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EFFECT OF MOLECULAR BINDING ON PRIMARY IONIZATION*

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ABSTRACT

Cross sections, differential in ejection energy and angle, for electron emission from methane, ethane, ethylene, acetylene and benzene molecules following proton impact have been measured for protons of 0.3 and 1.0 MeV. The purpose in making the measurements is to look for an effect on the electron yield attributable to the chemical form or molecular binding of the target atoms. The results for the five molecules indicate that for many practical situations involving energy transport by energetic secondaries there is no significant binding effect. However, when the results are compared with similar data for molecular hydrogen, one observes an apparent difference in the amount of ionization per carbon atom depending on the degree of saturation of the hydrocarbon. The more highly saturated molecules, (methane, ethane, ethylene) appear to produce, per carbon atom, more secondary electrons with energies up to 60 eV, than do the less saturated benzene and acetylene. The observation suggests that the amount of ionization produced in a hydrocarbon gas may be quite different from what one would calculate by summing the contributions of the atomic constituents of the gas.

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Introduction

Cross sections, differential in ejection energy and angle, for electron emission from methane, ethane, ethylene, acetylene and benzene molecules following proton impact have been measured for protons of 0.3, 1.0 and 2.0 MeV. The purpose in making the measurements is to look for an effect on the electron yield attributable to the chemical form or molecular binding of the target atoms. If such an effect is significant, it has implications for the additivity rules for ionization and energy loss in gaseous mixtures. For example, the ionization one observes in a "tissue equivalent" gas might then depend on whether methane or acetylene is used for the carbon component. The data for the several molecules have been compared by comparing the various moments of the energy and angular distributions as well as directly comparing the yields themselves.

Experimental Method

The apparatus and experimental technique used for ejected-electron yield measurements have been described in detail previously^(a) and therefore will be discussed here only briefly (Fig. 1). The proton beam from a Van de Graaff generator, after energy analysis and collimation is made to pass through a differentially pumped target cell before being collected in a Farady cup. Electrons ejected from the target gas are energy analyzed by a cylindrical-mirror electrostatic analyzer and detected by a continuous-channel electron multiplier. The electrostatic analyzer has an energy resolution of 3.5% and was collimated to accept electrons ejected in a given direction with an angular spread of approximately five degrees. Electron-energy spectra are measured by recording the number of electrons transmitted by the electrostatic analyzer with

a given analyzing voltage for a preset number of protons passing through the target cell. Analyzer voltage is automatically advanced and the process repeated. Data points are normally obtained at intervals of either 2 or 4 eV with each data point representing the electron yield for approximately 10^{12} protons. Energy spectra of ejected electrons are obtained at several angles from 20 to 130 degrees. Data were obtained for all five molecules at proton energies of 0.3 and 1.0 MeV and for benzene at 2.0 MeV also. Reduction and plotting of the large volume of data are accomplished with computers. Integration over ejection angle provides energy spectra of ionization electrons ejected at any angle.

Results

Fig. 2 shows the results for 2 MeV protons bombarding benzene; ejected-electron yield or cross section, multiplied by the electron energy is plotted on a log scale against ejected-electron energy. The purpose in multiplying by the respective electron energy is primarily to reduce the numerical range required to present the data. It also forms a quantity on the ordinate that is proportional to the energy loss or stopping power for production of first generation secondary electrons with the respective energy. The 10 different curves are for ejection of electrons at the indicated 10 angles between 20 and 125 degrees.

Several distinct features are evident in the energy distribution shown in Fig. 2. These are a) the very narrow peak appearing at all angles and occurring at a fixed electron energy of about 250 eV, b) the strong peaking of the distributions near zero electron energy at all angles, and finally c) the broad

maximum which occurs for forward ejected electrons and whose position varies in energy with emission angle. The narrow peak at 250 eV arises from Auger emission from carbon following the creation of an inner shell vacancy in a carbon atom. Auger emission is isotropic since it occurs at a time after the collision long in comparison to the collision time itself. The energy of the Auger electron is characteristic of the excited atom and is not influenced by the kinematics of the proton-molecule collision. Nothing further will be said about Auger emission except to point out that the area under the Auger peak can be used to obtain the total inner-shell ionization cross section, (K-shell ionization cross section for carbon in this case). The magnitude of the K-shell ionization cross section relative to the total ionization cross section will be important later. The peaking of the distributions near zero electron energy is associated with the distant collisions in which a small amount of energy is transferred to the molecule and the broad maximum results from essentially binary collisions between the proton and an atomic electron.

The main features of the benzene data of Fig. 2 are common to the data taken at 0.3 and 1.0 MeV proton energies and to all five hydrocarbon molecules studied. This example was selected for illustration, only because the features are somewhat more separated owing to the higher proton energy and are therefore more distinct. As the proton energy is decreased, the broad maximum shifts to lower electron energy, the relative size of the Auger-emission peak decreases and the overall yield of ejected electrons increases.

For proton energies of 0.3 and 1.0 MeV the distributions, differential only in ejected-electron energy obtained by

integrating over the emission angle, are scalable in terms of the number of outer or weakly bound electrons in the molecule. When the yields or cross sections in units of $\text{cm}^2\text{ev}^{-1}\text{molecule}^{-1}$ are respectively divided by the total number of valence electrons in the molecule (total electrons minus the K-shell electrons) the result is a single curve in units of $\text{cm}^2\text{ev}^{-1}\text{"electron"}^{-1}$. The distribution "per electron" is the same for all five molecules for secondaries with energies greater than 10 eV, (Fig. 3). Below 10 eV the data are too sparse to provide a good comparison. This scalability implies that the effective distribution per carbon atom is the same for all five molecules in the group studied, and that effective distribution is just four times the distribution per electron since each carbon atom has four contributing electrons. One can conclude from this that the variation in chemical environment of the carbon atoms within these five molecules makes little difference in the energy distribution of the first-generation secondary electrons having energies greater than 10 eV.

Also shown in Fig. 3 for comparison purposes are previously measured distributions for electron ejection from molecular hydrogen expressed as cross section per electron.⁽²⁾ There is a significant difference in the distributions, especially for low ejected-electron energies. From this, one can conclude that chemical environment or molecular binding in general can influence the yield of low energy secondary electrons, as one would expect.

This observation has implications for the validity of the additivity rule often used for obtaining stopping powers and ionization yields for gaseous mixtures. It is customary to

calculate the stopping power of a gaseous mixture by summing the contributions of the atomic constituents, each weighted in proportion to the amount of that atomic constituent present in the mixture. Let us use the additivity rule and the data of Fig. 3 to calculate an equivalent electron yield for the carbon atom.

When one constructs a secondary-electron energy distribution for carbon by taking $1/2$ the difference between the acetylene yield and molecular hydrogen yield [$1/2(C_2H_2 - H_2)$], one obtains a result different from that obtained by subtracting from the methane distribution 2 times the hydrogen distribution, [$CH_4 - 2H_2$], (Fig. 4). The difference shows up as a larger yield of secondary electrons for energies up to about 60 eV for the distribution synthesized from the methane-hydrogen data; the yield of 10 eV secondaries is 30% larger from methane than from acetylene by this method of analysis. Distributions synthesized in a similar manner from ethane-hydrogen and ethylene-hydrogen agree more closely with the distribution obtained from methane-hydrogen whereas the distribution obtained from benzene-hydrogen falls with the distribution for the acetylene-hydrogen, i.e., the saturated hydrocarbons produce similar secondary electron-energy distributions for carbon atoms and the unsaturated hydrocarbons indicate a different distribution.

In order to discuss the implications of Fig. 4 more quantitatively, one needs to define:

$$S(\Delta)_{KE} = \int_{\Delta}^{\infty} \epsilon \sigma(\epsilon) d\epsilon, \quad \text{the} \quad (1)$$

partial stopping cross section for first generation secondary electrons (FGSE) having initial kinetic energy greater than Δ .

Then $f(\Delta)_{KE} = S(\Delta)_{KE}/S(\Delta)_{KE} =$ fraction of total FGSE kinetic energy that exceeds Δ . If Δ is interpreted as the energy cutoff for nonlocally deposited energy then $f(\Delta)_{KE}$ is the fraction of the total K.E. that "escapes" and $1-f(\Delta)_{KE}$ is the locally imparted KE fraction. (2)

Similarly to Equations (1) and (2), define:

$$\sigma(\Delta)_I = \int_{\Delta}^{\infty} \sigma(\epsilon) d\epsilon, \quad \text{the} \quad (3)$$

partial ejection cross section for FGSE having initial kinetic energy greater than Δ ; and the fraction, $f(\Delta)_I = \sigma(\Delta)_I/\sigma(0)_I$ (4) is then the relative number of FGSE associated with $f(\Delta)_{KE}$.

Equations (1) - (4) were evaluated for a carbon atom in one case by assuming its scattering properties are represented by four effective electrons and using data from Fig. 3. This procedure gives the results in the first two columns of Table I.

For comparison, Equations (1) - (4) were evaluated using the additivity rule and the results for acetylene in one case and methane in the other. This gives respectively the last two

pair of columns in Table I. In the latter two cases, the quantities in the denominator of Equations (2) and (4) were evaluated using the universal curve, i.e., representing the carbon atom by four effective electrons. This procedure overemphasizes the inadequacy of the additivity rule somewhat.

The results shown in Table I indicate that use of the additivity rule can lead one to over-estimate both the energy and the number of electrons escaping a small absorption site. Perhaps more importantly, they indicate that different gas mixtures having the same carbon to hydrogen ratio may give different ionization results. Thus, one must be cautious about relating the ionization collected in proportional counters to the energy deposited in the counter when not all of the electrons are

TABLE I

1.0 MeV PROTONS ON HYDROCARBONS

Universal Curve			Additivity Rule			
C-atom $\equiv$ 4 H-C electrons			$(C_2H_2-H_2)^{1/2}$		(CH_4-2H_2)	
Δ (eV)	$f(\Delta)_{KE}$	$f(\Delta)_I$	$f(\Delta)_{KE}$	$f(\Delta)_I$	$f(\Delta)_{KE}$	$f(\Delta)_I$
0	1.0	1.0	1.05	1.07	1.21	1.28
10	.94	.53	.99	.57	1.13	.67
20	.86	.32	.91	.34	1.04	.39
60	.70	.12	.73	.13	.82	.14

References

- a) L. H. Toburen, Phys. Rev. A 3, 216 (1971).
- b) L. H. Toburen and W. E. Wilson, Phys. Rev. A 5, 247-256 (1972).

Figure 1

$\sigma(\theta, E)$

Figure 2

$\sigma(e) \quad [m^2 eV^{-1} electron^{-1}]$

Figure 3

Electron Energy, (eV)

"YIELD per CARBON ATOM" FOR 1.0 MeV PROTONS

Figure 4

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