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Electron emission from methane, ammonia, monomethylamine, and dimethylamine by 0.25 to 2.0 MeV protons*

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Absolute cross sections, differential in electron energy and emission angle, have been measured for ejection of electrons from methane, ammonia, monomethylamine, and dimethylamine by 0.25 to 2.0 MeV protons. Electron energy distributions are presented for 12 emission angles between 15° and 125°. The results indicate that emission cross sections for electrons ejected with energy greater than about 1 eV show no effects related to molecular structure for this group of molecules, within experimental uncertainty. The double-differential cross sections are found to be scalable in terms of the number of weakly bound electrons per molecule. Total ionization cross sections are determined by integration of the double-differential cross sections with respect to energy and angle. The results are compared with the results for other low-*Z* polyatomic molecules, and also in the case of methane, with results from electron impact ionization.

I. INTRODUCTION

The ionization of atoms and molecules by proton impact and the resulting energy and angular distribution of emitted electrons is of fundamental importance in connection with a number of fields such as atmospheric, plasma, and radiation physics.¹⁻³ The present work is part of a program to determine whether molecular structure has an important influence on the energy and angular distribution of secondary electrons produced by proton impact on low-*Z* polyatomic molecules. In an ionizing collision of a fast electron or proton with a molecule, it has often been assumed that the ionization cross section for the molecule is given as the sum of the corresponding ionization cross section of its constituent atoms (the additivity rule for ionization cross section).⁴⁻⁷ This is a generalization of the Bragg additivity rule of stopping power of molecular substances which has been investigated by a number of workers.⁸⁻¹¹

For atoms of low *Z*, the total ionization cross section is much greater than the inner (*K*) shell ionization cross section; ionization of the weakly bound valence electrons is, therefore, the dominant interaction.¹² If the molecular structure does not significantly influence the yield of electrons ejected at a given energy and angle, then the corresponding ionization cross sections, differential in energy and angle, should depend only on the number of weakly bound electrons, which was illustrated for a number of simple hydrocarbon molecules in earlier work.¹ Moreover, if the double differential ionization cross sections are scalable in terms of the number of weakly bound electrons per molecules, then the additivity rule for molecular ionization cross sections is also established. Watanabe has shown theoretically that ionization cross sections for electron impact on molecules should obey the additivity rule to within 20% for sufficiently high impact energies.⁵ Since ionization cross sections for electron and proton impact at the same velocity are expected to be equal in the energy range considered in the present work (0.25 to 2.0 MeV proton energy), the additivity rule should also apply in the present case to within a similar agreement.

Cross sections, differential in energy and angle, for electron emission following proton impact of methane (CH_4), ammonia (NH_3), monomethylamine (CH_3NH_2), and dimethylamine ($(\text{CH}_3)_2\text{NH}$) molecules were measured for protons of 0.25, 1.0, and 2.0 MeV energy. These cross sections, scaled by the number of weakly bound electrons per molecule, are compared with each other. Total ionization cross sections, obtained by integration of the double-differential cross sections with respect to energy and angle, are calculated. Total ionization cross section results from the present study are compared with previous work on other polyatomic molecules and also, in the case of methane, with electron impact ionization cross sections.

II. EXPERIMENTAL METHOD

In the present work, two distinct experimental techniques have been used, in combination, to determine cross sections, differential in energy and angle, for the emission of electrons from various target gases under proton impact. Absolute cross sections for ejected electrons with energies greater than ~20 eV were determined by a system which utilized a cylindrical-mirror electrostatic analyzer (CME) to measure electron energies. Relative cross sections for ejected electrons with energies ranging from ~1 eV to several hundred eV were determined by a system which used a time-of-flight (TOF) technique. By normalizing the relative TOF cross section to the absolute CME cross sections in the energy region where both give reliable results, absolute cross sections were determined for ejected electron energies greater than ~1 eV. Integration of these double-differential cross sections with respect to emission angle and electron energy yields total ionization cross sections for the various target gases.

A. Electrostatic analysis system

The apparatus and experimental technique used in the cylindrical-mirror electrostatic analyzer system (CME) shown schematically in Fig. 1 have been described previously,¹³ and, therefore, will be discussed only briefly

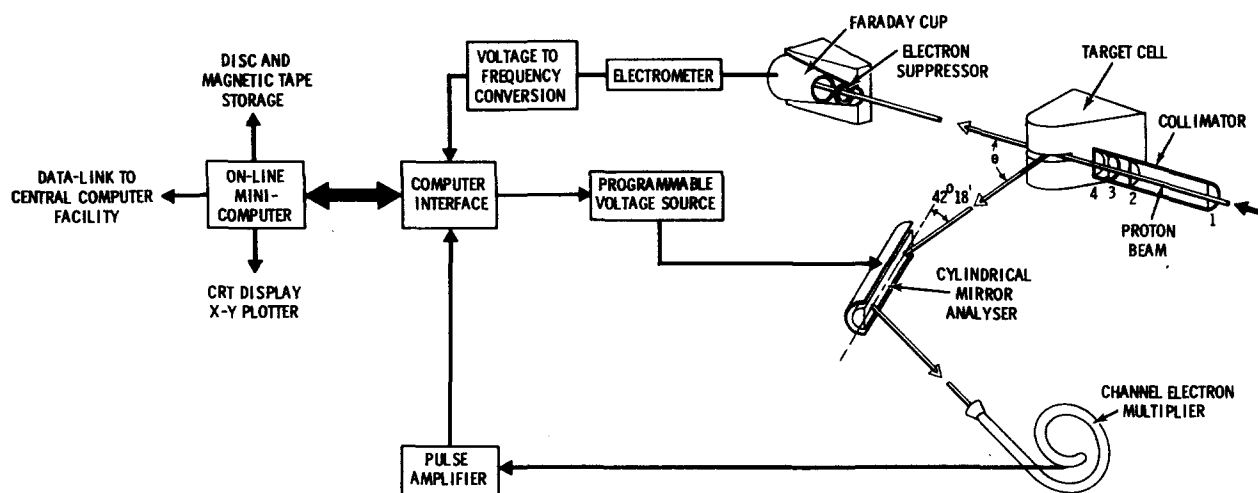


FIG. 1. Schematic diagram of the cylindrical mirror electrostatic analyzer apparatus and associated instrumentation.

here. A proton beam from a Van de Graaff generator, after momentum analysis and collimation, was passed through a differentially pumped target cell and collected in a Faraday cup. Electrons ejected from the target gas were energy analyzed by the electrostatic analyzer and detected by a continuous channel electron multiplier. The analyzer had an energy resolution of approximately 3.5% and an angular acceptance of approximately 5° . Electron energy spectra were obtained by recording the number of electrons transmitted by the electrostatic analyzer with a given analyzing voltage for a preset number of protons ($\sim 10^{12}$) collected in the Faraday cup. Energy spectra of ejected electrons were obtained at various emission angles ranging from 15° to 125° . The cross sections, differential in observation angle θ and the electron energy ϵ , were calculated from the following equation:

$$\sigma(\theta, \epsilon) = \frac{N_e e^{\alpha P x}}{N_p P dS \Delta E} 3.23 \times 10^{16} \text{ cm}^2/\text{eV sr molecule}, \quad (1)$$

where N_e is the number of electrons counted while a number of protons N_p passed through the target cell; P is the target gas pressure in Torr; ΔE is the energy spread of the electrons transmitted by the analyzer; dS is the product of solid angle subtended by the analyzer and the proton path length observed within this solid angle; α is the absorption coefficient for electrons of energy ϵ in the target gas; and x is the effective path length of the electrons through the target gas including the effects of differentially pumping the target cell.

B. Time-of-flight system

The time-of-flight apparatus and related experimental techniques have recently been described by Toburen and Wilson.¹⁴ In this method, ionization of target gas molecules was produced in an interaction region by a pulsed beam of protons which was obtained by chopping the dc proton beam from a Van de Graaff generator with an rf high voltage oscillator, as shown schematically in Fig. 2. The interaction region was formed by the intersection of the pulsed proton beam and a directed-flow gas beam target. Electrons ejected in collisions between

the pulsed proton beam and the target gas molecules were detected by a channel electron multiplier as a function of time following the proton pulse. The energy of an electron reaching the detector was determined by its time-of-flight and the path length from the interaction region to the detector, which was approximately 7.5 cm. A spectrum of the number of electrons reaching the detector as a function of time was converted to a spectrum of relative cross section for electron emission as a function of electron energy for various emission angles with respect to the proton beam directions, ranging from 50° to 125° . Physical limitations in the apparatus prevented measurements at smaller emission angles.

III. DATA REDUCTION

A thorough discussion of the method of estimating uncertainties in the absolute electron emission cross sections, differential in emission angle and electron energy, for the CME system, is given in Ref. 13. The resulting cross sections for proton impact on the target gases in the present study are estimated to have an uncertainty of $\pm 20\%$ in absolute value, and $\pm 10\%$ in relative value for ejected electron energies greater than 20 eV. Excellent agreement has been reported between the results of cross section measurements of Stolterfoht, Crooks, and Rudd, and Toburen for electron energies greater than about 20 eV in the case of proton impact on nitrogen.^{13,15,16} However, discrepancies exist in the reported low-energy electron ejection cross sections (below ~ 20 eV).¹⁵ The TOF method has been utilized in the present study to improve the low energy electron cross section measurements.

In both the CME and TOF methods of electron energy analysis used in the present measurements, energy spectra of double-differential cross sections were obtained for various emission angles. Figure 3 shows a typical example. The relative TOF spectrum has been normalized to agree with the CME spectrum in the range from ~ 20 eV to ~ 100 eV where both give reliable results. This normalization yields absolute TOF cross sections for electron energies greater than ~ 1 eV,

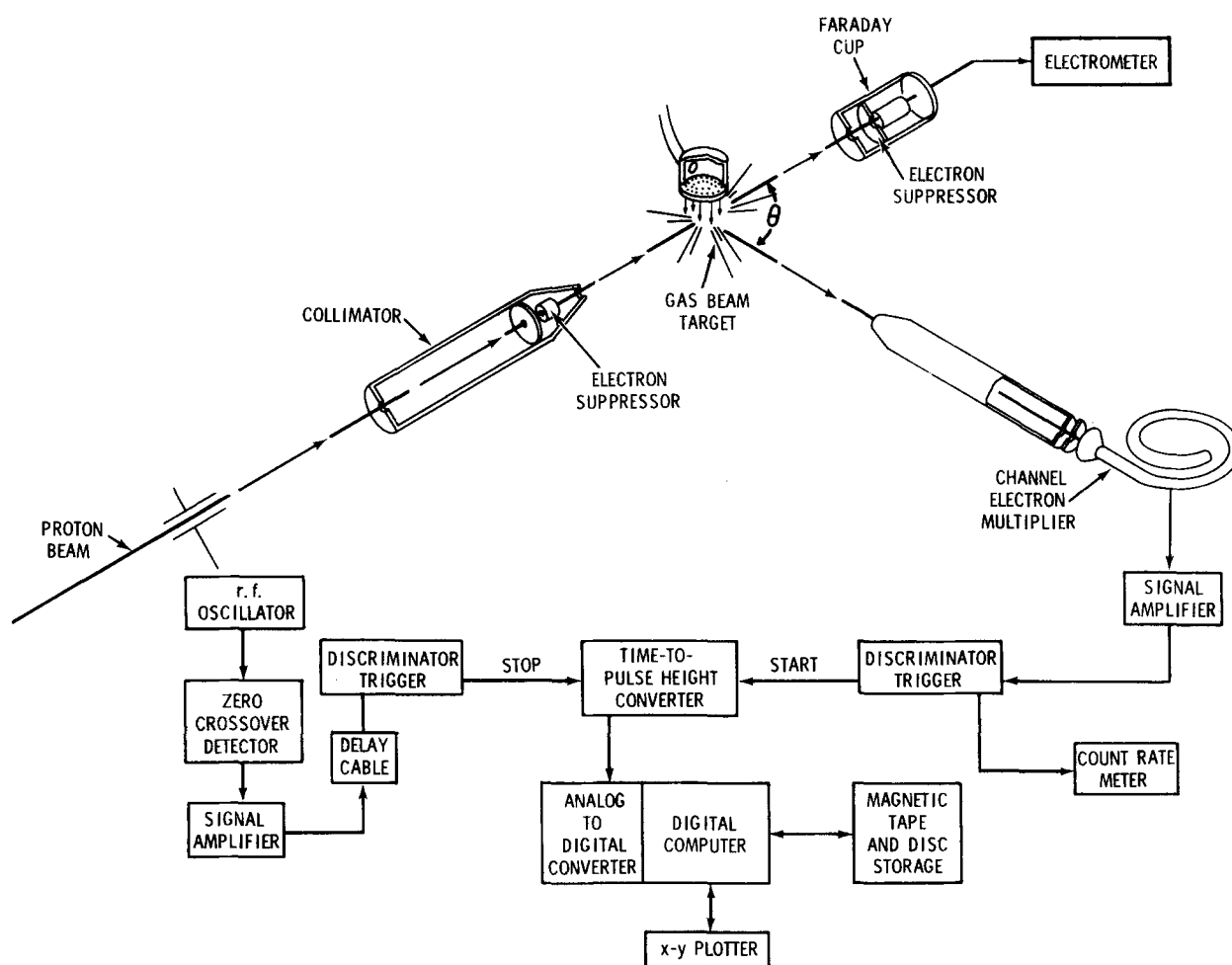


FIG. 2. Schematic diagram of the time-of-flight apparatus and associated instrumentation.

with an estimated uncertainty of 20% in the absolute values. Since the ionization cross sections fall off rapidly with increasing electron energy, the low energy portion of the spectrum contributes significantly to total ionization cross sections.

Unfortunately, we were not able experimentally to obtain a TOF spectrum at each of the twelve ejection angles studied with the CME system from 15° to 125° . Nonetheless, it is possible to use the TOF results for those angles studied (i.e., $\theta = 50^\circ, 70^\circ, 90^\circ$, and 125°) to estimate TOF corrections to the CME spectra for all other angles investigated (i.e., $\theta = 15^\circ, 20^\circ, 30^\circ, 40^\circ, 60^\circ, 80^\circ, 110^\circ, 120^\circ$). Figure 4 shows TOF spectra for 2 MeV H^+ on dimethylamine. It can be seen that the shapes of the low energy portion of the various spectra are nearly identical. The curves have been normalized to overlap in the region from ~ 10 to 20 eV. Since the TOF correction to the CME data depend only on the shape of the lower energy portion of the spectra and the shape does not vary greatly over a range of from 50° to 125° , the assumption was made that the *shape* of the low energy spectra will not be greatly different for the other angles studied. TOF corrections have been made to the low energy portion of the CME spectra for all angles studied based on this assumption. It should be emphasized that this assumption is in re-

gard to the shape of the spectra only, and does not imply that the absolute values of the double-differential cross sections are taken to be equal for low energy electrons.

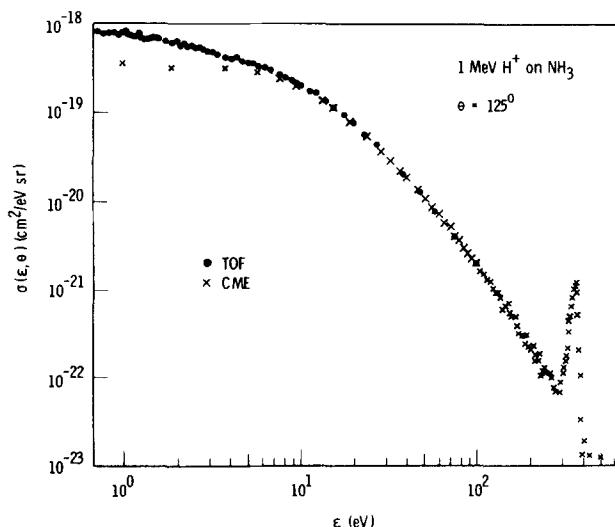


FIG. 3. TOF spectrum (●) normalized to CME spectrum (x) at $\theta = 125^\circ$ for 1 MeV protons on ammonia. θ is the emission angle and E is the electron energy.

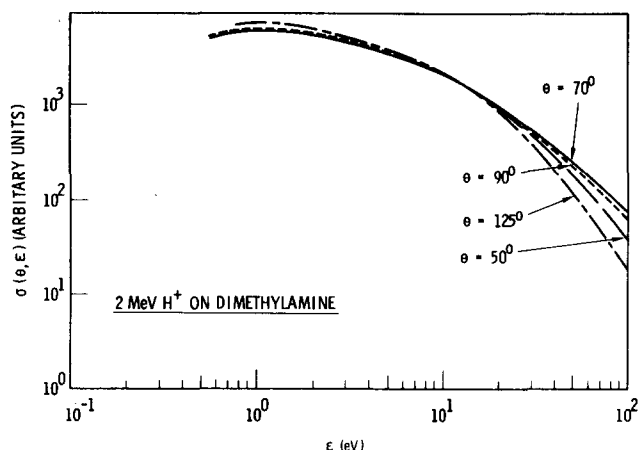


FIG. 4. TOF spectra for 2 MeV protons on dimethylamine. This figure shows that the shape of the curves at energies less than 20 eV is nearly independent of the emission angle θ . ϵ is the electron energy.

IV. RESULTS AND DISCUSSION

The double-differential ejected electron cross section multiplied by the electron energy, produced by 1 MeV proton impact on ammonia, is shown in Fig. 5 as an example of the data obtained.¹⁷ The purpose of multiplying the cross section by the respective electron energy is primarily to reduce the numerical range required to present the data from seven orders of magnitude to four. This operation also forms a quantity on the ordinate which is proportional to the energy loss or stopping power for production of first-generation secondary electrons of energy ϵ . The twelve different curves are for emission of electrons at the indicated angles

ranging from 15° to 125° . The general features of the ammonia data shown in Fig. 5 are common to the data obtained for the various target gases studied at proton energies of 0.25, 1.0, and 2.0 MeV. These include the following: a maximum in the energy distributions near zero electron energy for all angles, a broad maximum at large electron energies for small ejection angles, and either one or two narrow peaks appearing at all angles and occurring at fixed electron energies. The peaking of the distributions near zero electron energy is associated with distant collisions in which a small amount of momentum is transferred to the molecule, and the broad maximum at high energies arises from essentially binary collisions between the incident proton and an orbital electron. The narrow peaks correspond to Auger electrons emitted from carbon atoms (at 250 eV) and/or nitrogen atoms (at 365 eV) in the target molecules.

In Figs. 6–8, angular distributions of electron emission cross sections are shown for various electron energies. The cross sections are scaled by the number of outer weakly bound electrons per target molecule (total number of electrons minus the K -shell electrons of carbon and nitrogen). The energy and angular distributions per weakly bound electron are approximately the same, within experimental error, for all four molecules investigated, over the entire electron energy range studied. This result confirms the earlier findings of Wilson and Toburen,¹ where the same scalability was observed for ejected electron energies greater than 10 eV in the case of proton impact on various hydrocarbon molecules. The scaled angular distributions shown in Figs. 7 and 8 agree quantitatively with the re-

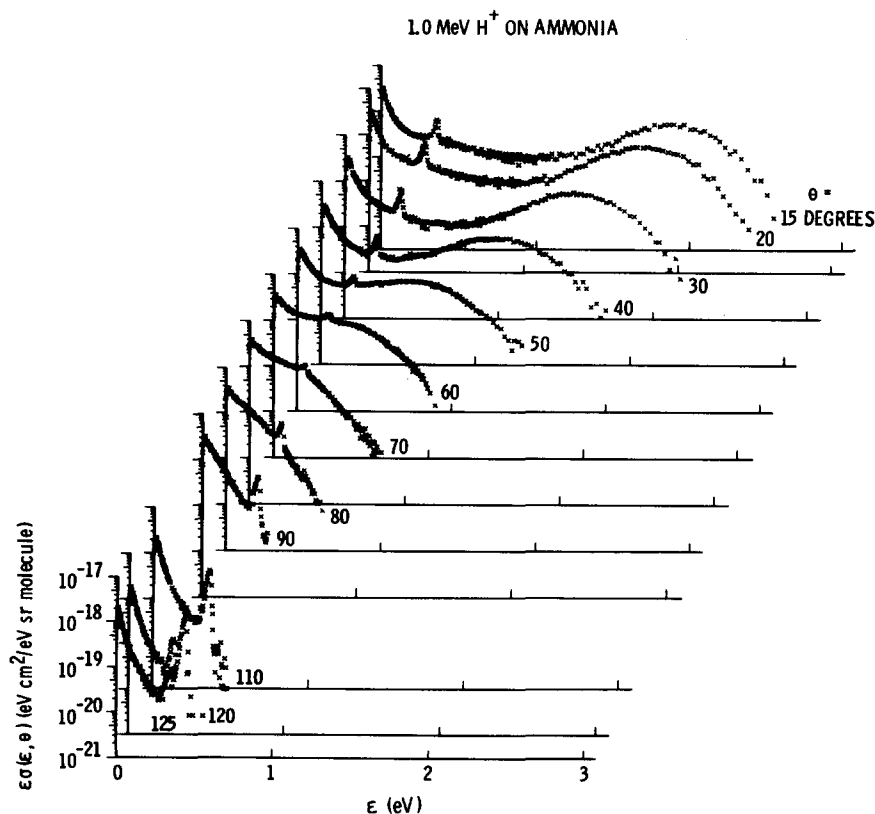


FIG. 5. Cross sections, differential in electron energy ϵ and emission angle θ , for ejection of electrons by 1 MeV protons on ammonia.

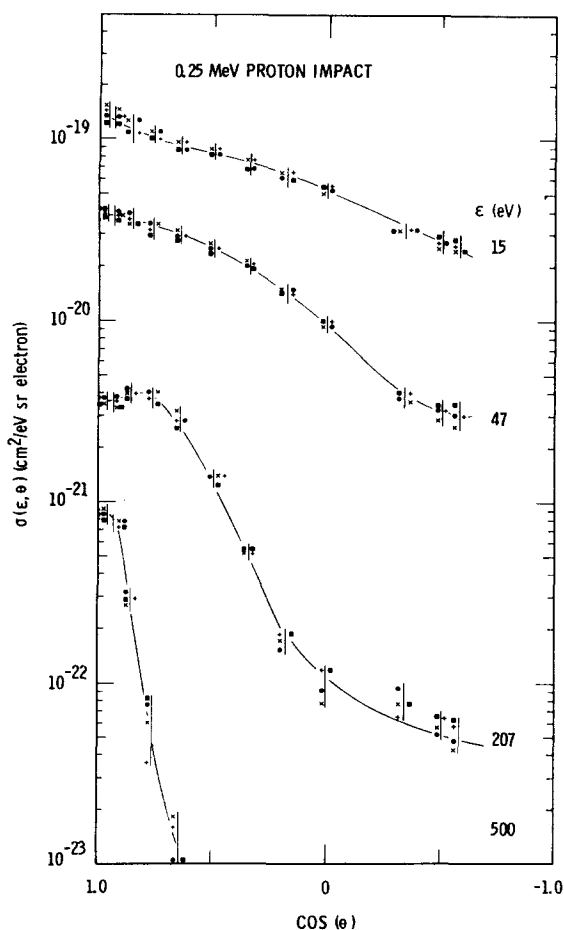


FIG. 6. Angular distributions of electrons of several energies ejected from methane (x), ammonia (●), monomethylamine (+), and dimethylamine (■) by 0.25 MeV protons. The cross sections are scaled according to the number of weakly bound electrons per molecule. The vertical lines indicate the exact angle; the data symbols are spread horizontally for clarity. θ is the emission angle and ϵ is the electron energy.

sults reported in Ref. 1 for 1 and 2 MeV proton impact of hydrocarbon molecules, respectively; the present work extends the previous observation of scalability to include ejected electron energies as low as 1 eV. Because of low beam intensity for 0.25 MeV protons, no TOF corrections were made to the CME results at this energy.

Further evidence of scalability of electron emission cross sections in terms of the number of weakly bound electrons per molecule is presented in Figs. 9–11, where total ionization cross sections are displayed for the various molecules studied in the present work and Ref. 1. The error bars shown represent $\pm 10\%$ relative uncertainty in the total ionization cross section, since all measurements were made at the same laboratory. Table I summarizes the total ionization cross section results of the present work. It has been pointed out previously that scalability is possible because the dominant interaction of the incident proton is with the outer electrons of the target molecule, the K -shell ionization cross section for carbon and nitrogen being about two orders of magnitude smaller than the total ionization cross sections of the molecules discussed

TABLE I. Total ionization cross sections (in units of 10^{-16} cm^2).

| Proton energy (MeV) | Methane | Ammonia | Monomethylamine | Dimethylamine | σ_e |
|---------------------|---------|---------|-----------------|---------------|------------|
| 0.25 | 3.1 | 3.4 | 5.4 | 6.9 | 0.39 |
| 1.0 | 1.3 | 1.4 | 2.4 | 3.6 | 0.17 |
| 2.0 | 0.93 | 0.82 | 1.6 | 2.2 | 0.11 |

σ_e is the cross section per weakly bound electron.

All values given in Table I have an estimated uncertainty of 20% in absolute value.

here.¹ In addition, binary encounter theory^{2,13} indicates that the variation of ionization potential within the group of molecules being considered (8.2 eV for dimethylamine to 12.8 eV for methane) is not great enough to make a significant difference in the respective electron yields.

The results of the present work suggest that the ionization cross section for low- Z polyatomic molecules, scaled by the number of weakly bound electrons, does not vary significantly with the ionization potential of the molecule for the incident proton energies considered

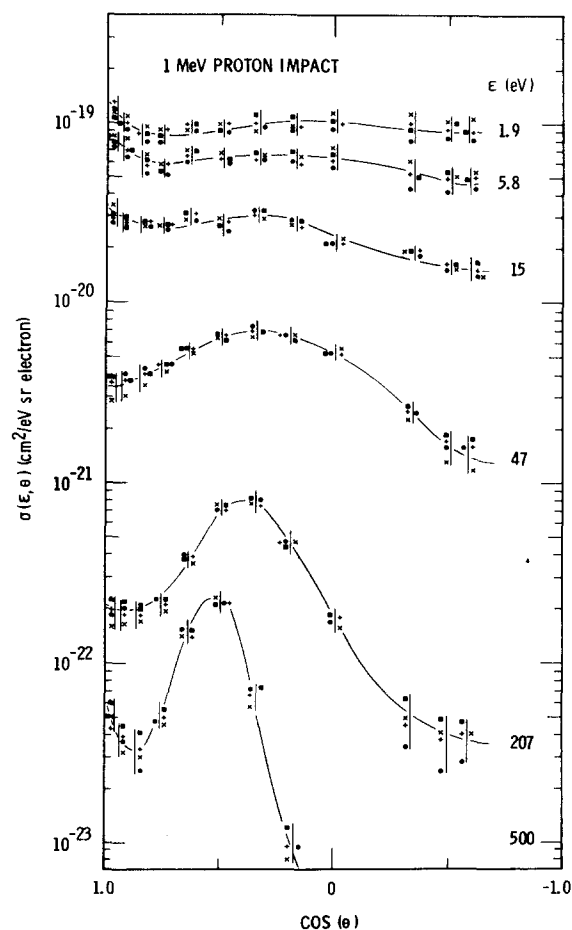


FIG. 7. Angular distributions of electrons of several energies ejected from methane (x), ammonia (●), monomethylamine (+), and dimethylamine (■) by 1.0 MeV protons. The cross sections are scaled according to the number of weakly bound electrons per molecule. The vertical lines indicate the exact angle; the data symbols are spread horizontally for clarity. θ is the emission angle and ϵ is the electron energy.

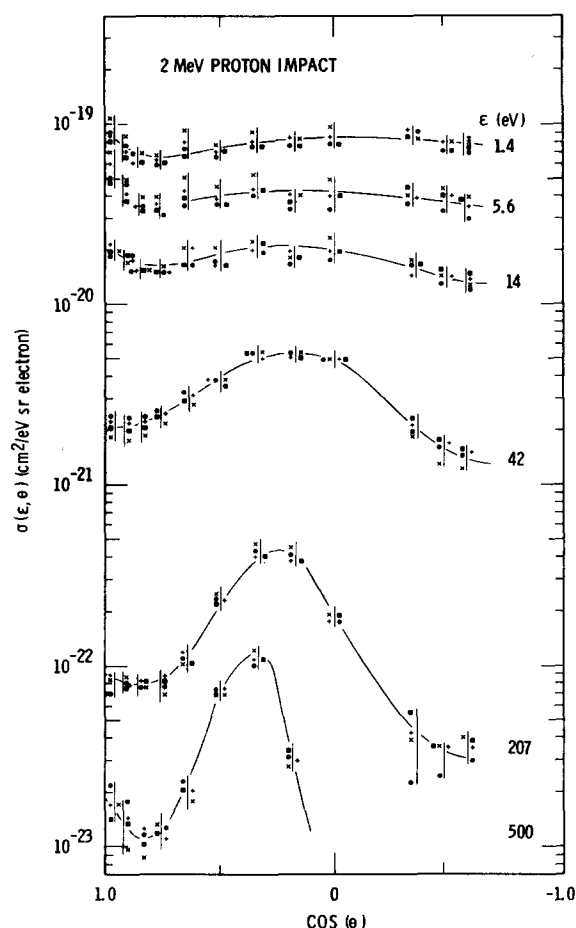


FIG. 8. Angular distributions of electrons of several energies ejected from methane (\times), ammonia (\bullet), monomethylamine ($+$), and dimethylamine (\blacksquare) by 2.0 MeV protons. The cross sections are scaled according to the number of weakly bound electrons per molecule. The vertical lines indicate the exact angle; the data symbols are spread horizontally for clarity. θ is the emission angle and ϵ is the electron energy.

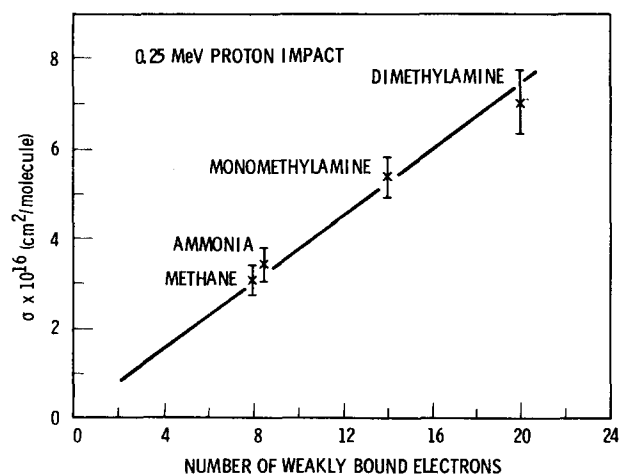


FIG. 9. Total ionization cross section for various low- Z polyatomic molecules by 0.25 MeV proton impact, plotted as a function of the number of weakly bound electrons per molecule. Error bars indicate 10% relative uncertainties.

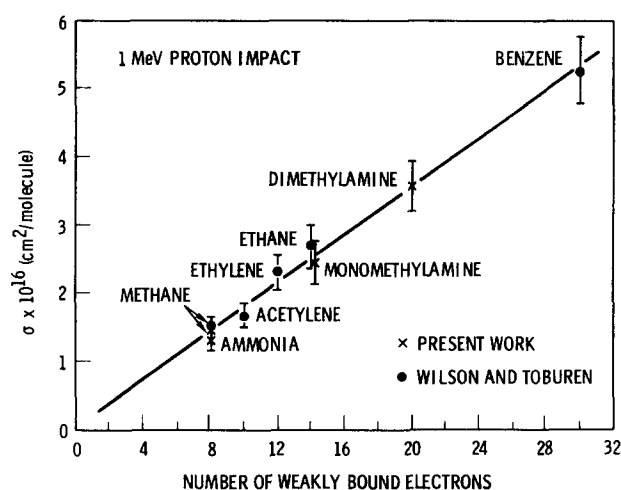


FIG. 10. Total ionization cross sections for various low- Z polyatomic molecules by 1.0 MeV proton impact, plotted as a function of the number of weakly bound electrons per molecule. Error bars indicate 10% relative uncertainties. The results of Wilson and Toburen are from Ref. 1.

here, to within experimental uncertainty. The observed scalability of molecular cross sections in terms of weakly bound electrons is consistent with the additivity rule for molecular cross sections which has been observed to hold to within experimental error of 15% in the case of ionization of water vapor by 0.1–20 keV electrons.¹⁸

In the limit of high projectile energy, the Born approximation predicts the total ionization cross section of a given atom or molecule to be the same for proton and electron impact at equal velocity.^{19–21} A comprehensive comparison of electron and proton impact ionization cross sections of various atoms has been carried out by Hopper *et al.*, which experimentally confirmed this behavior.²² Figure 12 shows a com-

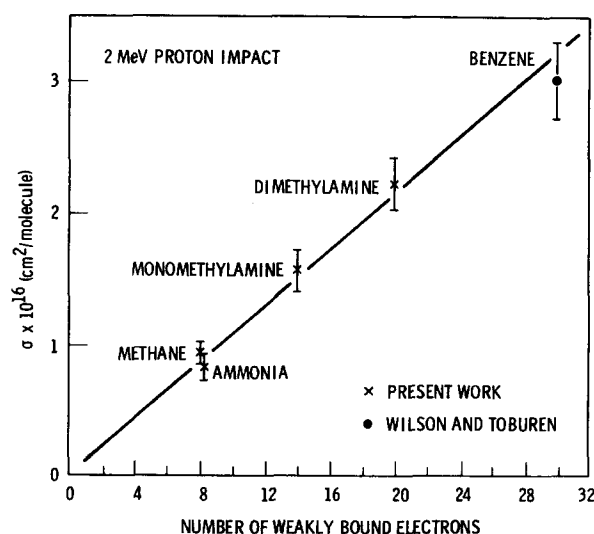


FIG. 11. Total ionization cross sections for various low- Z polyatomic molecules by 2.0 MeV proton impact, plotted as a function of the number of weakly bound electrons per molecule. Error bars indicate 10% relative uncertainties. The results of Wilson and Toburen are from Ref. 1.

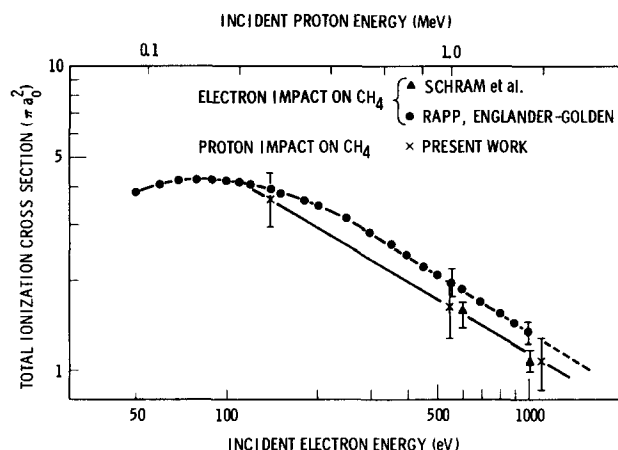


FIG. 12. A comparison of total ionization cross sections of methane for electron and proton impact at equal velocities. Error bars indicate estimated absolute uncertainties. The results of Rapp and Englander-Golden are from Ref. 23, and the results of Schram *et al.* are from Ref. 7.

parison of experimental measurements of the total ionization cross section for protons and electrons incident at the same velocities on methane.^{7,23} The agreement within experimental uncertainties between the proton impact results of the present work and those of the electron impact work confirms the validity of the TOF updating method used in the present work since the major portion of the total ionization cross section is contributed by low energy electrons. Furthermore, this agreement lends confidence to the absolute values of the cross sections obtained with the CME system.

V. CONCLUSIONS

Cross sections, differential in energy and angle, for ejection of electrons from methane, ammonia, monomethylamine, and dimethylamine following proton impact, have been measured for proton energies from 0.25 to 2.0 MeV. Total ionization cross sections were obtained from the double-differential cross sections by integration over energy and angle. The total ionization cross section results for methane were found to be in agreement with electron impact results at equal velocity, as predicted by theory.

For the limited group of molecules considered in the present work, the ejected electron cross sections,

differential in energy and angle, were observed to be proportional to the number of weakly bound electrons, to within experimental uncertainty. This result, combined with earlier work on hydrocarbon molecules, suggests that the structure of polyatomic molecules of low *Z* does not significantly influence the yield of secondary electrons with energies greater than ~1 eV.

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