Formation of Negative Ions in a Gas by Charge Transfer from a Fast Atomic Hydrogen Beam*

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Structure has been reported in the electron loss cross section for hydrogen atoms in H_2. Study of various gases shows that there is no structure for collisions with argon, but nine peaks of magnitude 10^{-16} cm^2 between 8 and 40 kev in CO. Analysis of these peaks support the idea advanced for hydrogen gas that the peaks are caused by formation of negative ions in the target gas by a process in which the electron is captured as though it were a free electron. Mass spectroscopic study reveals that negative ions are formed when hydrogen atoms pass through CO, O_2, and H_2O. The formation rate varies in CO as predicted from the σ_{01} structure and the cross section is $\sim 10^{-16}$ cm^2. The ions formed in CO are CO^- and O^-. The copious production of CO^- contradicts the simple model of the capture collision previously proposed.

I. INTRODUCTION

THE program to measure the cross sections for electron capture and loss by hydrogen atoms in the range of energy between 5 and 40 kev has been extended in this laboratory to argon and carbon monoxide. The reason for selecting these gases was that the cross section for electron loss, σ_{01},[1] for hydrogen atoms in hydrogen gas (H_2) had been found to show some structure as a function of the particle energy.[2] The most likely explanation for this structure appeared to be that the loss cross section was enhanced at certain energies by the processes

$$H+H_2 \rightarrow H^++H_2^-, \quad (1)$$

or

$$H+H_2 \rightarrow H^++H^-+H, \quad (2)$$

leading to negative ion formation in the target gas. An interesting aspect of the collision process was that the cross-section peaks occurred at almost the same velocity at which free electron capture,

$$e+H_2 \rightarrow H^-+H, \quad (3)$$

was most likely to occur. No negative ions should be formed in argon while a multitude of states involving C^-, O^- and CO^- are available in CO. Thus, according to the hypothesis advanced to explain the structure in H_2, a smoothly varying cross section for electron loss was expected for hydrogen atoms in argon and a rich structure was expected in carbon monoxide.

This is just what was found. A mass spectrograph was therefore constructed to analyze the ions left behind along the path of the atomic beam. The analysis of these ions confirms that negative ions are formed in CO as a result of collisions between fast hydrogen atoms and CO molecules. Furthermore the cross section for negative ion formation varies in the same way as σ_{01} for H in CO and is large enough to account for the structure. The details of the process are not understood, however, for the predominant negative ion formed is CO^- where O^- would have been expected from the analogy with free electron capture.

II. CAPTURE AND LOSS CROSS SECTION MEASUREMENTS

A. Procedure

The technique used to measure the electron capture and loss cross sections has been described in previous papers,[2–4] and will be described here only briefly. A beam of neutral atoms is prepared by subjecting a monoenergetic beam of protons to charge transfer and removing the residual proton beam. The neutral beam in the collision chamber passes between a linear array of nine identical sets of condenser plates to a detector. The detector is a foil thermocouple mounted inside a Faraday chamber. The thermocouple measures the total particle current, charged plus neutral. It is calibrated with a proton beam sent through the evacuated collision chamber so that current recorded in the Faraday cage

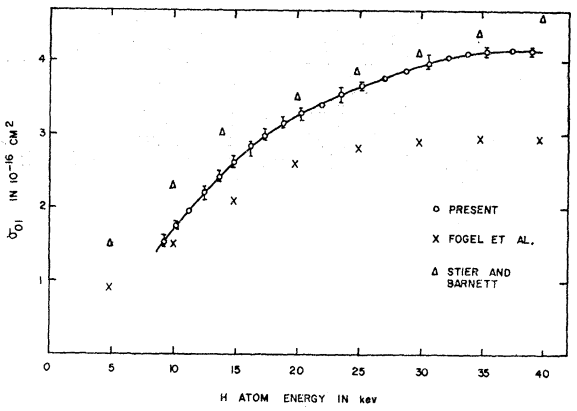

FIG. 1. Electron loss cross section for hydrogen atoms in argon.

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[1] σ_{if} is the cross section for charge transfer where i is the initial charge state of a beam particle and f its final state.

[2] R. Curran and T. M. Donahue, Phys. Rev. **118**, 1233 (1960).

[3] W. Kasner, thesis, University of Pittsburgh, 1957 (unpublished).

[4] R. Curran, T. M. Donahue, and W. H. Kasner, Phys. Rev. **114**, 490 (1959).

is in this case the total current. It is found that the thermocouple response is linear for the currents strengths used in these experiments and that the detector reading does not change as gas is admitted to the beam preparation chamber or the collision chamber, thereby changing the composition of the beam. Thus the calibration with protons is valid for hydrogen atoms of the same energy.

The sum of the electron loss and capture cross sections, $\sigma_{01}+\sigma_{0-1}$, is measured by sending the neutral beam into the scattering chamber and using high voltage on selected condensers to remove the charged component in the beam as quickly as it is formed. After the beam has traveled a distance x along which the ionic component has been removed in this manner, the residual neutral beam current is given by the expression

$$I(x)=I_0\exp[-(\sigma_{01}+\sigma_{0-1})nx], \tag{4}$$

where I_0 is the initial neutral beam current and n is the gas density. The distance x is varied by changing the number of condensers charged. The quantity $(\sigma_{01}+\sigma_{0-1})$ is thus readily and accurately measured. Only the ratios $I(x)/I_0$ need be evaluated and no detector calibration is necessary.

TABLE I. Values of σ_I for hydrogen atoms in argon.

H atom energy (kev)	$\sigma_I(10^{-16}\,\text{cm}^2)$	H atom energy (kev)	$\sigma_I(10^{-16}\,\text{cm}^2)$
10.27	8.72	18.88	7.22
12.54	7.72	20.39	7.25
13.75	6.72	23.60	7.30
14.94	7.47	27.04	5.67
16.29	7.73	28.84	5.55
17.42	7.33		

On the other hand, collection of the slow ions left along the path of the beam when low voltage is applied to the condensers permits the measurement of $\sigma_{01}-\sigma_{0-1}$ and σ_I, the cross section for production of ion pairs in the target gas. The technique is the same used in the measurement of σ_{10} when the incident beam contains only protons.[3,4] It involves the use of low pressure (0.2 to 0.8 μ) in the collision chamber and is based on the small beam absorption approximation that the current collected by m negative condenser plates is

$$J_+=I_0(0)n(\sigma_{0-1}+\sigma_I)(mx_c+x_0), \tag{5}$$

where x_c is the length of a condenser and x_0 is an end correction. The current to m positive plates is

$$J_-=I_0(0)n(\sigma_{01}+\sigma_I)(mx_c+x_0). \tag{6}$$

Measurement of $I_0(0)$ and the variation of J_+ and J_- with mx_c determines $\sigma_{0-1}+\sigma_I$, $\sigma_{01}+\sigma_I$ and thence $\sigma_{01}-\sigma_{0-1}$ and σ_I.[5]

[5] In this discussion we neglect the effect of impurities. For a more detailed treatment we refer to previous papers.[2,4]

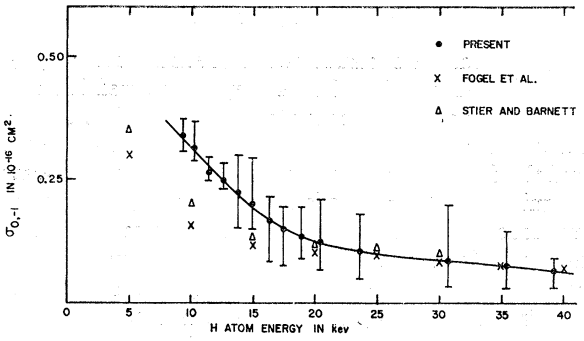

FIG. 2. Electron capture cross section for hydrogen atoms in argon.

B. σ_{01} and σ_{0-1} for H in Argon

The electron loss and capture cross sections for hydrogen atoms in argon are plotted in Figs. 1 and 2. They both vary smoothly. Two other groups have measured these cross sections previously.[6,7] Our values of σ_{01} agree with those of Fogel' *et al.* at low energy, and those of Stier and Barnett at high energy except, that our cross section levels off at 35 kev while that of Stier and Barnett continues to rise. This is not consistent with the case of H_2 where our measurements and those of the Fogel' group were in agreement and far below those of Stier and Barnett at all energies.

All measurements of σ_{0-1} for H in Ar are in agreement from 40 kev down to 15 kev. Below that energy the cross section as we measure it rises somewhat more steeply with decreasing energy than either of the other two determinations.

Values of σ_I obtained for hydrogen atoms in argon are listed in Table I. This cross section is actually the weighted sum of the cross sections for multiple ionization

$$\sigma_I(\text{Ar}^+)+2\sigma_I(\text{Ar}^{++})+3\sigma_I(\text{Ar}^{3+})+\cdots. \tag{7}$$

The measurement of σ_I is not corrected for secondary electron emission.

The uncertainties indicated in the plotted cross section measurements of Figs 1 and 2 are the probable errors resulting from a least-squares fit of the curves representing Eqs. (4)–(6) to the data. The scatter which occurs is a consequence of beam instability and pressure drifts. The absolute value of the cross section is also subject to an uncertainty arising from the measurement of the gas density n. This is obtained from the reading of a McLeod gauge of large volume. It causes an uncertainty of $\pm 1\%$ in $\sigma_{01}+\sigma_{0-1}$ and somewhat more in $\sigma_{01}-\sigma_{0-1}$. We estimate our accuracy at $\pm 2\%$ for the measurement of σ_{01}.

[6] I. M. Fogel', V. A. Ankuninow, D. V. Philipenko, and N. V. Topolia, J. Exptl. Theoret. Phys. (U.S.S.R.) translation: Soviet Phys. JETP **7**, 400 (1958).

[7] P. M. Stier and C. F. Barnett, Phys. Rev. **103**, 896 (1956).

C. σ_{01} and σ_{0-1} for H in CO

An abundance of structure is evident in both $\sigma_{01}+\sigma_{0-1}$ and $\sigma_{01}-\sigma_{0-1}$ for H in CO as they are plotted in Fig. 3. The reality of the effect is attested by the fact that the fluctuations occur at the same energies in both the sum and the difference of the cross sections and is of the same magnitude in both. This is true despite the fact that the methods of measuring the two quantities are completely different. Since the fluctuations are approximately the same for both $\sigma_{01}+\sigma_{0-1}$ and $\sigma_{01}-\sigma_{0-1}$ most of the structure is in σ_{01} (Fig. 4). At 9.31 kev there is an exception where a sudden increase in $\sigma_{01}+\sigma_{0-1}$ has no counterpart in $\sigma_{01}-\sigma_{0-1}$. The result (Fig. 5) is a large peak in σ_{0-1} at this energy. The structure in σ_{0-1} for CO is even more pronounced than that found in H_2.[1] There are two large maxima, one at 9.3 kev, the other at 13.75 kev.

In σ_{01} there are nine peaks between 8 and 40 kev. The cross section for electron loss is very large, attaining 4.7×10^{-16} cm^2, and the fluctuations are of the order of 10^{-16} cm^2.

III. MASS SPECTROMETER STUDIES

A. Purpose of the Studies

To test the proposition that the structure in σ_{01} is a consequence of negative-ion formation in the target gas, a mass spectrometer was designed to determine the nature of the ions left along the track of the beam particles. If negative ions were found, attributable to hydrogen atoms in the beam and varying like σ_{01} with energy, this would of course settle the question. A failure to detect negative ions would not be definitive. For an enhancement of the electron-loss cross section could occur even if the negative ions formed were molecular ions whose internuclear separation was such that autodetachment would cause them to disappear long before they could reach the detector of the mass spectrometer. In that case the difficult experiment of detecting the electrons produced in autodetachment and distinguishing them from electrons produced in other processes would have to be performed before a clear assessment could be made of the role of negative-ion production in causing the fluctuations in σ_{01}.

B. The Mass Spectrometer

Sketches of the collision chamber and mass spectrometer assembly are presented in Figs. 6 and 7. They were designed so that they could be joined to the beam preparation section of the instrument used for charge exchange cross section studies.[2–4] The scattering chamber is a cylindrical tube 5 cm in diameter and 40 cm long. At one end this tube was fitted to the beam preparation chamber including the beam limiting and differential pumping ports. Into the other end was inserted our standard detector assembly consisting of the thermal detector enclosed within a Faraday cage. Provisions were made for evacuating the chamber, for admitting gas through cold traps, and for measuring the gas pressure with ionization gauge and McLeod gauge.

To extract the ions formed along the path of the beam a pair of parallel plates was used in this preliminary survey. To the pusher plate, B in the figures, positive or negative voltage could be applied. The grounded plate A closed off the arm of the mass spectrometer. A slot S_1, 0.022 cm$\times$1.3 cm, was milled in this plate with the long dimension parallel to the beam axis.

Ions formed along the beam could be propelled by the field between B and A through S_1 and into the evacuated mass spectrometer. S_1 is the object for an analyzing magnet designed to deflect ions through 90° on a path of 8 cm radius. The magnetic lens was designed to provide focusing in the plane of the pole faces and also in the plane perpendicular to them. The magnetic field was measured with a flip coil which was in turn calibrated against a proton resonance probe.

Ions are focused 25 cm from the magnet on a slit S_2, 2 cm long and 0.41 cm wide. This is the size of the image of S_1. After passing through S_2 they fall on a collector P. Both P and S_2 are maintained at +45 volts to prevent

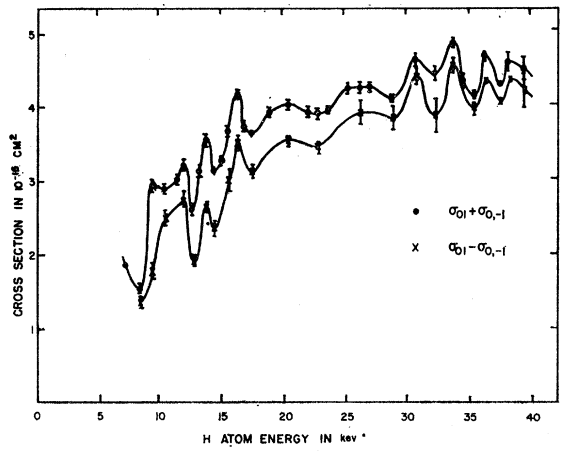

FIG. 3. Measured sum and difference of electron loss and capture cross sections for hydrogen atoms in carbon monoxide.

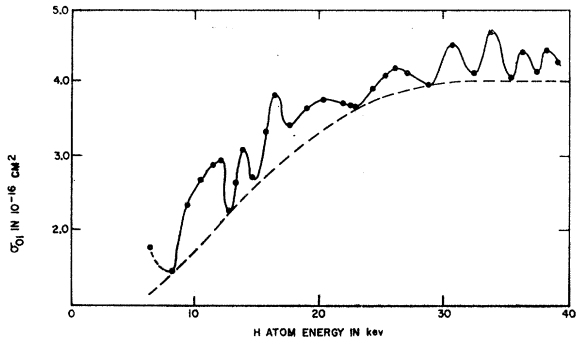

FIG. 4. Electron loss cross section for hydrogen atoms in carbon monoxide.

secondary electron emission. The current to P is measured by means of a micro-microammeter.

The mass spectrometer was calibrated by means of the positive helium ions produced through ionization of helium by an energetic neutral beam. The alignment was such that the beam passed close to plate B and almost the full extractor voltage was effective in accelerating ions through the slit S_1.

C. Negative Ions Formed in CO

It was found that with CO in the scattering chamber and a neutral beam incident on it that negative ions were indeed formed in the CO. A detailed analysis of these ions will be presented in subsequent sections. First it is necessary to demonstrate that the ion formation can be ascribed to the hydrogen atoms in the beam. The H/H^+ ratio was varied in the beam and it was found that for a fixed CO pressure the negative ion production rate increased with the H beam strength in the collection region while it remained independent of the proton current. It is necessary in checking this fact to keep in mind that even if protons are removed from the beam initially there is a certain amount of reconversion to protons by charge exchange between the beam preparation chamber and the mass spectrograph slit. The size of the reconverted current can be deduced from the reading at the Faraday cage and the known distances in the apparatus as well as from the value of σ_{01}. This is not necessarily an unimportant effect since negative ions may be produced in dissociative ionization:

$$H^+ + XY \rightarrow \begin{cases} H^+ + X^+ + Y^- \\ H^+ + X^- + Y^+. \end{cases}$$

On the other hand, it may be noted that incident hydrogen atoms may also cause such dissociation. To distinguish

$$H + XY \rightarrow H^+ + X^- + Y$$

from

$$H + XY \rightarrow H + X^- + Y^+$$

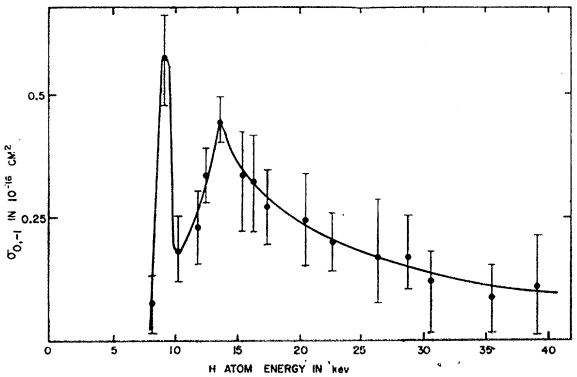

FIG. 5. Electron capture cross section for hydrogen atoms in carbon monoxide.

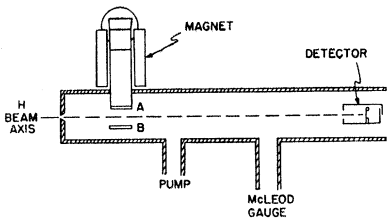

FIG. 6. Side view of mass spectrograph and scattering chamber. The beam detector is at the right.

in the presence of

$$H + XY \rightarrow \begin{cases} H + X + Y^+ + e \\ H + X^+ + Y + e \\ H + (XY)^+ + e \\ H^+ + XY + e \\ \text{etc.}, \end{cases}$$

requires an elaborate analysis. On the other hand, if the ions produced are $(XY)^-$ and the rate of production is linear with pressure, there can be no doubt that the reaction is

$$H + XY \rightarrow H^+ + (XY)^-.$$

At any rate, if the cross section for production of $(XY)^-$, X^-, and Y^- should be found to follow the fluctuations in σ_{01} for H in XY, this would have to be taken as strong evidence that the negative ions are formed by direct transfer from the fast atom to the XY molecule.

In Fig. 8 is plotted the negative ion current obtained as a function of the pusher voltage for a fixed value of the magnetic field in the mass spectrograph. The incident beam was neutralized and the beam energy was 16.3 kev. The pressure in the collision chamber was 0.346 μ. The positive ion spectrum measured under the same conditions, except for the reversal of the fields in the mass spectrograph, is also shown in the same figure. The positive ions appear to be predominantly CO^+ and C^+ while the negative ions are CO^- and O^- at this energy. The resolution of the mass spectrometer, as indicated on the figure where the expected peaks due to O_2, CO, and CN are marked, is not high. It is not possible to exclude categorically that the diatomic ion is

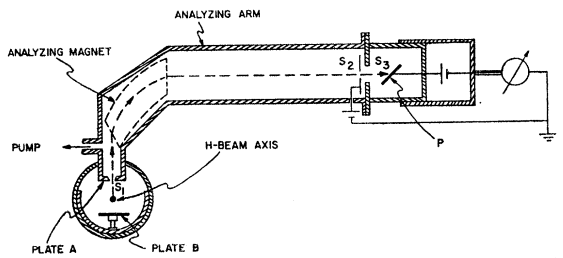

FIG. 7. Mass spectrograph and scattering chamber viewed along the beam axis.

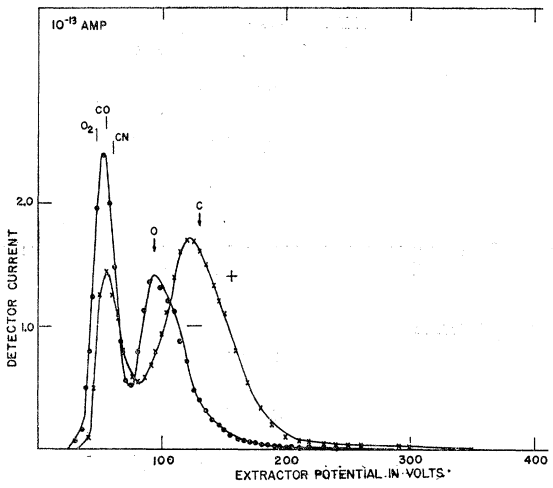

FIG. 8. Mass spectrometer response as function of draw-out voltage for H and CO at 16.3 kev and a CO pressure of 0.346 μ. Positive- and negative-ion results are both plotted. Scale is in 10^{-11} amp for positive ions and 10^{-13} amp for negative ions.

O_2^- or CN^-. However, a careful study of a great quantity of data leads us to prefer CO^- very definitely with the exception of some special cases which will be mentioned in the sequel.

Another negative ion spectrum for a different energy and pressure, 14.34 kev and 0.560 μ, is presented in Fig. 9. Again there is little doubt that the ions are CO^- and O^-.

At all energies up to 33.8 kev these two negative ions were the only ones identified as arising from the H–CO collisions. At this energy the monatomic peak became broader and exhibited structure. This suggested the presence of a third negative ion with a mass slightly less than that of O^-. An attempt to resolve the two peaks in the way illustrated in Fig. 10 indicates that this new ion cannot be as light as C^- unless it is formed with considerable kinetic energy. Eight separate runs gave for the masses of the three ions 28.3 m_H, 16.2 m_H, and 13.1 m_H, on the assumption of zero initial kinetic energy. This would indicate CO^-, O^-, and CH^-. However, the third peak certainly could be ascribed to C^-, formed

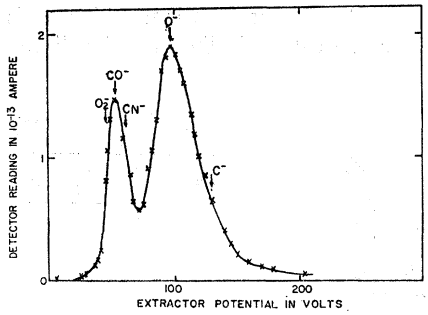

FIG. 9. Negative-ion spectrum for 14.34-kev hydrogen atoms incident on CO at 0.560 μ. Arrows show the expected position of O_2^-, CO^-, CN^-, and O^- ions.

with about 8 ev of kinetic energy. This is the interpretation favored.

During this survey there was a certain amount of water vapor and air present in the scattering chamber. The consequence was that it was always possible to detect a strong H_2^- signal arising from the reaction

$$H+H_2O \rightarrow H^++H_2^-+0.$$

This was demonstrated by deliberately introducing water vapor at controlled pressures into the system. The H_2^- peak proved to be in one way a boon since it gave a useful fiducial mark for mass measurements. The O_2 present in the air gave rise to O_2^- from the reaction

$$H+O_2 \rightarrow H^++O_2^-.$$

This peak in fact masked the CO^- at very low CO pressures; that is for total pressures below 0.1 μ.[8]

D. Cross Sections for Negative-Ion Formation

The relative cross section for negative-ion formation was measured at several energies selected for being

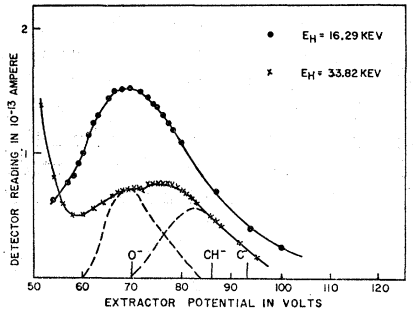

FIG. 10. Negative-ion spectrum for 33.82-kev H atoms incident on CO compared to the spectrum at 16.3 kev.

either maxima or minima in the electron loss cross section. The procedure was to hold the pusher voltage constant and to scan the negative ion spectrum by varying the magnetic field in the mass spectrometer. A sample spectrum obtained in this way is presented in Fig. 11. The areas under the CO^- and O^- portions of the curve, normalized for unit beam current, were obtained and the procedure repeated for several values of the pressure between 0.05 and 0.3 μ. Plots of the areas against pressure for several energies are shown in

[8] Results reported in this survey have been checked since, with a very much cleaner and more reliable system. [J. Nolan (private communication)]. The absence of background impurities has not been found to change the results reported here. Attention is drawn, however, to the mistakes in negative ion identification in a preliminary note, [T. M. Donahue and F. Hushfar, Nature **186**, 1038 (1960)]. These were the result of the asymmetric location of the beam with respect to the pusher plates and a misinterpretation of the helium ion calibration data. We are indebted to James Nolan and M. A. Biondi for their help in recalibrating the spectrograph, cleaning up the vacuum system, and generally improving the reliability of the observations with the mass spectrometer.

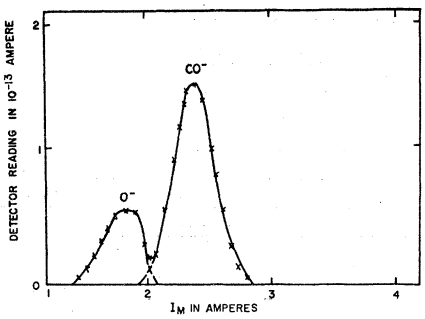

FIG. 11. Negative-ion spectrum for hydrogen atoms of 16.29-kev energy in CO at 0.115 μ. The extractor voltage is fixed at 37 v and the magnetizing current I_M is varied.

Figs. 12 and 13. The slope of the resulting curves is taken to be proportional to the cross section for formation of the corresponding ion by hydrogen atoms incident on CO. The cross sections for negative-ion formation measured relative to that at 14.34 kev are listed in Table II along with the percentage of the cross section due to CO^- formation and the percentage due to O^- formation.

In the curves of Figs. 12 and 13 the large intercept in the CO^- curve is caused by the O_2^- signal which could not be resolved in a clear-cut way from the CO^- peak. Similarly the non vanishing intercept for O^- at 17.42 kev is to be attributed to the background gas. The cross section of the residual gas for O_2^- and O^- production clearly varies with energy as the variation of the intercept with energy shows.

The bending of the curve at 16.29 kev is rather puzzling. It suggests that some of the CO^- formed at this energy are lost, presumably by collisional detachment, on the path through the mass spectrometer. However, the curvature does not appear at other energies, perhaps because some CO^- is formed at 16.29 kev in excited vibrational states. Effects of this sort must be investigated much more thoroughly in more refined experiments than this preliminary survey.

In Table II the height of the σ_{01} cross section above the arbitrarily drawn smooth curve of Fig. 4 is also listed. It is clear that the cross section for production of negative ions, σ_-, tends to follow the fluctuations in

TABLE II. Cross sections for negative-ion formation measured relative to that at 14.34 kev, together with the percentage of the cross section due to CO^- formation and the percentage due to O^- formation. Also listed is $\Delta\sigma_{01}$, the height of the σ_{01} cross section above the arbitrarily drawn smooth curve of Fig. 4.

Energy (kev)	σ_- relative	σ_- (10^{-16} cm^2)	$\Delta\sigma_{01}$ (10^{-16} cm^2)	CO^- (%)	O^- (%)
12.0	2.5	0.3	0.8	77	23
13.75	3.2	0.4	0.6	70	30
14.34	1	0.12	0.1	83	17
16.29	5.8	0.7	0.95	94	6
17.42	1	0.12	0.2	66	34
28.70	0.94	0.1	0.0	41	59

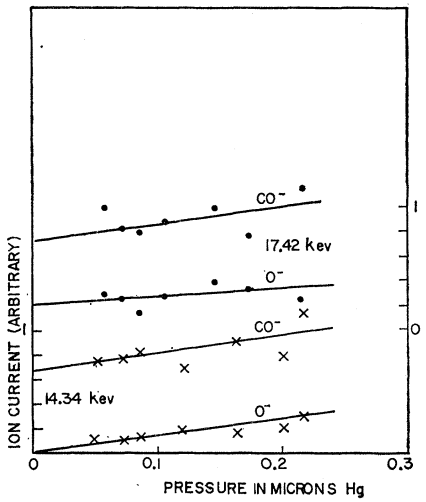

FIG. 12. Integrated and normalized negative-ion current plotted against CO pressure for hydrogen atoms at 14.34 and 17.42 kev. The zero for the latter energy is shifted upward as indicated on the right.

σ_{01}. It is also noticeable that the predominant ion formed is the molecular ion CO^-, particularly in the largest peak at 16.3 kev.

The absolute cross section was measured also at several energies. This was done by comparing the total positive ion current (I_+) collected by the mass spectrometer to the total negative ion current collected (I_-) after normalization to the same beam current.

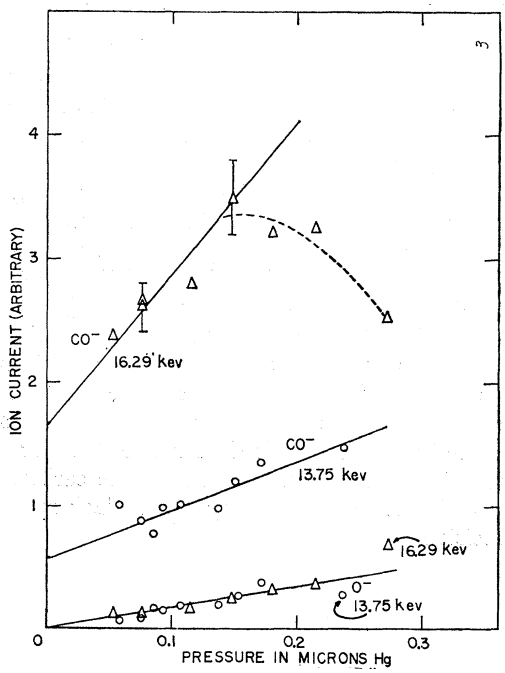

FIG. 13. Integrated and normalized negative-ion current (I_-/I_0) plotted against CO pressure at hydrogen atom energies of 13.75 and 16.29 kev.

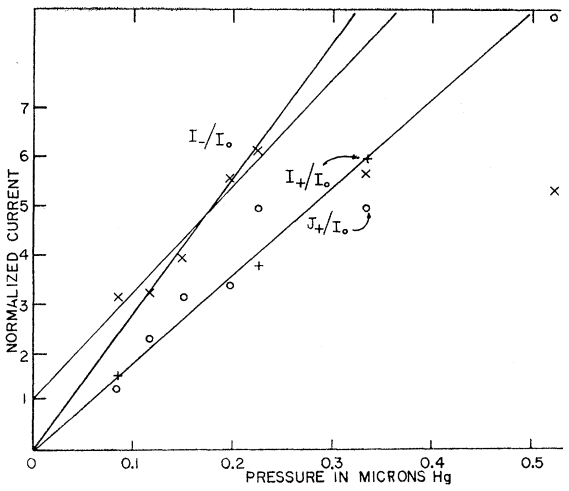

FIG. 14. Measurement of cross section for negative-ion formation in CO by hydrogen atoms at 14.34 kev. J_+/I_0 is the positive-ion current collected by a negatively charged collector plate divided by the beam current. For J_+/I_0 the scale is to be multiplied by 10^{-2}. I_+ and I_- are the integrated mass-spectrometer collecter currents for positive and negative ion, respectively. For I_-/I_0 the scale is 10^{-2} that for I_+/I_0.

The ratio of these two normalized currents will be $(\sigma_{0-1}+\sigma_I)/\sigma_-$. The cross section $\sigma_{0-1}+\sigma_I$ is not known yet for CO. It had to be obtained relative to the known cross section for argon by measuring the current of positive ions collected by plate B. This current J_+ is given by a version of Eq. (5)

$$J_+=I_0(\sigma_{0-1}+\sigma_I)nx+\Delta I_+(0) \tag{8}$$

where I_0 is the neutral beam current, n the gas density, and x the effective condenser length $\Delta I_+(0)$ is a (presumably) constant current from impurities. J_+ for CO was compared to that for argon to give $(\sigma_{0-1}+\sigma_I)$ for CO. At 14.34 kev the value of $\sigma_{0-1}+\sigma_I$ obtained turned out to be 11×10^{-16} cm^2.

In Fig. 14 are plotted I_+/I_0, I_-/I_0, and J_+/I_0 as functions of the pressure at 14.34 kev. These represent the best of several measurements of the cross section σ_-. The value obtained here is 0.12×10^{-16} cm^2. It is estimated to be good to no better than 25%.

Using this value for σ_- at 14.34 kev and the cross sections measured relative to it at other energies, the values of σ_- which result are also given in Table II. These measurements leave little doubt that the structure found in σ_{01} for CO is the result of transfer of the electron from the hydrogen atom to the carbon monoxide molecule. However, they clearly lack something in precision.

IV. DISCUSSION AND CONCLUSIONS

The fact that CO^- molecular ions are formed in great quantities in these electron loss collisions appears to offer great difficulties for a simple intepretation of the collision process such as was given in previous papers discussing the electron loss measurements.[2,9] If it is assumed that the electron at the time it is captured is simply accompanying the proton at about the same speed and that it forms negative ions in accordance with the Franck-Condon principle, then a good correspondence is obtained between the kinetic energy of the electron and the energy necessary to form the excited states of the molecular CO^- ion. However stable negative ions formed in such a process would have to be atomic; the molecular ions would quickly lose the electron by autodetachment. It is interesting that the model predicted the formation of C^- only near 34 kev and that it was only at this energy that there was evidence for its formation. However the evidence is against this simple model. On the other hand, it seems quite definite that the negative-ion formation cross sections for

$$H+XY\rightarrow\begin{cases}H^++XY^-\\ H^++X+Y^-\end{cases}$$

can be very large, of the order of 10^{-16} cm^2—and varies with energy in such a way as to cause oscillations in the cross section for electron loss by hydrogen atoms in electronegative gases. The automatic presence of the third body makes this an effective way of forming molecular negative ions. The process should be important in atmospheric, astrophysical, and plasma physics problems. In particular it could lead to large scale formation of O_2^- or even of O^- low in the ionosphere during solar proton events leading to polar blackouts.

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[9] T. M. Donahue and F. Hushfar, Phys. Rev. Letters 3, 470 (1959).