

Effect of the molecular environment on the C, N, and O Auger-electron yields induced by MeV H^+ and He^+ ions

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The *KLL* Auger-electron yields from a number of C-, N-, and O-bearing compounds have been measured for either H^+ or He^+ bombardment in the incident energy range of 0.6–2.0 MeV. The yields are seen to vary significantly with the chemical environment with variations of greater than 30% observed between CH_4 and CF_4 yields. These variations seem to be reproducible by two simple scaling laws, one based on the inelastic scattering cross sections of the various molecular components, while the second uses the effective number of valence-shell electrons about the site of the *K*-shell vacancy. The cross sections are reported for the He^+ -induced carbon and nitrogen Auger-electron yields from CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , CO, CO_2 , C_2F_6 , CF_4 , $(CH_3)_2NH$, NH_3 , N_2 , and N_2O , as well as for the H^+ -induced carbon and oxygen Auger-electron yields from C_2H_6 , CO, CO_2 , N_2O , and O_2 .

I. INTRODUCTION

Measurements of the heavy-ion-induced Auger-electron cross sections have been carried out for a number of years, but the effect of the chemical environment on the Auger yield has generally assumed to be small.¹ This has in part been due to the large experimental errors in the cross-section measurement which make comparisons from author to author difficult. However, relative electron-yield measurements carried out with the same apparatus have much smaller systematic errors, making minor changes much more noticeable. In a previous work² we have reported large variations ($> 30\%$) in the *KLL* Auger-electron yields of several carbon-containing compounds, which confirmed earlier reports by Toburen³ and Matthews *et al.*⁴ In related work, Chaturvedi *et al.*⁵ claim they have seen significant changes ($> 10\%$) in the relative yields of fluorine-containing compounds. The observed variations were much greater than those expected from chemical shifts in the *K*-shell binding energies under the E^2 dependence of the binary encounter approximation (BEA).⁶ Detailed descriptions of the inner-shell ionization cross sections by heavy-ion impact can be found in Refs. 6 and 7 for the BEA and in Ref. 8 for the plane-wave Born approximation (PWBA).

We were somewhat successful in reproducing the observed yield variations using either of two simple models. In this discussion we refer to the site of the inner-shell vacancy as the primary atom while all other molecular components are referred to as secondary atoms. The first model utilized a simple electron inelastic scattering scheme, similar to that of Matthews *et al.*,⁴ where the Auger electron emitted from the primary atom scatters from the electron clouds of the secondary atoms. The second and simpler scaling related the relative Auger-electron yields to the effective number of valence-shell electrons of the primary atom. This model

utilizes the Mulliken charges from Ref. 9 associated with the various molecular components.

The changes in the Mulliken charge are roughly linearly related to the chemical shifts in the *K*-shell binding energy. From this it is reasonable to assume that the close agreement of the simple charge scaling of Ref. 2 indicates that there is an additional dependence on the *K*-shell binding energy not accounted for by the BEA predictions. However, the equal success of the scaling based on electron loss through scattering would indicate that the E^2 dependence of the BEA was sufficient. We hoped that an expanded study of the Auger-electron yield variations would clarify the situation.

II. EXPERIMENTAL PROCEDURE

The experimental procedure has been described previously in Ref. 2. Briefly, 0.45–2.0-MeV He^+ and 0.6–2.0 H^+ , H_2^+ , and H_3^+ ions with typical beam currents of 0.5 μA passed through a differentially pumped gas cell containing research-grade gases (see Tables I–III) of purities 99.5% or higher from Matheson Co., La Porte, Texas, and with background pressure less than 10^{-5} Torr. Pressure within the gas cell, typically 3 mTorr, was measured with a capacitance manometer. The ejected electrons entered an electrostatic analyzer positioned at 90° to the incident ion beam. The analyzer was a 160° spherical-sector analyzer operated in constant transmission mode with a pretarding lens, and with a microchannel-plate detector at the exit port. Detector efficiency was calculated using the detector geometry and a microchannel-plate efficiency of 60%. Measurements revealed no noticeable effects on electron transmission by the preretarding lens. The electron spectra were acquired with resolutions of 0.6–1.5 eV depending upon target gas and projectile. Comparison of our cross-section values with Ar, CH_4 , and N_2 values by Matthews¹⁰ and Stolterfoht¹¹ gives the same energy

TABLE I. Carbon Auger-electron production cross sections in 10^{-20} cm²/atom induced by 0.45–2.1-MeV He⁺ bombardment. Errors given are relative errors only. Absolute errors may be obtained by adding an additional 10% of the cross section to the relative errors.

E/A (keV/amu)	C ₂ H ₆	CH ₄	C ₂ H ₄	C ₂ H ₂	CO	CO ₂	C ₂ F ₆	CF ₄	CCl ₄	(CH ₃) ₂ NH
112.5	111±12		111±10	116±13	107±17					
150	187±16	179±14	203±14	189±15	159±14	121±15	147±18	129±26		
175	261±20									
200	315±23	300±20	296±19	282±19	262±19	237±20	232±24	214±32	183±37	288±17
250	407±23	429±26	378±23	348±22	344±24	288±23	279±27	264±33	320±30	415±23
300	469±28	451±28	461±27	401±25	398±27	361±32	347±30	300±34	345±34	438±23
350	497±29	457±28	476±28	432±27	414±29		341±35		325±35	456±25
400	490±30	527±31	507±30	457±28	442±31	395±31	399±42			514±25
450	517±31	511±31	496±30	487±30	461±32	404±30	418±33			557±28
487.5			517±30			394±30				
500	494±42	479±39		465±29	439±31		395±38	374±58	379±62	550±34
512.5			514±41							
525					471±47	403±61				

TABLE II. Nitrogen Auger-electron production cross sections in 10^{-20} cm² induced by 0.6–1.8-MeV He⁺ bombardment. Errors given are relative errors only. Absolute errors may be obtained by adding an additional 10% of the cross section to the relative errors.

E/A (keV/amu)	N ₂	N ₂ O	(CH ₃) ₂ NH	NH ₃
150	28±4	30±4		46±5
250	123±8	105±7	140±11	144±10
300	167±10	151±9	172±15	204±15
350	182±10	193±12	233±16	230±16
400	204±10	210±13	230±17	242±16
450	217±11	226±13	233±17	251±16

TABLE III. Carbon and oxygen Auger-electron production cross sections induced by 0.6–2.0-MeV H₁⁺, H₂⁺, and H₃⁺ bombardment. Errors given are relative errors only. Absolute errors may be obtained by adding an additional 10% of the cross section to the relative errors. The bombarding ion is given in parentheses for each target gas.

E/A (keV/amu)	Carbon Auger-electron cross sections (10^{-20} cm ² /atom)					Oxygen Auger-electron cross sections (10^{-21} cm ² /atom)				
	C ₂ H ₆ (H ₁ ⁺)	CO(H ₁ ⁺)	CO ₂ (H ₁ ⁺)	O ₂ (H ₁ ⁺)	CO(H ₁ ⁺)	CO(H ₂ ⁺)	N ₂ O(H ₂ ⁺)	CO ₂ (H ₁ ⁺)	CO ₂ (H ₂ ⁺)	CO ₂ (H ₃ ⁺)
267										71±9
300						76±14	61±9			
333										88±10
400						147±20	149±22			143±12
467										176±14
500						173±20	164±18		155±14	
600	127±10	113±10	92±11	193±19	168±18	232±20	182±17	162±19	182±14	
700						192±34	214±30		177±17	
800	135±7	112±7	92±10	233±15	214±17			187±18		
900					262±30	222±31	284±38	206±12		
1000	131±7	112±7	96±9	249±14	258±17	267±33	276±38	198±15		
1200	125±7	112±7	83±8	251±14	254±17			230±15		
1400	129±6	110±7	87±7	256±14	242±16			222±14		
1600	121±6	103±6	84±7	247±14	253±17			242±15		
1800	111±6	106±6	82±7	253±16	246±17			258±28		
2000	98±7	87±6	76±6	233±17	254±18			233±17		

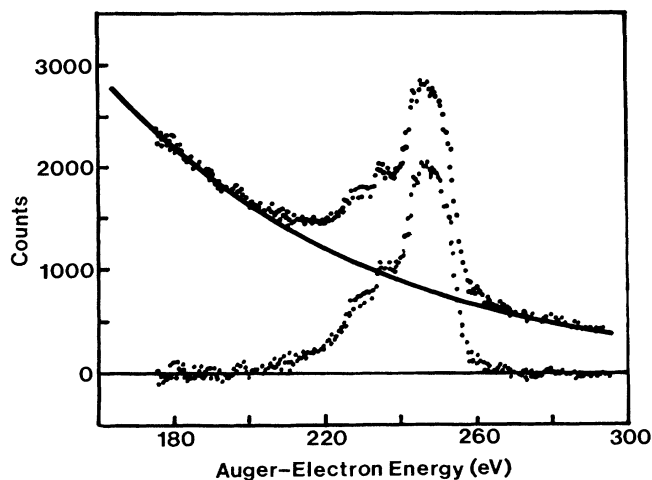


FIG. 1. Auger-electron-energy spectrum produced by bombardment of C₂H₆ by 1.8 MeV protons and acquired with a resolution of 1.5 eV. The solid line represents a second-order polynomial curve fit to the electron background, where the curve-fit regions are 175–195 and 275–295 eV respectively.

dependence, thereby revealing that our calculated detector response is correct. Our reported cross sections are for total Auger-electron production at 90° to the incident ion beam. Several authors^{3,4,12} have assumed that the Auger emission is isotropic; Stolterfoht¹² indicated the Auger emission is essentially isotropic for H⁺ impact on Ar at 90° and 150°, and Matthews and Hopkins⁴ indicat-

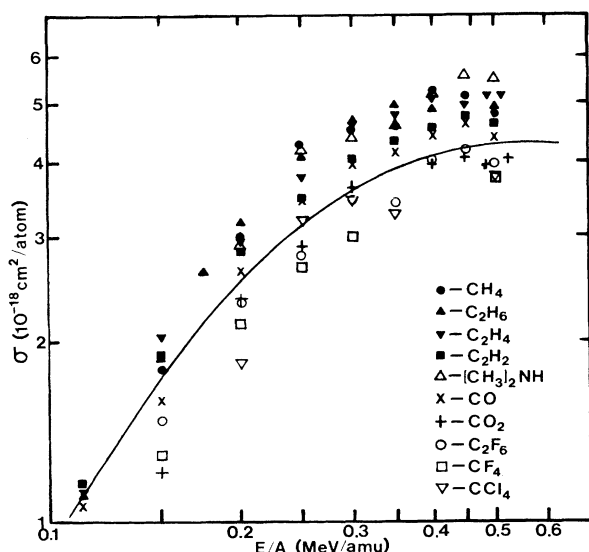


FIG. 2. Carbon Auger-electron production cross sections vs reduced bombarding energy for 0.45–2.0-MeV He⁺ ions incident upon CH₄, C₂H₆, C₂H₄, C₂H₂, (CH₃)₂NH, CO, CO₂, C₂F₆, CF₄, and CCl₄. Errors in the individual data points are typically 15%. The solid line represents the BEA prediction for the carbon K-shell ionization cross section from CH₄ with a carbon binding energy of 290.7 eV.

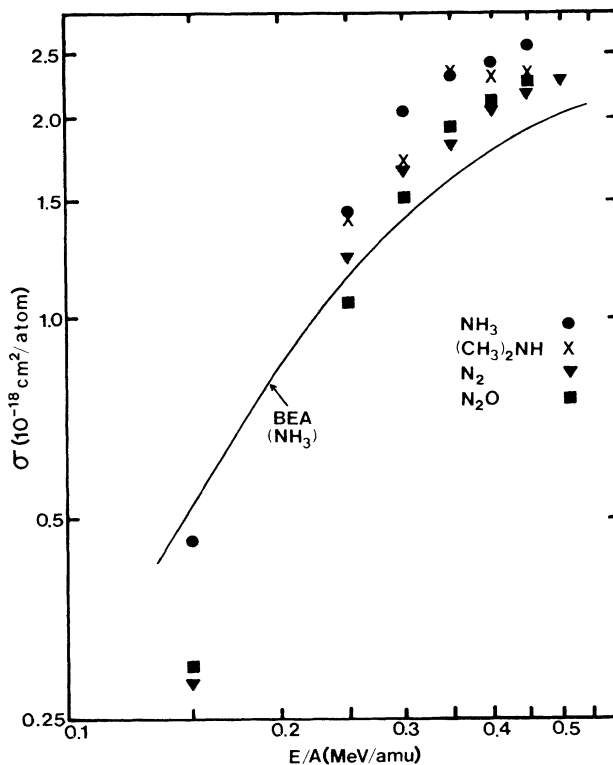


FIG. 3. Nitrogen Auger-electron production cross sections vs reduced bombarding energy for 0.6–2.0-MeV He⁺ ions incident upon N₂, N₂O, NH₃, and (CH₃)₂NH. Typical errors in each data point are 15%. The solid line represents the BEA prediction of the nitrogen K-shell ionization cross sections from NH₃.

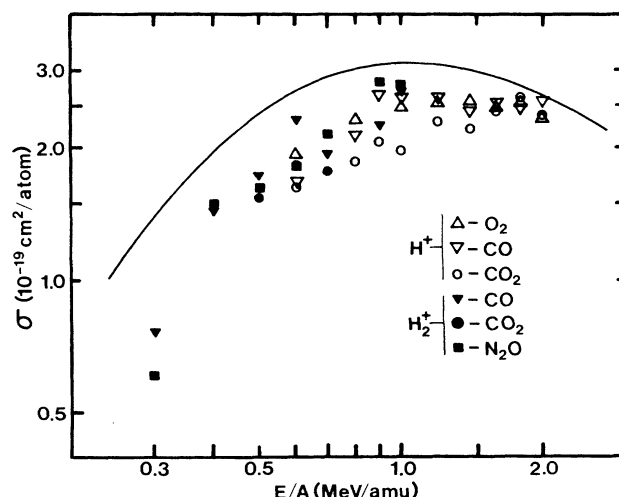


FIG. 4. Oxygen Auger-electron cross sections vs reduced bombarding energy for 0.6–2.0 MeV for H₁⁺ and H₂⁺ bombardment of O₂, CO, CO₂, and N₂O. Typical errors for the individual data points are 14% for H⁺ and 20% for H₂⁺ bombardment. The results for the different oxygen-bearing gases are less parallel than for carbon or nitrogen, which is due to the larger uncertainty in the H₂⁺ beam current.

ed isotropy for SF₆ spectra at 90° and 160°. We have, therefore, along with these other authors, assumed isotropy for the total Auger-electron cross sections presented in this paper.

III. RESULTS

The major difficulty in these Auger-electron yield measurements is the large error associated with a given cross-section value, although measurement at many bombarding energies tends to alleviate this problem somewhat by means of a better determination of the background subtraction, which typically is about 5% and is the largest source of error in the measured Auger yields. A typical Auger-electron spectrum from the 1.8-MeV H⁺ bombardment of C₂H₆ is shown in Fig. 1, before and after the subtraction of a second-order polynomial curve fit. This background subtraction is not entirely random since it depends on the limits and nature of the polynomial curve fit. For the heavier target gases, evidence of electron elastic-scattering peaks have been observed which vary in electron energy and He⁺ or H⁺ (atomic or molecular) bombarding energy. Acquisition of Auger-electron spectra at several ion-bombarding energies provides a better knowledge of these secondary effects and a better knowledge of how to handle the background spectrum. An additional benefit of obtaining spectra at many energies is to identify trends in the cross sections. Other less important errors in the relative yields are the target-gas pressure and beam-current measurements, estimated to be 3% and 1%, respectively. Error in the absolute cross-section measurement includes an additional error of 10% from the calculated detector efficiency. The error in the background electron subtraction was determined by variation of the fit input parameters and was typically 5% for the carbon *KLL* spectra. In some cases, such as the CCl₄ yields for low He⁺ bombarding energies, this error was as high as 20%.

However, the error in the relative yield measurements was generally less than 10% for any given measurement at a particular bombarding energy.

In our previous paper,² the Auger-electron production cross sections for eight carbon-containing compounds were presented in graphical form only, and were normalized to the cross-section measurements for 0.6-MeV He⁺ bombardment of CH₄ and Ar of Refs. 10 and 11. Since then we have calculated the efficiency of our detector system. A summary of the cross section measurements based on this calculation is given in Tables I–III. The Auger-electron yields for the carbon- and nitrogen-containing molecules were induced by 0.45–2.0-MeV He⁺ ions, while the oxygen spectra were induced by either H₁⁺, H₂⁺, or H₃⁺ ions with incident energies from 0.6 to 2.0 MeV. The use of different hydrogen molecular ions was dictated primarily by three considerations: (1) to obtain Auger-electron yields in the maximum momentum transfer region, (2) to obtain convenient counting rates, and (3) no appreciable differences were observed in trends, shapes, and yields for the oxygen Auger-electron spectra. The Ar *LMM* yields induced by 75- and 150-keV H⁺ ions compared to those at 150 and 300 keV H₂⁺ by Stolterfoht *et al.*¹² likewise showed no appreciable differences. A comparison of the present results with those of Refs. 10 and 11 for 0.6-MeV He⁺ bombardment of Ar, CH₄, and N₂ indicates our values are generally 10–20% greater than theirs. Better agreement is seen between the 1.0 and 2.0-MeV H⁺ bombardment of CO, CO₂, and C₂H₆ measurements of Toburen³ and the present work.

We have also measured the sulfur *LMM* spectra from H₂S, SO₂, and SF₆ induced by both H⁺ and He⁺ ions, but the large background prevented accurate subtraction of the electron continuum. Matthews *et al.*⁴ were able to acquire cleaner spectra at a backward angle of 160° to the incident beam, but their treatment of the SF₆ background may be somewhat questionable because they used

TABLE IV. Relative total carbon *KLL* Auger-electron yields.

Target gas ^a	E_b^b (eV)	H ⁺ induced ^{c,d}	H ⁺ induced ^{c,e}	He ⁺ induced ^{c,e}	Average H ⁺ and He ⁺	Expected values		Mulliken charge ^f
						Y_s	Y_q	
CH ₄	290.7	0.97(7)		0.98(2)	0.98(3)	1.06	1.06	−0.74
C ₂ H ₆	290.9	1.00(3)	1.00(2)	1.00(2)	1.00(2)	1.00	1.00	−0.48
C ₂ H ₄	291.7	0.96(2)		0.99(2)	0.98(2)	0.98	0.97	−0.35
C ₂ H ₂	292.2	0.92(3)		0.93(2)	0.93(2)	0.95	0.94	−0.26
(CH ₃) ₂ NH				1.00(2)	1.00(2)	0.98	0.98	−0.40*
CO	296.2	0.95(5)	0.87(3)	0.86(3)	0.89(2)	0.94	0.81	+0.20
CO ₂	297.5	0.87(5)	0.71(4)	0.74(4)	0.77(2)	0.86	0.73	+0.59
C ₂ F ₆	298.8			0.75(4)	0.75(4)	0.70	0.70	+0.70*
CF ₄	301.7	0.8(1)		0.68(6)	0.72(6)	0.75	0.63	+0.94
CCl ₄	296.2	0.66(8)		0.70(6)	0.68(5)	0.70	0.69	+0.80*

^aBond lengths from Refs. 18 and 19.

^bCarbon 1s binding energies from Ref. 13, and binding energy for (CH₃)₂NH is taken to be the same as C₂H₄.

^cNumbers in parentheses indicate error in last digit.

^dH⁺ measurements: 0.3, 1.0, 2.0 MeV, CH₄, . . . , CO₂, Toburen, Ref. 3; 1.5 MeV, CH₄, CF₄, CCl₄, Matthews *et al.*, Ref. 4.

^ePresent measurements.

^fMulliken charges from Ref. 9. The asterisk refers to our estimated values.

TABLE V. Relative total nitrogen and oxygen *KLL* Auger-electron yields.

Target gas ^a	E_b ^b (eV)	He ⁺ induced ^c	Expected values Y_s	Expected values Y_q	Mulliken charge ^d
Nitrogen yields					
NH ₃	406.6	1.00(3)	1.00	1.00	-0.86
(CH ₃) ₂ NH	~406.6	0.94(3)	0.87	0.93	-0.56*
N ₂	409.9	0.83(3)	0.88	0.84	0.00
N ₂ O	411.1	0.81(3)	0.85	0.81	+0.15
Oxygen yields					
Target gas ^a	E_b ^b (eV)	H and H ₂ ⁺ induced ^c	Expected values Y_s	Expected values Y_q	Mulliken charge ^d
O ₂	543.1	1.00(2)	1.00	0.96	0.00
N ₂ O	545.8	1.01(4)	0.99	1.00	-0.29
CO	546.8	0.98(2)	0.97	0.98	-0.20
CO ₂	545.4	0.93(2)	0.98	1.00	-0.29

^aBond lengths from Ref. 18.

^bNitrogen and oxygen 1s binding energies from Ref. 13. E_b for (CH₃)₂NH is approximated as E_b for NH₃.

^cNumbers in parentheses indicate error in last digit.

^dMulliken charges from Ref. 9. The asterisk indicates our estimated value.

the SO₂ background spectrum along with what appears to be discontinuous subtraction of a portion of the spectrum (see Fig. 1, Ref. 4) to obtain the SF₆ spectrum. We have found that the shape of the electron background in hydrocarbons changes even between methane and ethane, so it is somewhat difficult to believe their subtraction is adequate for gases as dissimilar as SF₆ and SO₂ even though the major contribution to the background electrons is from sulfur. The difficulty may be mitigated somewhat because the background from a proton-induced spectrum taken at a backward angle is lower than our background taken at 90°, but errors are still present. Nevertheless, the 50% reduction in sulfur *LMM* yield in SF₆ compared to sulfur *LMM* yield in H₂S that they reported is not incompatible with the 32% reduction in these yields that is predicted with the two simple scaling models discussed in Sec. IV of this paper.

Examination of Tables I–III shows that the quoted values for the relative errors are typically much larger than the observed energy-to-energy fluctuations in any particular target gas. This is caused in part to a minor degree by the inclusion of a $\pm 3\%$ error in pressure and a $\pm 1\%$ error in beam-current measurement, and to a greater degree by a larger error assignment to the background subtraction than may have been necessary.

The results of the Auger-electron yield measurements as a function of incident bombarding energy are presented in Figs. 2–4, while the average relative yields for the various compounds are given in Tables IV and V. Table IV includes a reanalysis of some of the information previously presented in Ref. 2 and also includes new measurements on CCl₄ and (CH₃)₂NH.

Table IV includes a comparison of the present carbon *KLL* Auger yields with those of Refs. 3 and 4. The values for the hydrocarbons are in excellent agreement and only the CO and CO₂ yields of Ref. 3 are

significantly different from the present measurements. We have measured the C₂H₆, CO, and CO₂ *KLL* yields for both H⁺ and He⁺ projectiles and obtained values consistent within experimental error. It is possible that the discrepancy arises from the different methods of background removal. Toburen performs the background subtraction based on a corresponding section of the oxygen Auger-electron spectrum. We, unfortunately, did not record a similar spectrum to make a comparison since the background changes noticeably from molecule to molecule even among the hydrocarbons.

IV. DISCUSSION

We are concerned with yield variations much larger than can be accounted for by changes in the inner-shell binding energies, where these energies have been measured by photoabsorption.¹³ The discussion is simplified since the inner-shell ionization cross sections are small enough to localize effectively the ionization process to a small volume within the molecule, in that the incident ion must pass extremely close to the nucleus of the primary atom. This localization may be explained from classical arguments, since the impact parameter for *K*-shell ionization is roughly a factor of 10 less than for *L*-shell ionization. The *K*-shell ionization requires that an incident H⁺ or He⁺ ion approach within a fraction of an atomic radius to the nucleus in the case of carbon, compared to a molecular distance of 1–2 atomic radii. Thus, the *K*-shell ionization process is localized to a fractionally small volume of the molecule. The Auger-electron yield variations in the molecule may be divided into two classes, internal and external. The internal processes are those that affect the inner-shell ionization probability while the external processes are associated with the emission of the Auger electron.

The internal processes include chemical shifts in the inner-shell binding energy, multiple ionization, molecular dissociation, and screening of the projectile by the secondary atoms of the molecule. As has been noted, the chemical shifts in the inner-shell binding energies are insufficient to account for the large-scale variations in the Auger yields. Screening of the primary atom's inner shells by those of the secondary atom's nuclei and inner shells can be neglected, since in order that the other components of the molecule affect the primary atom's K -shell ionization probability, there must be a large deflection of the incident ion, which in turn requires a small impact parameter or close approach to the inner shell of the other components. The solid angle subtended by these scattering cross sections at the primary atom's K -shell will be very small indeed (<0.005).

Spohr *et al.*¹⁴ conducted a study of the e^- -induced Auger spectra of the bromocarbons and found final-state effects on the Auger line shapes due to the dissociation of a proton from methane. It is possible that dissociation may occur with heavy-ion impact, such as H^+ or He^+ particles, before the inner-shell ionization. The effect of this would be a change in inner-shell binding of several eV, altering the Auger yields by a few percent. The Auger line structures do not show evidence of such transitions.²

Multiple ionization is simply the ejection of more than one electron by the incident ion. For the molecules under study here, we are concerned with the ejection of a K -shell electron and one or more L -shell electrons. In the BEA the ejection of the electrons is treated as individual events so that the L shell must be ionized before the K shell to affect the K -shell binding. There is a strong Z_1 and incident-energy dependence of the multiple-ionizing probability.¹⁵ The probability of multiple ionization can be estimated as follows. The L -shell ionization cross sections can be estimated from the BEA.⁶ An effective atomic radius is estimated using the molecular bond lengths and from this a cross-sectional area is calculated. The ratio of the L -shell cross section to the effective atomic area enables one, with standard probability methods, to calculate the probability for emission of an individual L -shell electron with the K -shell ionization. From this value an average number of emitted L -shell electrons per K -shell ionizing event was then estimated. On the average, 1.3 L -shell electrons can be expected with each K -shell electron in CH_4 under 1.0-MeV He^+ bombardment, and 0.6 L -shell electrons at 2.0 MeV. For H^+ bombardment, the multiple-ionization probability is down to 0.10 at 1.0 MeV and is negligible at 2.0 MeV incident proton energy. Since there is no significant energy dependence observed for the He^+ (Fig. 5) on carbon yields and no major difference between the H^+ and He^+ yields, it would seem that multiple ionization does not have a large effect upon the Auger yields.

The external effects on Auger-electron yields would include any processes that would prevent the detection of the emitted electron. The fluorescence yields of carbon, oxygen, and nitrogen are less than 1%, and so a K -shell vacancy must then be filled by the emission of an Auger electron. An electron may scatter inelastically from the

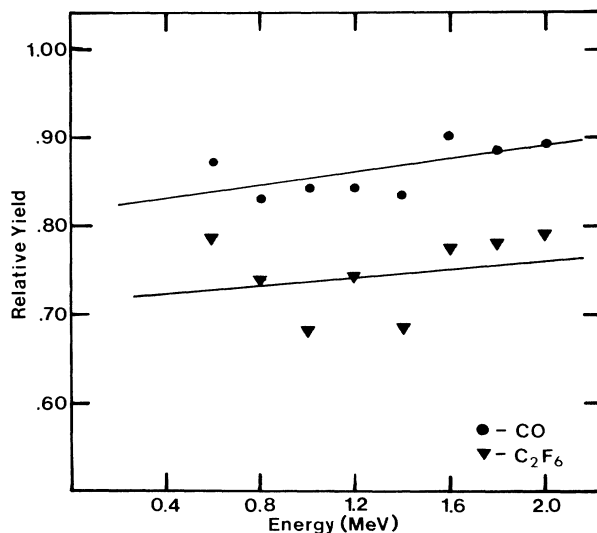


FIG. 5. Plot of the $C_2H_6:CO$ and $C_2H_6:C_2F_6$ ratios for He^+ bombarding as a function of bombarding energy. The straight lines are linear fits to the data, and the large error for each point (see Table I) indicates that the apparent energy dependence is not significant.

electron clouds of the secondary atoms. If the Auger electron knocks out a second electron, then both of these electrons will become immersed in the continuous electron background and be undetectable as an Auger event. Matthews *et al.*⁴ estimate the scattering cross sections from the electron-induced ionization cross sections of Ref. 16, but these values do not reproduce the large variations in the observed yields of Ref. 4 or the present results. By using a simple ball-and-stick model of the molecules, where the scattering cross section is taken as πR_n^2 and R_n is the covalent atomic radius of the various molecular components, we can reproduce the observed relative yields quite well. The relative Auger yield between molecules i and j is given by the simple form

$$Y_s = (E_i/E_j)^2 [1 - (R_n/d_n)^2/4]_j / [1 - (R_n/d_n)^2/4]_i,$$

where d_n is the interatomic spacing between the primary and secondary atoms. The atomic radii were obtained from Ref. 17, and the spacings from Refs. 18 and 19. We also assume that the electrons are emitted radially outward from the primary atom, and that the hydrogen atoms have a radius equal to zero. These results are heavily dependent upon the choice of the atomic radii. However, in this case it is the general behavior of the model rather than its actual results that is important.

A more realistic model would incorporate accurate shapes of the molecular orbitals and better estimates of the electron-electron interaction cross section. But, with only a few exceptions, this simple model does extremely well. For instance, the CO and CO_2 yields are overestimated by this model, perhaps because the high bond orders place the electrons in much closer proximity to each other, thereby increasing the solid angle for scattering. Also, the yield ratio for $CH_4:C_2H_6$ was found to be

about unity when it was expected to be approximately 1.06:1. Examination of the carbon yields suggests that the CH_4 yield is lower than expected, although the same does not appear to be the case for the $\text{NH}_3:(\text{CH}_3)_2\text{NH}$ yield ratio. A possible explanation may come from the dissociation of a proton by the incident ion which in turn could increase the effective carbon K -shell binding.

Tables IV and V list the predicted values from the valence-shell electron scaling based upon the Mulliken charge. Bissinger *et al.*²⁰ at first attempted to explain the variations of the fluorescence yields with molecular environment of several carbon-containing compounds by demonstrating that these yields were more or less linearly related to either the Pauling or Mulliken charge on the carbon atom. In a follow-up paper, Bissinger *et al.*²¹ then showed that the variations in fluorescence yield were, to a large extent, offset by normalizing with the corresponding relative Auger-electron yields. From this approach, we attempted to reproduce the observed variations in Auger-electron yields by scaling to an effective number of carbon valence-shell electrons. This scaling is represented by the following ratio:

$$Y_q = (E_i/E_j)^2(q_0 - q_j)/(q_0 - q_i),$$

where q_0 is the number of valence electrons in the free atom, and q_i and q_j are the Mulliken charges on the primary atoms of the two molecules. Although the effective charge has been observed to be roughly linearly related to the K -shell binding energy, the BEA indicates a $1/E^2$ dependence on the charge. A linear effect is insufficient to explain the observed variations in carbon Auger yield from, for example, C_2H_6 to CF_4 . Other effects such as the X-ray fluorescence yields or double Auger emission are small.²⁰ This means that the inner-shell vacancy must be filled by the emission of an Auger electron, so that the Mulliken charge is expected only to affect the line shapes and widths of the Auger spectrum. With this in mind, the results of Tables I–III are even more surprising when there appears to be no obvious connection between Mulliken charge and relative Auger-emission probabilities. An attraction and/or repulsion of the emitted electron by the local charge-density distribution about the molecule seems unlikely since the binding energy for the emitted Auger electron is less than 20 eV for any of the molecules, whereas the Auger-electron energy is greater than 100 eV and the electron should still appear in the spectrum. The calcu-

lation of Mulliken charge involves the population of overlapping molecular orbitals (see, for instance, Ref. 22) to estimate the fraction of time an electron remains in the vicinity of each of the molecular components, so no matter how long it takes the target molecule to emit an Auger electron, only the spectral shape should be affected, not the intensity. Perhaps for the simple molecules involved in the present study, the Mulliken charges are emulating the scattering approach in some way that is not apparent.

Either of the two empirical models discussed here seems to predict adequately the observed relative Auger-electron yield variations. Despite the slightly better performance of the Mulliken-charge scaling, the physical simplicity of the scattering-loss model suggests that it may be a more reasonable representation of the nature of the observed variations in yield. The deviations from the simple scattering model are expected due to the crude estimations of scattering cross sections and electron distributions. For instance, the electron-electron scattering cross section is expected to decrease with increased electron energy, so that for the heavier elements KLL Auger-electron yields will probably show less and less variation with the molecular environment. We also have not considered the effect of the He^+ electron upon the yields, but since the yields presented here do not show a marked difference between H^+ , H_2^+ , or He^+ projectiles, it seems to have little, if any, effect upon the electron yield.

Our earlier results² on the Auger-electron yields of carbon confirmed the results of Toburen and Matthews *et al.*, and although we still do not have a satisfactory explanation for these results, either of these two models might be used to predict the Auger yield for an unknown compound such as, for example, a higher n alkane or alkyne, or for predicting inner-shell ionization cross sections. Since these values still suffer from relatively large experimental uncertainties ($\sim 20\%$), these corrections will not generally be significant, except for uses such as fluorescence yields and measurements made on large or complex molecules.

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