

Ionization of phosphine and deuterated phosphine by electron impact from threshold up to 180 eV

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Electron impact ionization has been studied in PH_3 and in a mixture of PH_3 and PD_3 as a function of electron energy up to 180 eV, with a double focusing mass spectrometer. Absolute partial ionization cross sections have been obtained in PH_3 for the production of the parent ion PH_3^+ , for the fragment ions PH_2^+ , PH^+ , P^+ , H_2^+ , and H^+ and for the doubly charged ions PH_3^{2+} , PH_2^{2+} , PH^{2+} , and P^{2+} by normalization against the Ar ionization cross section. From the measured partial ionization cross sections the total ionization cross section function of PH_3 has been deduced. In addition, it has been possible to obtain the cross section ratios $q(\text{PD}_3^+)/q(\text{PD}_3^+)$, $q(\text{PD}_2^+)/q(\text{PD}_2^+)$, $q(\text{PD}^{2+})/q(\text{PD}_3^+)$, and $q(\text{P}^{2+})/q(\text{PD}_3^+)$ as a function of electron energy. The ion D_3^{2+} , produced by the process $\text{PD}_3 + e$, has been found for the first time and an estimate of the ionization cross section is given. Using n th root extrapolation the following ionization and appearance potentials have been derived from the low energy cross section functions: I.P. (PH_3^+) = 10.1 ± 0.1 and 12.5 ± 0.2 eV; I.P. (PD_3^+) = 10.15 ± 0.1 and 12.75 ± 0.2 eV; A.P. (PH_2^+) = 14.2 ± 0.2 eV; A.P. (PD_2^+) = 14.3 ± 0.2 eV; A.P. (PH^+) = 13.0 ± 0.2 eV; A.P. (PD^+) = 13.3 ± 0.2 eV; A.P. (P^+) from PH_3 = 17.2 ± 0.3 , 18.8 ± 0.3 , and 23.5 ± 0.3 eV; A.P. (P^+) from PD_3 = 17.7 ± 0.3 , 19.5 ± 0.3 , and 22.0 ± 0.3 eV; A.P. (H_2^+) = 14.8 ± 0.2 and 24.8 ± 0.5 eV; A.P. (D_2^+) = 14.9 ± 0.2 and 24.8 ± 0.5 eV; A.P. (H^+) = 25.3 ± 0.5 eV; A.P. (D^+) = 25.3 ± 0.5 eV; I.P. (PH_3^{2+}) = 30.0 ± 1.0 eV; I.P. (PD_3^{2+}) = 29.8 ± 0.5 eV; A.P. (PH_2^{2+}) = 35.0 ± 0.5 eV; A.P. (PD_2^{2+}) = 34.9 ± 0.5 eV; A.P. (PH^{2+}) = 33.0 ± 1.0 eV; A.P. (PD^{2+}) = 34.4 ± 0.5 eV; A.P. (P^{2+}) from PH_3 = 45.6 ± 0.5 eV; and A.P. (P^{2+}) from PD_3 = 46.7 ± 0.5 eV. In all double ionization cases a square law has been found from threshold up to some 5–10 eV above threshold. The ionization and appearance potentials obtained are compared with previous results where available. It is possible to resolve a yet unexplained discrepancy of the ionization potentials of the doubly ionized ions of PH_3 .

I. INTRODUCTION

Only a relatively few mass spectrometric studies have been made of the phosphorus compound phosphine. The majority of the previous studies has been restricted to the investigation of the ionization potential of the singly charged parent ion^{1–7} and of the appearance potentials of the fragment ions^{1,3,4,5,7,8} of PH_3 . The authors are aware of only one previous report about the occurrence and the measurement of the ionization potentials of doubly charged ions of PH_3 .⁴ Thus our knowledge of fragmentation processes for this tetratomic molecule is still incomplete, especially when considering that no measurements exist of total and/or partial ionization cross section functions of PH_3 , save a measurement of the relative abundance at 60,³ 70,⁵ and 100 eV¹ electron energy and one measurement of the total ionization cross section at 75 eV of PH_3 .⁹ Only one study exists of the ionization potentials of deuterated phosphine.⁵

In an attempt to gain more knowledge of the mass spectral cracking patterns of this phosphorus compound, electron impact ionization of the parent ion and of all fragment ions has been studied as a function of electron energy E up to 180 eV of PH_3 and also in a mixture of PH_3 and PD_3 . Results reported in the present paper include absolute partial ionization cross section functions $q(E)$ for the processes $\text{PH}_3 + e \rightarrow \text{PH}_3^+$, $\text{PH}_3 + e \rightarrow \text{PH}_2^+$, $\text{PH}_3 + e \rightarrow \text{PH}^+$, $\text{PH}_3 + e \rightarrow \text{P}^+$, $\text{PH}_3 + e \rightarrow \text{H}_2^+$, $\text{PH}_3 + e \rightarrow \text{H}^+$, $\text{PH}_3 + e \rightarrow \text{PH}_3^{2+}$, $\text{PH}_3 + e \rightarrow \text{PH}_2^{2+}$, $\text{PH}_3 + e \rightarrow \text{PH}^{2+}$, and $\text{PH}_3 + e \rightarrow \text{P}^{2+}$, also the total ionization cross section function in PH_3 , and the ratios of the cross section functions $q(\text{PD}_3^+)/q(\text{PD}_3^+)$, $q(\text{PD}_2^+)/q(\text{PD}_2^+)$, $q(\text{PD}^{2+})/q(\text{PD}_3^+)$, $q(\text{P}^{2+})/q(\text{PD}_3^+)$, and $q(\text{P}^{2+})/q(\text{PD}_3^+)$.¹⁰ Values of the ionization and appearance potentials of the various par-

ent and fragment ions of PH_3 and PD_3 are also presented and compared with previous data.

II. APPARATUS AND TECHNIQUE

The experimental setup in the present study is identical with that previously described in detail.^{12,13} In short, it consists of a molecular type of electron impact source Varian MAT Intensitron M, and a high resolution double focusing mass spectrometer, Varian MAT CH5, with a total dynamic range of 1×10^6 . In the course of earlier work, the extracting conditions in the ion source have been improved¹⁴ in order to reduce disturbing instrumental effects. It thus became possible to obtain quite accurate relative ionization cross section functions $q(E)$ of the various ions of PH_3 and PD_3 . The improvement has been achieved by studying the extracting conditions for singly and multiply ionized rare gases¹⁴ and adjusting the various extracting potentials to such a value that reproducible and reliable relative cross section functions have been obtained. Consistency checks necessary in electron impact studies and the energy scale calibration used have been reported previously.¹³

Normalization of the measured relative cross section functions $q(E)$, to yield absolute values, has been made by the method described previously,^{12,13} in which the relative cross section under study is compared at a particular electron energy with that of the measured value for $q(\text{Ar}^+/\text{Ar})$ for which absolute cross sections are known from the literature. The comparison has been usually made near the maximum of $q(\text{Ar}^+/\text{Ar})$, i. e., at an electron energy of 90 eV, setting the presently measured values of $q(\text{Ar}^+/\text{Ar}) + 2q(\text{Ar}^{2+}/\text{Ar})$ equal to the total ionization cross section reported by Rapp *et al.*,¹⁵ from

which $q(\text{Ar}^+/\text{Ar}) = 2, 43 \times 10^{-16} \text{ cm}^2$ is obtained. A correction has been made to this $q(\text{Ar}^+/\text{Ar})$ for the isotopic abundances of argon ($^{40}\text{Ar} = 99, 6\%$).¹⁶

The measurement of the ratio of the gas density of argon to the gas under study in the collision chamber necessary for this absolute calibration has been made by means of the method of effusive flow.^{13,15,16} The gas pressure in the gas reservoir is measured with an absolute capacitance manometer. According to Rapp *et al.*¹⁵ and Märk *et al.*¹³ the results thus obtained are believed to be more accurate than those based on absolute McLeod-gauge measurements in each gas. In all normalization procedures the ion currents have been measured either with a Faraday collector cup or with a 16 dynode electron multiplier. In the latter case corrections for the different secondary emission coefficients γ for the different ions have been made by calibration with the Faraday cup.¹⁷

The accuracy of the measured ion currents was in general better $\pm 1\%$. However, for very low ion currents, e.g., as in the case for PH_3^+ , PH_2^+ , PH^+ , P^+ , and H_2^+ , the statistical error could be as large as $\pm 5\%$. The accuracy of the density ratio necessary for the absolute calibration of the cross section values depends on the accuracy of measurement of the pressure (capacitance manometer Barocel $\pm 0,05\%$) and on the adequacy of the assumption of effusive flow. In accordance with Rapp *et al.*¹⁵ and Märk *et al.*¹³ the accuracy for repeated measurements at different effusive flow conditions was found to be about $\pm 4\%$. These error bars have been recently confirmed by an electron impact study of the rare gases in this laboratory.¹⁴ Thus, the estimated maximum possible error, excluding that of the absolute value for $q(\text{Ar}^+/\text{Ar})$, is about 10%.

The phosphine samples used were obtained from Professor E. Mayer, Institut für Anorganische Chemie, Universität Innsbruck and distilled *in vacuo* through a -79°C cold trap and purified of N_2 and O_2 contaminants *in vacuo* with help of a -180°C cold trap. Impurities still present have been determined mass spectrometrically ($\text{H}_2\text{O} < 0,5\%$, $\text{N}_2 < 0,2\%$ and $\text{O}_2 < 0,05\%$) and allowed for in the calibration procedures (e.g., the PH_3^+ signal had to be corrected by about 25% at an electron energy of 90,5 eV, see also below). As the known hydrides of phosphorus consist also of P_2H_2 and P_2H_4 a mass spectrometric search at higher masses has been made in order to correct the phosphine results. Whereas in PD_3 higher hydrides were $< 0,01\%$, in PH_3 higher hydrides were present in the order of 5% of the PH_3^+ signal. This gives, according to the measured fragmentation pattern³ of diphosphine, contributions to the phosphine fragment ion signals of $< 1\%$.

III. RESULTS AND DISCUSSION

A. Ionization cross section functions

The absolute ionization cross sections obtained for the processes $\text{PH}_3 + e \rightarrow \text{PH}_3^+$, $\text{PH}_3 + e \rightarrow \text{PH}_2^+$, $\text{PH}_3 + e \rightarrow \text{PH}^+$, $\text{PH}_3 + e \rightarrow \text{P}^+$, $\text{PH}_3 + e \rightarrow \text{H}_2^+$, $\text{PH}_3 + e \rightarrow \text{H}^+$, as well as $\text{PH}_3 + e \rightarrow \text{PH}_3^{2+}$, $\text{PH}_3 + e \rightarrow \text{PH}_2^{2+}$, $\text{PH}_3 + e \rightarrow \text{PH}^{2+}$, and finally $\text{PH}_3 + e \rightarrow \text{P}^{2+}$ are shown semilogarithmically as a function of

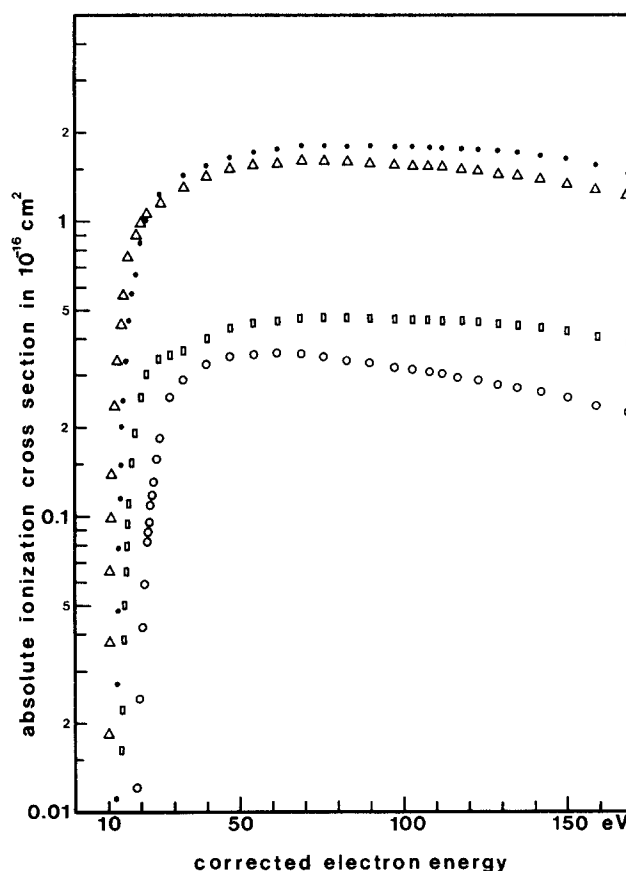


FIG. 1. Absolute partial ionization cross section $q(\text{PH}_3^+/\text{PH}_3)$, designated Δ ; $q(\text{PH}_2^+/\text{PH}_3)$, designated \square ; $q(\text{PH}^+/\text{PH}_3)$, designated \bullet ; and $q(\text{P}^+/\text{PH}_3)$, designated \circ , as a function of corrected electron energy. The energy scale of the present data has been calibrated by means of the linear extrapolation method, taking the ionization potential of Ar^+ as 15,76 eV (spectroscopic value).

electron energy in Figs. 1–3, respectively. It can be seen that the PH_3^+ curve peaks near 70 eV, PH_2^+ near 80 eV, PH^+ near 80 eV, P^+ near 60 eV, H_2^+ near 70 eV, H^+ near 65 eV, whereas the PH_3^{2+} curve has its peak near 105 eV, PH_2^{2+} near 90 eV, PH^{2+} near 95 eV, and P^{2+} near 90 eV. A representative set of values of all absolute cross sections measured in PH_3 is given numerically in Tables I and II.

Table I also contains $q'(\text{PH}_3) = q(\text{PH}_3^+) + q(\text{PH}_2^+) + q(\text{PH}^+) + q(\text{P}^+) + q(\text{H}_2^+) + q(\text{H}^+) + 2q(\text{PH}_3^{2+}) + 2q(\text{PH}_2^{2+}) + 2q(\text{PH}^{2+}) + 2q(\text{P}^{2+})$ for different electron energies. Saalfeld *et al.*,³ who have studied carefully the positive ion fragmentation pattern for several group VB hydrides (including PH_3), have found that if the fragment ions contained excess kinetic energy it was negligible. Because no discrimination due to initial kinetic energy will thus occur in the ion source of the mass spectrometer, partial ionization cross sections of the fragment ions obtained in the present study are true cross sections and the above sum of all cross sections q' is equal to the total ionization cross section $q_t(\text{PH}_3)$.

There exist no previous absolute determinations of the total ionization cross section function in PH_3 , only a measurement relative to that of Ar at an electron energy

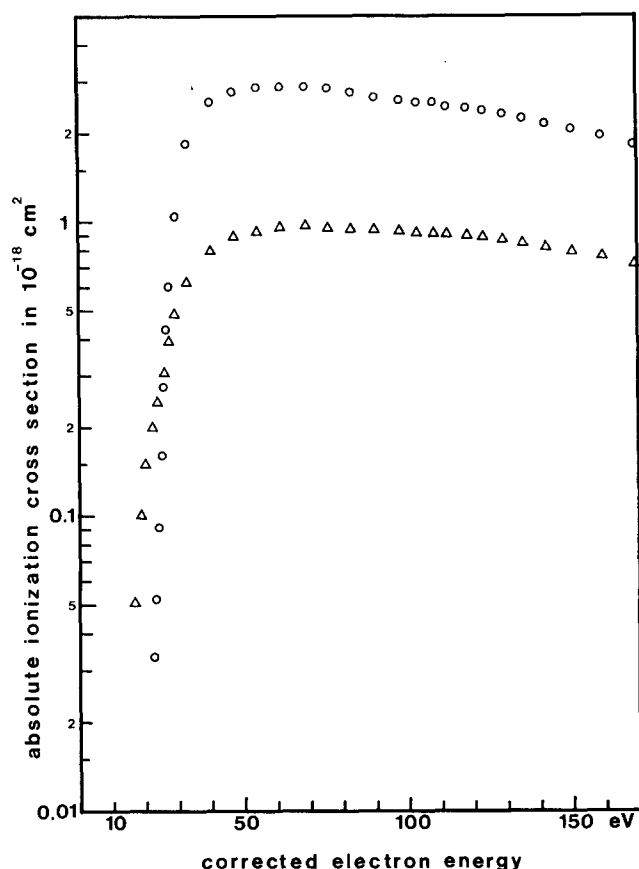


FIG. 2. Absolute partial ionization cross section $q(\text{H}_2^+/\text{PH}_3)$, designated Δ ; and $q(\text{H}^+/\text{PH}_3)$, designated \circ , as a function of corrected electron energy.

of 75 eV by Otvos *et al.*⁹ These authors determined this relative total cross section from the sum of the specific intensities of the ions of the resolved mass spectra of PH_3 , the mass spectra being obtained with the Westinghouse Type LV $\pi/2$ sector analyzer mass spectrometer. Because Otvos *et al.*⁹ have expressed their values in relative units of a calculated total argon cross section, for intercomparison a conversion of their values to the units used in the present paper is required, i. e., using the total cross section of argon measured by Rapp *et al.*¹⁵ This gives a value for $q_t(\text{PH}_3)$ at an electron energy of 75 eV of $3.80 \times 10^{-16} \text{ cm}^2$, which is in good agreement with the present value of $(4.28 \pm 0.43) \times 10^{-16} \text{ cm}^2$.

The partial single ionization cross section functions in PH_3 obtained in the present study can be compared only with previous measurements by Neuert *et al.*,¹ Saalfeld *et al.*,³ and Wada *et al.*⁵ These authors, however, have only reported the relative ion intensities in PH_3 as a result of a mass spectrometric study of the products of ionization and dissociation in phosphine at one particular electron impact energy, i. e., Neuert *et al.* at 100 eV, Saalfeld *et al.* at 60 eV, and Wada *et al.* at 70 eV electron energy. Table III gives for comparison at each of these energies the partial ionization cross section of the fragment ions relative to that of the parent ion PH_3^+ of the present study and of that of each of the above mentioned authors. It can be seen from Table III that the present values of PH_2^+ , PH^+ , and P^+ at an electron energy of 70

and 100 eV agree with those of Wada *et al.* and Neuert *et al.* to within 10%, except for $q(\text{P}^+/\text{PH}_3)$ (the present values are lower by 30%). The latter could be due to a possible presence of higher hydrides of phosphorus in the gas samples of these authors, which would lead, according to the fragmentation patterns of P_2H_2 and P_2H_4 reported,³ to an increased signal of P^+ . The present results can also be compared with results obtained in deuterated phosphine. Because the available sample was not pure PD_3 , but rather a mixture of PH_3 and PD_3 [e. g., $p(\text{PD}_3):p(\text{PD}_2\text{H}):p(\text{PDH}_2):p(\text{PH}_3)=100:11:?:?$, the latter two $<1\%$] it was not possible to analyze the measured ion current data in a way to obtain accurate absolute cross section values of the deuterated ions. However, the fragmentation pattern of deuterated phosphine obtained, compares well within the experimental error of $\pm 5\%$ with that of the normal phosphine.

The agreement in Table III between the present values at an electron energy of 60 eV and the experimental values of Saalfeld *et al.* is generally poor, i. e., for all fragment ions their values are considerably higher. This relatively high fraction of fragment ions could be due to the high electron current used in their ion source (95 μA as compared to 15 or 50 μA used in the present study). At this high electron current secondary processes are present and could falsify the electron impact fragmentation pattern.

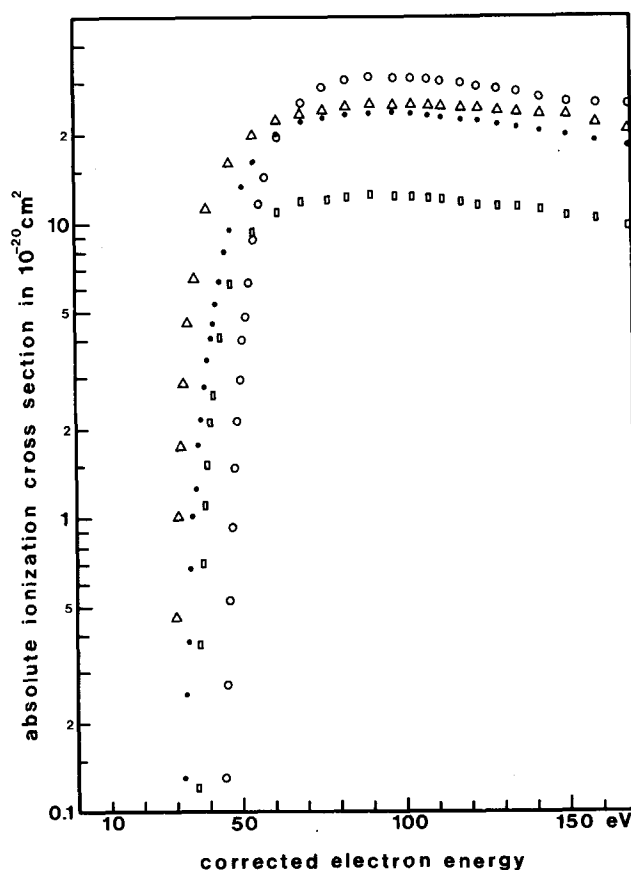


FIG. 3. Absolute partial double ionization cross section functions of PH_3 : Δ — $q(\text{PH}_3^{2+}/\text{PH}_3)$; \square — $q(\text{PH}_2^{2+}/\text{PH}_3)$; \bullet — $q(\text{PH}^{2+}/\text{PH}_3)$, and \circ — $q(\text{P}^{2+}/\text{PH}_3)$.

TABLE I. Absolute partial single ionization cross sections and the sum $q' = q(\text{PH}_3^+) + q(\text{PH}_2^+) + q(\text{PH}^+) + q(\text{P}^+) + q(\text{H}_2^+) + q(\text{H}^+) + 2q(\text{PH}_3^{2+}) + 2q(\text{PH}_2^{2+}) + 2q(\text{PH}^{2+}) + 2q(\text{P}^{2+})$ for different corrected electron energies.

| E eV | $q(\text{PH}_3^+)$ 10^{-16} cm^2 | $q(\text{PH}_2^+)$ 10^{-16} cm^2 | $q(\text{PH}^+)$ 10^{-16} cm^2 | $q(\text{P}^+)$ 10^{-16} cm^2 | $q(\text{H}_2^+)$ 10^{-18} cm^2 | $q(\text{H}^+)$ 10^{-18} cm^2 | $q' = q_t$ 10^{-16} cm^2 |
|-----------|---|---|---|--|--|--|---------------------------------------|
| 183 | 1.14 | 0.360 | 1.38 | 0.203 | 0.659 | 1.65 | 3.12 |
| 170.5 | 1.21 | 0.385 | 1.48 | 0.222 | 0.717 | 1.82 | 3.34 |
| 159.5 | 1.28 | 0.407 | 1.57 | 0.237 | 0.760 | 1.95 | 3.54 |
| 150.5 | 1.34 | 0.423 | 1.63 | 0.252 | 0.788 | 2.07 | 3.69 |
| 142.5 | 1.39 | 0.434 | 1.68 | 0.264 | 0.815 | 2.16 | 3.81 |
| 135.5 | 1.43 | 0.443 | 1.71 | 0.274 | 0.845 | 2.25 | 3.90 |
| 129.5 | 1.45 | 0.450 | 1.74 | 0.279 | 0.865 | 2.32 | 3.97 |
| 123.5 | 1.48 | 0.454 | 1.75 | 0.289 | 0.882 | 2.39 | 4.02 |
| 118.5 | 1.49 | 0.459 | 1.77 | 0.296 | 0.896 | 2.43 | 4.07 |
| 112.5 | 1.51 | 0.461 | 1.78 | 0.303 | 0.906 | 2.48 | 4.11 |
| 108.5 | 1.52 | 0.463 | 1.78 | 0.308 | 0.913 | 2.52 | 4.12 |
| 103.5 | 1.52 | 0.463 | 1.79 | 0.311 | 0.916 | 2.53 | 4.14 |
| 98 | 1.54 | 0.467 | 1.80 | 0.318 | 0.923 | 2.59 | 4.18 |
| 90.5 | 1.56 | 0.470 | 1.81 | 0.330 | 0.936 | 2.67 | 4.20 |
| 83.5 | 1.58 | 0.471 | 1.81 | 0.337 | 0.946 | 2.74 | 4.25 |
| 76.5 | 1.59 | 0.472 | 1.82 | 0.347 | 0.957 | 2.82 | 4.28 |
| 69.5 | 1.60 | 0.470 | 1.81 | 0.355 | 0.967 | 2.87 | 4.29 |
| 62.1 | 1.57 | 0.463 | 1.78 | 0.357 | 0.953 | 2.87 | 4.22 |
| 54.9 | 1.54 | 0.452 | 1.73 | 0.352 | 0.926 | 2.85 | 4.12 |
| 47.7 | 1.50 | 0.432 | 1.66 | 0.345 | 0.882 | 2.77 | 3.98 |
| 40.5 | 1.42 | 0.400 | 1.55 | 0.325 | 0.788 | 2.56 | 3.73 |
| 33.3 | 1.30 | 0.365 | 1.42 | 0.289 | 0.622 | 1.84 | 3.40 |
| 26.1 | 1.15 | 0.340 | 1.23 | 0.181 | 0.308 | 0.273 | 2.91 |
| 22.5 | 1.05 | 0.302 | 1.01 | 0.081 | 0.199 | 0.033 | 2.45 |
| 19.0 | 0.887 | 0.189 | 0.661 | 0.013 | 0.116 | 0 | 1.75 |
| 15.1 | 0.561 | 0.038 | 0.108 | 0 | 0 | | 0.707 |
| 12.3 | 0.235 | 0 | 0 | | | | 0.235 |
| 11.2 | 0.098 | | | | | | 0.098 |
| 10.3 | 0.018 | | | | | | 0.018 |

By comparing in Table III the present values of $q(\text{H}_2^+/\text{PH}_3)$ and $q(\text{H}^+/\text{PH}_3)$ with those of Neuert *et al.*¹ it may be seen that there is poor agreement (factor of 20 and 3, respectively). There exist, however, two arguments in favor of the present results. First, the present results can be compared with electron impact ionization studies by Märk *et al.*¹⁰ in ammonia, a molecule which also belongs to the group V monohydrides. Although the fragmentation pattern of the heavier fragments in both gases is quite different, the fractions of H_2^+ and H^+ produced are about the same according to these measurements. It is also possible to prove reliability of the present determination by comparing it with the results obtained in deuterated phosphine. Although the latter are only estimates, because of difficulties in the calibration (see above), they are in the same order of magnitude, i. e., $q(\text{D}_2^+/\text{PD}_3)/q(\text{PD}_3^+/\text{PD}_3) = 0.59\%$ and $q(\text{D}^+/\text{PD}_3)/q(\text{PD}_3^+/\text{PD}_3) = 2.0\%$ at an electron energy of 100 eV.

Due to the high dynamic range of the mass spectrometer it was possible to detect also at mass number 6 the ion D_3^+ , which had been produced by the process $\text{PD}_3 + e$. Assuming $q(\text{PH}_3) = q(\text{PD}_3)$, a partial ionization cross section at an electron energy of 90.5 eV could be deduced from the measured ratio $q(\text{PD}_2^{2+}/\text{PD}_3)/q(\text{D}_3^+/\text{PD}_3) = 26$ in the order of $q(\text{D}_3^+/\text{PD}_3) = 5 \times 10^{-21} \text{ cm}^2$.

As already mentioned there exist no previous measure-

TABLE II. Absolute partial double ionization cross sections, $q(\text{PH}_3^{2+}/\text{PH}_3)$, $q(\text{PH}_2^{2+}/\text{PH}_3)$, $q(\text{PH}^{2+}/\text{PH}_3)$, and $q(\text{P}^{2+}/\text{PH}_3)$ for different corrected electron energies.

| E eV | $q(\text{PH}_3^{2+})$ 10^{-18} cm^2 | $q(\text{PH}_2^{2+})$ 10^{-18} cm^2 | $q(\text{PH}^{2+})$ 10^{-18} cm^2 | $q(\text{P}^{2+})$ 10^{-18} cm^2 |
|-----------|--|--|--|---|
| 183 | 0.188 | 0.089 | 0.171 | 0.249 |
| 170.5 | 0.207 | 0.097 | 0.183 | 0.252 |
| 159.5 | 0.218 | 0.103 | 0.190 | 0.253 |
| 150.5 | 0.230 | 0.105 | 0.199 | 0.256 |
| 142.5 | 0.232 | 0.110 | 0.204 | 0.265 |
| 135.5 | 0.236 | 0.113 | 0.210 | 0.276 |
| 129.5 | 0.239 | 0.114 | 0.215 | 0.285 |
| 123.5 | 0.244 | 0.116 | 0.221 | 0.289 |
| 118.5 | 0.245 | 0.118 | 0.226 | 0.296 |
| 112.5 | 0.248 | 0.120 | 0.228 | 0.301 |
| 108.5 | 0.249 | 0.121 | 0.230 | 0.305 |
| 103.5 | 0.251 | 0.121 | 0.231 | 0.307 |
| 98 | 0.250 | 0.124 | 0.234 | 0.308 |
| 90.5 | 0.250 | 0.125 | 0.234 | 0.312 |
| 83.5 | 0.248 | 0.123 | 0.231 | 0.301 |
| 76.5 | 0.241 | 0.120 | 0.228 | 0.287 |
| 69.5 | 0.233 | 0.118 | 0.220 | 0.256 |
| 62.1 | 0.222 | 0.109 | 0.200 | 0.196 |
| 54.9 | 0.197 | 0.093 | 0.162 | 0.088 |
| 47.7 | 0.160 | 0.062 | 0.095 | 0.009 |
| 40.5 | 0.112 | 0.015 | 0.034 | 0 |
| 33.3 | 0.029 | 0 | 0.003 | |
| 26.1 | 0 | | 0 | |

TABLE III. Partial ionization cross sections of the fragment ions of PH_3 divided by that of the parent ion PH_3^+ in % at three different electron energies as measured by Saalfeld *et al.*,³ Wada *et al.*,⁵ Neuert *et al.*,¹ and in the present study.

| Electron energy Author | 60 eV | | 70 eV | | 100 eV | |
|---|---------------------------|------------------|-----------------------|------------------|-------------------------|------------------|
| | Saalfeld <i>et al.</i> | Present study | Wada <i>et al.</i> | Present study | Neuert <i>et al.</i> | Present study |
| $q(\text{PH}_2^+/ \text{PH}_3)/q(\text{PH}_3^+/ \text{PH}_3)$ | 37 | 29.5 | 29 | 29.4 | 32.4 | 30.3 |
| $q(\text{PH}^+/ \text{PH}_3)/q(\text{PH}_3^+/ \text{PH}_3)$ | 147 | 112.8 | 133 | 113.1 | 117.5 | 116.8 |
| $q(\text{P}^+/ \text{PH}_3)/q(\text{PH}_3^+/ \text{PH}_3)$ | 59 | 22.8 | 32 | 22.2 | 29.4 | 20.5 |
| $q(\text{H}_2^+/ \text{PH}_3)/q(\text{PH}_3^+/ \text{PH}_3)$ | ... | 0.60 | ... | 0.60 | 11.3 | 0.60 |
| $q(\text{H}^+/ \text{PH}_3)/q(\text{PH}_3^+/ \text{PH}_3)$ | ... | 1.83 | ... | 1.79 | 4.7 | 1.67 |

ments of the absolute ionization cross section function for the production of doubly ionized parent and fragment ions in phosphine. Again, the present results can only be compared with the presently obtained results in deuterated phosphine. It was however only possible to measure accurately the ion current ratio $\text{PD}_3^{2+}/\text{PD}_3^+$, $\text{PD}_2^{2+}/\text{PD}_2^+$, $\text{PD}^{2+}/\text{PD}^+$, and P^{2+}/P^+ for different electron energies as listed in Table IV in terms of cross section values. By comparing each of the four columns of PH_3 and PD_3 of Table IV it may be seen that the sets of experimental values are identical in shape and magnitude within the experimental error.

It is further interesting to note, that the maximum of the cross section ratio $q(\text{PH}_3^{2+}/\text{PH}_3)/q(\text{PH}_3^+/ \text{PH}_3)$ is within the experimental error equal to the maximum of $q(\text{NH}_3^{2+}/\text{NH}_3)/q(\text{NH}_3^+/ \text{NH}_3)$, as measured by Märk *et al.*,¹⁸ both gases being group V monohydrides. The relative NH_2^+ , NH^+ , and N^+ signals, however, are much smaller than the relative PH_2^+ , PH^+ , and P^+ signals.

B. Ionization and appearance potentials

From the behavior of the single ionization cross section functions near threshold ionization and appearance potentials have been derived by means of the linear extrapolation method. Moreover, due to excited states of the produced ions and due to different dissociation processes (both with a relatively high transition probability) some of the ionization cross section functions exhibit distinct breaks corresponding to higher ionization or appearance potentials. The obtained values are listed in Table V, and are compared with those of other investigators.

In general, the values measured for phosphine in the present work are, within the experimental error, in good agreement with those of deuterated phosphine, the latter tending to slightly higher values. This result is to be expected, because a possible difference between the ionization or appearance potentials could only be related to

TABLE IV. Cross section ratios of the doubly ionized ions divided by the parent ion in PH_3 and PD_3 as a function of corrected electron energy.

| E eV | $q(\text{PH}_3^{2+})/$ $q(\text{PH}_3^+)$ % | $q(\text{PD}_3^{2+})/$ $q(\text{PD}_3^+)$ % | $q(\text{PH}_2^{2+})/$ $q(\text{PH}_2^+)$ % | $q(\text{PD}_2^{2+})/$ $q(\text{PD}_2^+)$ % | $q(\text{PH}^{2+})/$ $q(\text{PH}^+)$ % | $q(\text{PD}^{2+})/$ $q(\text{PD}^+)$ % | $q(\text{P}^{2+})/$ $q(\text{P}^+)$ % | $q(\text{P}^{2+})/$ $q(\text{PD}_3^+)$ % |
|-----------|---|---|---|---|---|---|---|--|
| 183.0 | 0.164 | 0.147 | 0.0781 | 0.0818 | 0.150 | 0.138 | 0.218 | 0.198 |
| 170.5 | 0.169 | 0.150 | 0.0793 | 0.0823 | 0.151 | 0.136 | 0.207 | 0.188 |
| 159.5 | 0.169 | 0.151 | 0.0800 | 0.0809 | 0.148 | 0.137 | 0.197 | 0.179 |
| 150.5 | 0.170 | 0.150 | 0.0783 | 0.0810 | 0.148 | 0.138 | 0.190 | 0.178 |
| 142.5 | 0.166 | 0.149 | 0.0791 | 0.0817 | 0.146 | 0.139 | 0.190 | 0.178 |
| 135.5 | 0.164 | 0.148 | 0.0786 | 0.0820 | 0.147 | 0.141 | 0.192 | 0.182 |
| 129.5 | 0.163 | 0.150 | 0.0782 | 0.0828 | 0.148 | 0.142 | 0.196 | 0.187 |
| 123.5 | 0.163 | 0.151 | 0.0784 | 0.0836 | 0.149 | 0.144 | 0.195 | 0.188 |
| 118.5 | 0.163 | 0.151 | 0.0785 | 0.0837 | 0.151 | 0.146 | 0.197 | 0.190 |
| 112.5 | 0.163 | 0.145 | 0.0794 | 0.0838 | 0.151 | 0.145 | 0.199 | 0.192 |
| 108.5 | 0.163 | 0.153 | 0.0797 | 0.0841 | 0.151 | 0.145 | 0.200 | 0.191 |
| 103.5 | 0.164 | 0.154 | 0.0795 | 0.0846 | 0.152 | 0.145 | 0.201 | 0.192 |
| 98 | 0.161 | 0.153 | 0.0801 | 0.0848 | 0.152 | 0.144 | 0.199 | 0.191 |
| 90.5 | 0.159 | 0.153 | 0.0799 | 0.0850 | 0.150 | 0.145 | 0.199 | 0.190 |
| 83.5 | 0.156 | 0.152 | 0.0774 | 0.0835 | 0.146 | 0.144 | 0.190 | 0.187 |
| 76.5 | 0.150 | 0.149 | 0.0751 | 0.0821 | 0.143 | 0.140 | 0.179 | 0.181 |
| 69.5 | 0.145 | 0.145 | 0.0735 | 0.0803 | 0.138 | 0.135 | 0.160 | 0.163 |
| 62.1 | 0.140 | 0.141 | 0.0690 | 0.0769 | 0.127 | 0.129 | 0.124 | 0.126 |
| 54.9 | 0.127 | 0.133 | 0.0600 | 0.0665 | 0.105 | 0.105 | 0.057 | 0.056 |
| 47.7 | 0.106 | 0.113 | 0.0412 | 0.0473 | 0.063 | 0.066 | 0.006 | ... |
| 40.5 | 0.078 | 0.077 | 0.0105 | 0.0153 | 0.024 | 0.022 | | |
| 33.3 | 0.022 | 0.015 | ... | ... | 0.001 | ... | | |

TABLE V. Ionization and appearance potentials in phosphine and in a mixture of phosphine and deuterated phosphine (see text) obtained by electron impact studies. The method of experimental technique used is indicated in the abbreviated form: LE (linear extrapolation), EC (energy compensation), VC (vanishing current), EVD (extrapolated voltage difference), SL (semilog plot), FDP (first differential plot).

| Ionization and appearance potentials in eV | | |
|--|------------------------------|--|
| Ion | | |
| Present study | Previous results and methods | |
| $\text{PH}_3(^2A_1)$ | 10.1 ± 0.1 | 10.0 ± 0.2 (LE ¹), 10.3 (EC ²), 11.5 ± 0.3 (LE ³), 10.3 ± 0.5 (LE ⁴), 10.4 ± 0.3 (VC ⁴), 10.2 ± 0.2 (EVD ⁵), 10.4 ± 0.3 (SL ⁶), 10.0 (FDP ⁷) |
| $\text{PH}_3(^2E)$ | 12.5 ± 0.2 | ... |
| PH_2^+ | 14.2 ± 0.2 | 13.9 ± 0.3 (LE ¹), 14.4 ± 0.2 (LE ³), 14.4 (LE ⁴), 14.0 ± 0.2 (VC ⁴), 13.2 ± 0.2 (EVD ⁵), 13.2 (LE ⁶), 13.4 (FDP ⁷) |
| PH^+ | 13.3 ± 0.2 | 12.0 ± 0.3 (LE ¹), 12.4 ± 0.2 (LE ³), 13.6 (LE ⁴), 13.1 ± 0.2 (VC ⁴), 13.3 ± 0.2 (EVD ⁵), 12.9 (FDP ⁷) |
| P^+ | 17.2 ± 0.3 | 16.7 ± 1 (LE ¹), 16.5 ± 0.2 (LE ³), 20 ± 1 (LE ⁴), 16.0 ± 1 (VC ⁴), 17.2 ± 0.2 (EVD ⁵), 16.3 (FDP ⁷) |
| | 18.8 ± 0.3 | 20.8 ± 0.3 (LE ³) |
| | 23.5 ± 0.3 | |
| H_2^+ | 14.8 ± 0.2 | 15.6 ± 0.2 (LE ¹) |
| | 24.8 ± 0.5 | |
| H^+ | 25.3 ± 0.5 | |
| $\text{PD}_3(^2A_1)$ | 10.15 ± 0.1 | 10.1 ± 0.2 (EVD ⁵) |
| $\text{PD}_3(^2E)$ | 12.75 ± 0.2 | ... |
| PD_2^+ | 14.3 ± 0.2 | ... |
| PD^+ | 13.3 ± 0.2 | 13.1 ± 0.2 (EVD ⁵) |
| P^+ | 17.7 ± 0.3 | 17.1 ± 0.3 (EVD ⁵) |
| | 19.5 ± 0.3 | |
| | 22.0 ± 0.3 | |
| D_2^+ | 14.9 ± 0.2 | |
| | 24.8 ± 0.5 | |
| D^+ | 25.3 ± 0.5 | |

a difference in zero point energies. By comparing in Table V the present results with previous data where available (several A.P.'s have been determined for the first time), it may be seen that for the first I.P.'s and A.P.'s there is generally good agreement, except for PH^+ and P^+ . The first appearance potential for PH^+ in

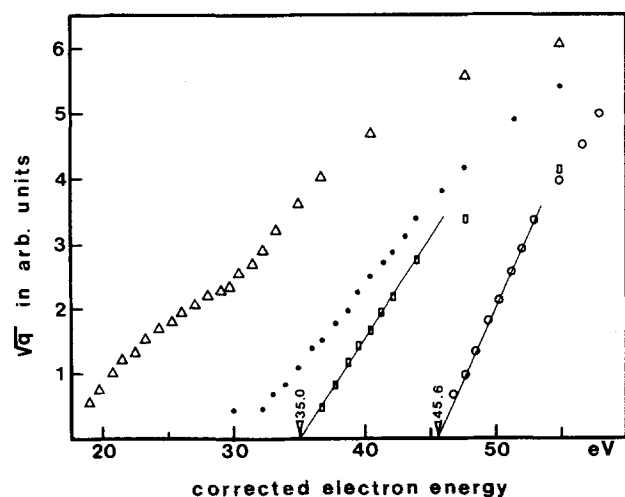


FIG. 4. Square root of the double ionization cross section functions of PH_3 near threshold vs corrected electron energy: Δ — PH_3^+ , \square — PH_2^+ , \bullet — PH^+ and \circ — P^+ .

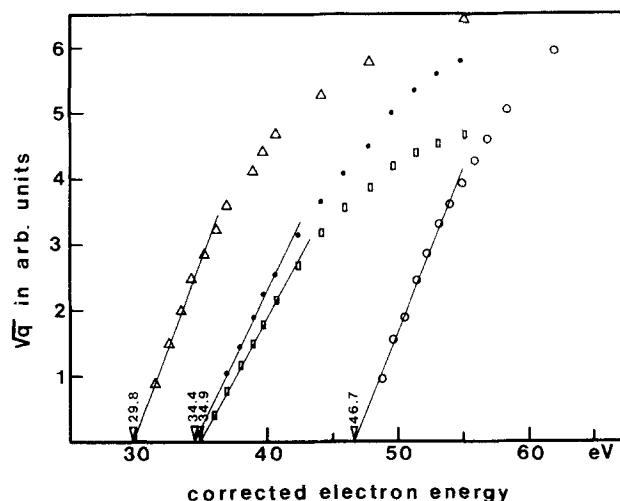


FIG. 5. Square root of the double ionization cross section function of PD_3 near threshold vs corrected electron energy: Δ — PD_3^+ , \square — PD_2^+ , \bullet — PD^+ , and \circ — P^+ .

the present study found to be 13.3 ± 0.2 eV, is slightly greater than the adiabatic ionization energy of 12.64 eV for the $1e$ valence orbital.¹⁹ In contrast, some authors report^{1,3} from their electron impact studies first A.P.'s of PH^+ smaller than this adiabatic ionization energy, and a second A.P. greater. The reason for these discrepancies could be that the PH^+ curve exhibits a curvature near the threshold, which makes an interpretation dependent on the method used. The P^+ curve, like that of PH^+ , also fails to show clearly defined breaks, thus making both difficult to analyse. The presently measured first and third appearance potential of P^+ in PH_3 and PD_3 may be consistent with the two dissociation processes: $\text{PH}_3 + e \rightarrow \text{P}^+ + \text{H}(\Sigma^+) + \text{H}_2(1\Sigma^+)$ and $\text{PH}_3 + e \rightarrow \text{P}^+ + 3\text{H}(^2S)$.

Particularly worthy of note is the analysis of the low energy behavior of the double ionization cross section functions in PH_3 and PD_3 . Figures 4 and 5 show plots of the square root of the partial cross sections for the production of the doubly ionized parent and fragment ions of PH_3 and PD_3 as a function of electron energy. It can be seen that in all cases, except for PH_3^{++} and in a lesser degree for PH^{++} (for the explanation of this anomaly see below), a quadratic threshold law is followed for some 5–10 eV above onset. This fact is of great significance in theory, because it is proof that the n th power rule of Wannier²⁰ and Geltman²¹ applies also to doubly ionized fragment ions, i.e., the probability for the occurrence of these ions varies above threshold as the 2nd power of the excess electron energy.

By comparing the low energy cross section functions of PH_3^{++} and PH^{++} with those of PD_3^{++} and PD^{++} it may be seen that the curves of PH_3^{++} and to a lesser degree of PH^{++} extend to lower electron energies than the respective curves of the deuterated ions. Attention should also be directed to the fact that the curves in contrast to those of the other doubly ionized ions cannot be approximated by a square root threshold law but rather by a linear threshold law. Fischler *et al.*,⁴ who also studied the low energy ionization efficiency curves of the doubly ionized phosphine ions, have shown in their paper a plot of the

TABLE VI. Ionization and appearance potentials of doubly ionized parent and fragment ions in phosphine and deuterated phosphine. LE: linear extrapolation method, SRP: square root plot method.

| | Ionization or appearance potential in eV | |
|---|--|-------------------------------------|
| | Present result | Fischler <i>et al.</i> ⁴ |
| I. P. (PH ₃ ²⁺ /PH ₃) | 30.0 ± 1.0 | 15.0 (LE), 15.6 (SRP) |
| A. P. (PH ₂ ²⁺ /PH ₃) | 35.0 ± 0.5 | 32.7 (LE), 34.0 (SRP) |
| A. P. (PH ²⁺ /PH ₃) | 33.0 ± 1.0 | 21.2 (LE), 25.1 (SRP) |
| A. P. (PH ⁺ /PH ₃) | 45.6 ± 0.5 | 42 ± 2 (LE), 42 ± 2 (SRP) |
| I. P. (PD ₃ ²⁺ /PD ₃) | 29.8 ± 0.5 | |
| A. P. (PD ₂ ²⁺ /PD ₃) | 34.9 ± 0.5 | |
| A. P. (PD ²⁺ /PD ₃) | 34.4 ± 0.5 | |
| A. P. (P ²⁺ /PD ₃) | 46.7 ± 0.5 | |

ion current against the electron current. From this figure can be seen that the curves of PH₃²⁺ and PH²⁺ fall off linearly with electron energy, whereas the curves of PH₂²⁺ and P²⁺ have in this plot a very long tail. Fischler *et al.*⁴ do not mention this crucial difference and derive for all ions appearance potentials in two ways, namely by linear extrapolation and square root plot.²² Their results (see Table VI) show a surprisingly low ionization potential of 15.6 eV for PH₃²⁺ and appearance potential of 21.2 eV for PH²⁺ as compared to their values for the appearance potentials of PH₂²⁺ and P²⁺. Similar results would be derived in the present study of PH₃, depending on the method used. However, when the results are intercompared with the data obtained in deuterated phosphine, a considerable discrepancy exists between the values for PH₃²⁺ and PD₃²⁺ and the values for PH²⁺ and PD²⁺. Thus it was possible to draw the conclusion that part of the ion signal observed for $m/e=17$ is due to OH⁺ from the process $H_2O + e \rightarrow OH^+$ and part of the ion signal observed for $m/e=16$ is due to O⁺ from the process $O_2 + e \rightarrow O^+$ and to a lesser degree from the process $H_2O + e \rightarrow O^+$. All the other doubly ionized ions PH₂²⁺, P²⁺, PD₂²⁺, PD²⁺ occur at m/e with half numbers, and thus their signal is not obscured by impurity ions. The above explanation is further supported by the facts (1) that the threshold law of the ion signal at $m/e=16$ and 17 is linear, (2) that the appearance potential for the process $H_2O + e \rightarrow OH^+$ with 18.3 eV²³ is close to the observed values of 15.0 eV (Fischler *et al.*⁴) and 17.0 eV (present study) and the appearance potential of processes $O_2 + e \rightarrow O^+$ with 18.9 eV²³ is close to the observed value of 21.2 eV by Fischler *et al.*, and (3) that the impurity signals of H₂O and O₂ observed mass spectrometrically are in the corresponding orders of magnitude.

On the assumption that the n th power rule is correct, the minimum double ionization potential was taken in the present study as the point to which the square root of the extrapolated double ionization cross section function met the energy axis. In case of PH₃²⁺ and PH²⁺ the ion signals have been corrected for the impurity signals OH⁺ and O⁺, respectively. Table VI gives the present results and the results of Fischler *et al.*⁴ From this table it may be

seen that the double ionization and appearance potentials in phosphine agree within the experimental error with those in deuterated phosphine, as a possible difference could only be related to a difference in zero-point energies. The agreement between the present values in PH₃ and the experimental values of Fischler *et al.*⁴ is good for PH₂²⁺ and P²⁺ and poor for PH₃²⁺ and PH²⁺. An explanation for the discrepancy of the two latter has been given above.

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