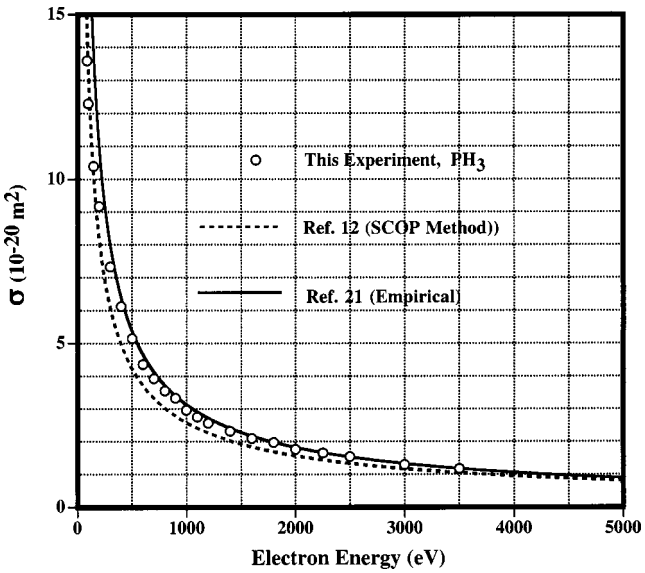


FIG. 2. Total electron scattering cross sections of $PH_3$ in $10^{-20}$ $m^2$. The dashed curve is the theoretical predictions by Jain and Baluja [12] while the solid curve is the predictions by Garcia and Manero [21].

ment with those of Sueoka, Mori, and Hamada [13], it is apparent that the cross sections at 200 eV and lower energies are in agreement with the present measurements, but those at 300 and 400 eV are about 10% higher than the present cross sections. A comparison of the cross section between $SiH_4$ and $PH_3$ reveals that the $PH_3$ cross sections are consistently lower than those of $SiH_4$ up to about 1400 eV. At energies higher than 1400 eV, the two cross sections tend to merge together. A similar type of behavior was observed by Zecca, Karwasz, and Brusa [11] in the measurement of cross sections of $SiH_4$ and $H_2S$: at higher energies the cross section of $H_2S$ merged with that of $SiH_4$.

Recently, Garcia and Manero [21] proposed an empirical formula for the cross sections at intermediate energies (0.5–5 keV) for molecules with 10–22 electrons. This model predicts the cross section $\sigma$ at energy $E$ as

$$\frac{\sigma}{a_0^2}=\left(0.4z+0.1\frac{\alpha}{a_0^3}+0.7\right)\left(\frac{E}{1\ \text{keV}}\right)^{-0.78}, \qquad (2)$$

where $z$ and $\alpha$ are, respectively, the number of electrons in the target molecule and the polarizability (in units of $a_0^3$) of the target molecule. In order to compare the $SiH_4$ cross sections with the predictions by this empirical formula, the present cross sections are scaled as a function of energy along with Garcia and Manero's predictions in Fig. 1. In the same figure, the experimental cross sections produced in other laboratories [11,13] as well as other existing theoretical predictions [12,22] are given for comparison. As can be seen from this figure, the predictions by Garcia and Manero are in good agreement with the present cross section at energies 300 eV and above. Theoretical predictions made by Jain and Baluja [12], based on the spherical-complex-optical-potential method (SCOP), are consistently lower (15–30 %) than the experimental values. The theoretical predictions by Jiang, Sun, and Wan [22], available only up to 1000-eV energy, are also in closer agreement with the present experimental cross sections and those of Zecca, Karwasz, and Brusa [11].

Displayed in Fig. 2 are the present cross sections of $PH_3$ as a function of electron energy. In this figure, existing theoretical predictions are given for comparison. Again the predictions by the model proposed by Garcia and Manero [21] are in good agreement with the experimental cross sections for energies 300 eV and higher, but those of Jain and Baluja [12] are 15–30 % lower than the experimental cross sections. However, at energies 200 eV and lower, the predictions by Jain and Baluja [12] are in good agreement with the present measurements.

In Ref. [11], where Zecca, Karwasz, and Brusa have reported the cross sections of several hydrides including $SiH_4$, the electron scattering cross section ($\sigma$) of hydrides is related to energy ($E$) by a two-parameter ($\sigma_0$ and $B$) formula,

$$\sigma=\frac{\sigma_0 B}{B+\sigma_0 E}. \qquad (3)$$

According to this relationship, the reciprocal of the cross section must linearly increase with increasing energy. In order to test the validity of this relationship, the reciprocals of the present cross sections are scaled with energy as shown in Fig. 3, where it can be seen that the present cross sections deviate from this formalism at energies higher than 1200 eV for both gasses.

For fast-moving charged particles, the Bethe theory gives an asymptotic formula for the total inelastic cross section [23,24] while the Born approximation gives the total elastic

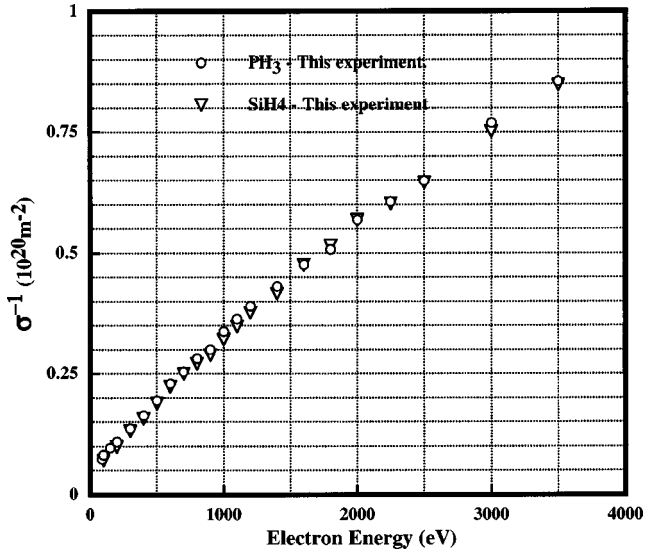


FIG. 3. The variation of the reciprocal of present $SiH_4$ and $PH_3$ cross sections with increasing energy.

cross section [25]. The combined Bethe-Born theory of Inokuti [23] expresses the total cross section ($\sigma$) in terms of the following formula:

$$\frac{E}{R}\frac{\sigma}{\pi a_0^2} = A_{\mathrm{el}} + B_{\mathrm{el}}\frac{R}{E} + C_{\mathrm{el}}\left(\frac{R}{E}\right)^2 + 4M_{\mathrm{tot}}^2 \ln\left[4c_{\mathrm{tot}}\frac{E}{R}\right], \quad (4)$$

where $E$ is the incident energy in eV, $R$ is the Rydberg energy, $a_0$ is the Bohr radius, and $A_{\mathrm{el}}$, $B_{\mathrm{el}}$, $C_{\mathrm{el}}$, $M_{\mathrm{tot}}$, and $C_{\mathrm{tot}}$ are constants depending on the physical properties of the target molecule. Jain and Baluja [21] used Bethe-Born theory in the following form:

$$\frac{E}{R}\frac{\sigma}{a_0^2} = d\ln\left(\frac{E}{R}\right) + b\left(\frac{R}{E}\right) + c \quad (5)$$

and determined the constants $a$, $b$, and $c$ using their theoretical cross sections, determined by the SCOP method, of $PH_3$ and $SiH_4$. However, these constants cannot be used to compare the present cross sections because the theoretical cross sections in Ref. [12] are 15–25 % lower than present cross sections as displayed in Figs. 1 and 2. Instead, the general formalism of Eq. (5) is used to compare the present results with the Bethe-Born theory in the form of Bethe plots: $E\sigma/Ra_0^2$ versus $\ln(E/R)$.

In Fig. 4, the present $SiH_4$ cross sections along with those of Zecca, Karwasz, and Brusa [11] and Sueoka, Mori, and Hamada [13] are displayed in the form of Bethe plots. As can be seen from this figure, the present cross sections closely agree with the Bethe-Born formalism for the entire energy range while those in Ref. [11] agree only up to about 1500 eV. At energies higher than 1500 eV, the increase in the cross sections reported in Ref. [11] with increasing energy is lower than the predictions in the Bethe-Born theory. As displayed in Fig. 5, the $PH_3$ cross sections also follow the general trend of the predictions of Bethe-Born theory for the entire energy range in this work.

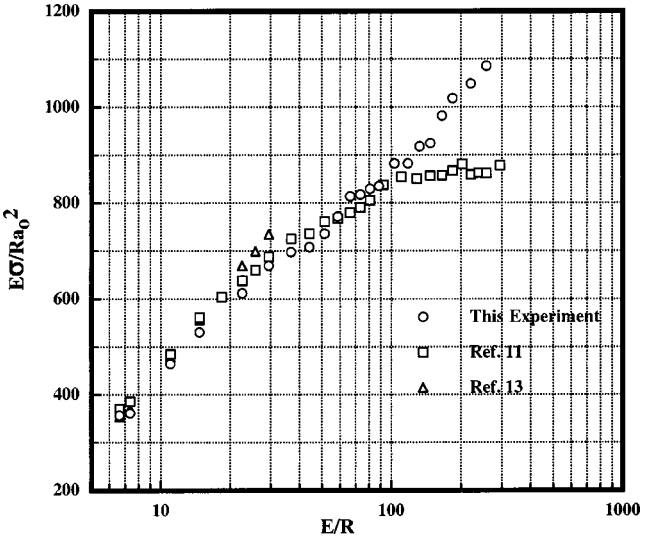


FIG. 4. The Bethe plot of $SiH_4$ cross sections. The circles are the present measurements. The squares and the triangles are, respectively, the measurements by Zecca, Karwasz, and Brusa [11] and Sueoka, Mori, and Hamada [13].

Next, the present cross sections are compared to the predictions of a model, based on the additivity rule, introduced by Joshipura and Vinodkumar [26]. This model predicts the cross section ($\sigma$) for energies ($E$) above 100 eV as

$$\frac{\sigma}{a_0^2} = A\left(\frac{E}{1\ \mathrm{keV}}\right)^{-B}, \quad (6)$$

where $A$ and $B$ are parameters that depend on the molecular properties of the target gas and $a_0$ is the Bohr radius. According to this model, the cross section on a logarithmic scale is proportional to the energy on the logarithmic scale. In Fig. 6, the present cross sections of $SiH_4$ and $PH_3$ as well as the $SiH_4$ cross sections of Zecca, Karwasz, and Brusa [11] are displayed on logarithmic scales. It is apparent from this

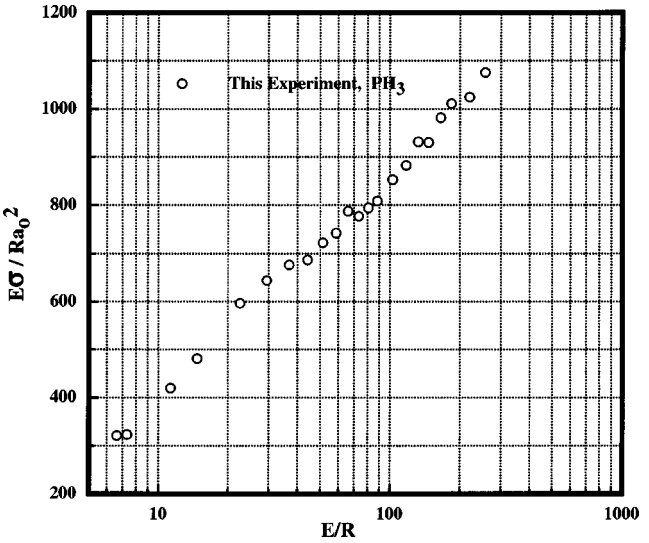


FIG. 5. The Bethe plot of present $PH_3$ electron scattering cross sections.

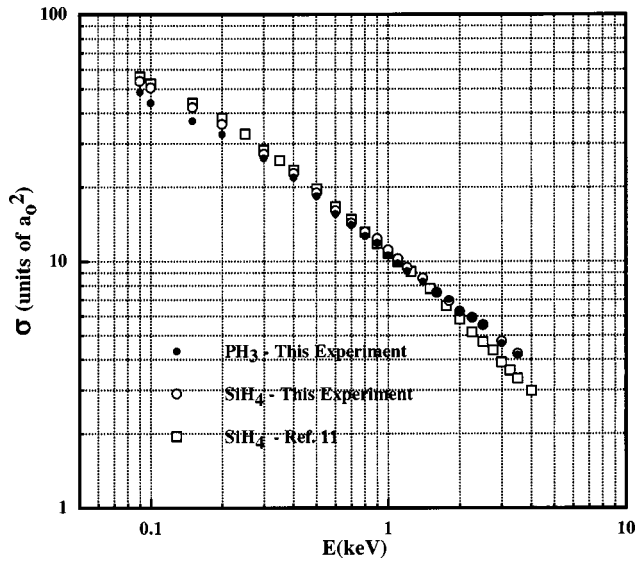


FIG. 6. The variation of the electron scattering cross sections with energy in the log-log scale. The open circles and the solid circles are, respectively, the present measurements for $SiH_4$ and $PH_3$ while open squares are the measurements reported in Ref. [11].

figure that the cross sections reported in Ref. [11] deviate from the general trend predicted by this model at energies 2000 eV and greater while those produced in this work follow the general trend of it for energy up to 3500 eV.

In the past, Garcia and Manero [16,27] have compared the cross sections of $CH_4$ and $NH_3$ with those reported by Zecca, Karwasz, and Brusa [28,29] and found that the cross sections reported by Garcia and Manero agree with the Bethe-Born formalism while those of Zecca, Karwasz, and Brusa were lower than the predictions of Bethe-Born formalism at energies larger than 1250 eV. It is important to mention here that the present cross-section measurements and those of Garcia and Manero are based on the linear beam transmission technique, while those of Zecca, Karwasz, and Brusa are based on the Ramsauer-type technique, and the differences in the cross sections may have resulted from the poor angular resolution of the Ramsauer-type apparatus.

## VI. CONCLUSION

Total electron scattering cross sections of $PH_3$ and $SiH_4$ have been measured for 90–3500-eV electrons. The cross sections of these two molecules are essentially the same at energies 1600 eV and higher, but at lower energies $SiH_4$ has a greater cross section than $PH_3$. The measured cross sections of $SiH_4$ are in agreement with those reported by Zecca, Karwasz, and Brusa [11] for energies between 90 and 1200 eV. At energies above 1200 eV, the present cross sections are higher than those in Ref. [11], reaching the greatest difference of 25% at 3500 eV. $PH_3$ and $SiH_4$ cross sections produced in the present work agree well with results calculated using the empirical formula proposed by Garcia and Manero [21], the theoretical predictions by Bethe-Born theory, and the formalism proposed by Joshipura and Vinodkumar [26].

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