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DETERMINATION OF THE EXCITATION FUNCTIONS OF THE RARE GASES AND DIATOMIC MOLECULES BY ELECTRON IMPACT

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DETERMINATION OF THE EXCITATION FUNCTIONS FOR METASTABLE STATES OF THE RARE GASES AND DIATOMIC MOLECULES BY ELECTRON IMPACT

John Olmsted III, Amos S. Newton and K. Street Jr.

August, 1964

DETERMINATION OF THE EXCITATION FUNCTIONS FOR METASTABLE STATES OF THE RARE GASES AND DIATOMIC MOLECULES BY ELECTRON IMPACT *

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ABSTRACT

An apparatus is described for the determination of the excitation functions for formation of metastable states by impact of electrons of precisely defined energies in the energy range from threshold to the ionization potential. Results are given for studies on Ne, Ar, Kr, H_2, N_2, and CO. Two sharp resonances are observed in each of the rare gas excitation functions, which correspond to excitation by electron exchange of the first two excited configurations of these atoms. For diatomic molecules, no such resonances are observed, except in nitrogen, where there is a resonant process with an onset energy of 11.8 eV. A partial explanation for the shapes of the excitation functions is offered, based on the location and character of the various excited triplet states of the materials studied.

I. INTRODUCTION

Studies of the formation of atomic and molecular excited states by the impact of electrons with energies below the ionization threshold have been pursued by a number of workers in several different ways. Dorrestein determined excitation functions for metastable states in helium and neon by measuring the electrons ejected from a metal surface by impingement of the metastable atoms.[1] Lichten has used the same detection method for measurements on metastable nitrogen[2] and hydrogen[3] molecules, among others; and Schulz and Fox made some more refined measurements on helium using this method.[4] Milatz and Ornstein measured the excitation function for one state of neon by measuring the absorption of one of the spectral lines terminating in that state.[5] This same technique has been used subsequently in several studies, the most recent being determinations of electronic excitation functions for helium excited states by Smit, Heideman and Smit.[6] Another means of measuring electronic excitation functions has been to study the spectrum of inelastically scattered electrons. This technique has been utilized by Schulz to study helium, nitrogen and carbon monoxide.[7] Other workers have concentrated mainly on inelastic scattering of electrons with initial energies well above the ionization threshold.

We report here the results of determinations of electronic excitation functions for metastable states of several atoms and molecules, using the metastable detection technique of Dorrestein in a crossed electron beam-molecular beam configuration.

II. APPARATUS

The apparatus used in this study was a molecular beam system shown schematically in Fig. 1. The substance being studied was admitted into the main vacuum chamber of the apparatus in the form of a molecular beam, defined by effusion from the source and collimated by a slit in a bulkhead. The bulkhead made it possible to reduce the operating pressure by permitting the effused gas that was not part of the beam to be pumped away by a system separate from the pumping system of the main vacuum chamber.

In the main vacuum chamber, the molecular beam traversed an electron beam directed perpendicular to its direction of travel and finally impinged on a metal surface that was the first stage of an electron multiplier.

The pressure in the source, and hence the molecular concentration within the beam, was maintained constant during a run to within 1/2% by a servo-loop regulator consisting of a Decker model 306 differential pressure meter whose output voltage (proportional to the source pressure) was balanced against a preset voltage to generate an error signal. This error signal drove a two-phase servo-motor to open or close a Granville-Phillips variable leak valve controlling the rate of flow of gas into the source chamber.

The electron gun was a retarding-potential-difference (RPD) gun very similar to that described by Fox, Hickam, Grove and Kjeldaas.[8] It was not necessary to use the pulse technique of Fox et al. inasmuch as ion extraction was not needed in this experiment; metastable neutrals formed in the gun continued to move in the beam direction with their thermal velocity and were unaffected by the small electric fields in the gun.

Since the operation of an RPD gun has been outlined in the literature several times,[4,8] it will not be detailed here. However, one refinement in operation was made in order to simplify the measurement of signal changes resulting from the incremental variation of the retarding potential. Onto the constant negative potential applied to the retarding grid was superimposed a 23 cps square wave signal of 0.055 V peak to peak amplitude. The anode current in the gun then possessed a 23 cps component that was made up entirely of electrons possessing energies within a small energy range (somewhat greater than 0.055 V owing to energy spread introduced by the collimating axial magnetic field supplied to the gun). This component of the anode current was measured by a-c amplification and display of the voltage that was developed across a 50 K load resistor. In addition, the detector signal possessed a 23 cps component due to metastables formed by bombardment with electrons composing this fluctuating current. This component of the detector signal was determined as outlined below.[9]

Detection of the metastable states formed depended on Auger de-excitation of the metastables at a metal surface, with ejection of an electron.[10] The metal surface used in the experiments reported here was a silver-magnesium alloy with a work function of about 4.5 V. Electrons so ejected from the metal detector surface were accelerated into a 16-stage Allen-type electron multiplier with a gain of 10^6.[11] The resulting pulses were fed through a pulse amplifier into a scaler system where they were displayed as counts.

The same function generator that supplied the square wave to the retarding grid of the electron gun also supplied a square wave gating signal to the counting network, such that one counter registered only those pulses occurring during the negative portion of the square wave, while a second counter registered only those pulses occurring during the positive portion. The pulses that were the result of the modulated

portion of the electron beam then were found by subtraction of the counts registered on the negative-gated counter from those on the positive-gated one.

III. PROCEDURE

All data presented in this paper were taken only after several days' operation of the electron gun. After such a "run-in" time, the gun displayed stable emission and energy characteristics. At the start of a run, the gaseous substance being studied, supplied from Matheson gas cylinders with no further purification, was admitted into the source to a specified preset pressure of between 0.2 and 1.5 mm. The total energy of the electrons was then varied, in 0.05 V increments, from an energy below the onset of the first metastable level to an energy somewhat above the ionization potential of the substance. At each energy setting, two quantities were determined: the modulated electron beam current reaching the anode of the electron gun, and the number of counts registered on the two counters during a time interval of from 2 to 5 minutes' duration.

Stability of the source pressure was monitored by periodic checks of the voltage output of the differential pressure meter. The stability of the multiplier was also monitored by periodic readings taken at the same electron energy setting. Except when hydrogen was being run, no variation in multiplier stability was noted; for hydrogen, it was necessary to run a very high intensity beam in the apparatus for about a half hour prior to making a run, in order to stabilize the detector surface of the multiplier. Under those conditions, the multiplier was stable to within ± 2% during a run.

In addition to metastable atoms or molecules whose excitation energy lay higher than the work function of the detector surface, ions with electron affinities greater than the work function and photons of energy greater than the work function also possessed the capability of giving rise to signal pulses from the multiplier. In the experiments described here, ions were prevented from reaching the detector surface by the electric field conditions in the gun-detector region. Photons could not be entirely eliminated as a signal source; however, the molecular beam geometry of the apparatus provided a very high discrimination factor against photons. Inasmuch as the emitted photon distribution in space is generally isotropic for molecules or atoms of random alignment, the detector surface, which subtended an extremely small solid angle, could detect only a correspondingly small percentage of the total photon emission. On the other hand, the detector surface intercepted virtually the entire molecular beam.

IV. RESULTS AND DISCUSSION

A. Neon

The excitation function for metastable neon atoms is shown in Fig. 2. It shows two distinct resonance maxima, the first of which coincides with the $2p^5 3s$ states and the second with the $2p^5 3p$ states. No resonance phenomena were observed at any higher energies, although scatter in the data points indicates there may be some other small resonances that are obscured by the already high cross section at higher energies. The curve obtained is in excellent agreement with that determined by Dorrestein,[1] with the exception that our threshold breaks are more sharply defined owing to better electron energy resolution.

The detailed explanation of the excitation function above the threshold for the $2p^5 3p$ states depends on knowledge of the relative probabilities of excitation to each of the many excited states that can radiate to a metastable state, as well as on knowledge of the optical transition probabilities to the metastable and radiating states. However, in the energy region between the onset of the first metastable state (16.62 eV) and the onset of the lowest $2p^5 3p$ state (18.38 eV) the possible modes of population of metastable states are sufficiently limited that an explanation of the shape of the curve can be sought.

A diagram of the neon energy levels in this region is shown in Fig. 3. The L-S coupling notation fails to give a totally adequate description even of the lowest excited states, as indicated by the considerable mixing of $^1P_1$ with $^3P_1$ that permits the observation of the $^3P_1 - {}^1S_0$ transition with a lifetime only about one order of magnitude longer than the L-S allowed transition $^1P_1 - {}^1S_0$.[12] Accordingly, the designation resulting from J-j coupling of the core electronic system with the excited electron is also indicated.[12] The rigorous selection rule $\Delta J = 0, \pm 1$, $0 \not\leftrightarrow 0$ for dipole radiation insures that both the 3/2, 1/2, 2 state at 16.62 eV and the 1/2, 1/2, 0 state at 16.72 eV are metastable, inasmuch as transition among the four $2p^5 3s$ states are rigorously forbidden by dipole radiation by operation of the Laporte selection rule $\Delta(\Sigma\, l_i) = \pm 1$.

Furthermore, in the electron energy region below 18.38 eV there can be no radiation cascading mechanism populating the metastable states, since on the one hand the Laporte selection rule prohibits radiation to

these states from the other $2p^5 3s$ states and on the other, no higher states can be populated with electrons of these energies. Therefore, the excitation function from threshold to onset of the second peak at 18.4 eV represents simply the sum of the excitation functions for direct formation by electron impact of the two states 3/2, 1/2, 2 ($^3P_2$) and 1/2, 1/2, 0 ($^3P_0$).

The feature that must be explained is the clear indication of the presence of two maxima occurring at different energies in this function. The first is the observed resonance peak at 17.05 eV, while the second must occur at some higher energy than 18.38 eV, for the cross sections for formation of these states eventually to fall to low values at higher energies. This second maximum is rendered unobservable by the population of metastable states through excitation to higher levels.

There exist two alternative explanations for this twin-peaked cross-sectional behavior: that the observed curve is the sum of two curves, one peaking at the lower energy, the other somewhat higher, each representing excitation to one of the two metastable states; or that the individual excitation functions for the two states each display this twin-peaked character, owing to the operation of two different mechanisms for excitation of each of them.

Penney has made a calculation of the excitation functions of the analogous excited states of the mercury atom, for which the extent of L-S coupling breakdown is much the same as for the neon levels.[14] The results of his calculations show neither a twin-peaked character for the $^3P_0$ and $^3P_2$ states, nor a maximum at a different energy for one state than for the other. The theory as he developed it is therefore inadequate, whichever of the alternative explanations is correct.

The possibility exists that the maximum for the J = 2 state is shifted to higher energies than that for the J = 0 state. The transition

from the ground state to the J = 2 metastable involves addition to the atomic system of two units of angular momentum, whereas transition to the J = 0 metastable involves no angular momentum change. The incoming electron must therefore possess at least two units of angular momentum in the electron - atom system for the transition to J = 2 to occur, but it need have no angular momentum for the transition to J = 0 to occur. This requirement might shift the maximum for the J = 2 transition to higher energies, inasmuch as the higher the energy of the incoming electrons, the greater the angular momentum of the system for any given impact parameter.

That the alternative explanation, involving two distinct mechanisms for excitation of the metastable levels, one operating at electron energies near threshold and the other at higher electron energies, may be correct is indicated by some experimental evidence and has some basis in theory as well. Maier-Leibnitz derived an excitation curve for the excitation of the 2^1S level of helium that shows twin peaking character similar to what we have observed.[15] Recently, Smit et al. have measured a similar shaped curve for excitation of the 4^1S level and other S levels of helium.[6] Finally, Thieme observed strongly doubly-peaked excitation functions for the 3^1S_0 and 4^1S_0 levels of the mercury atom.[16] These curves can be explained by assuming that the initial sharp peak is the result of electron exchange excitation, whereas the second broader maximum is due to excitation of the level through a direct interaction. Mott and Massey indicate that in singlet excitation both of these modes of excitation must be taken into account.[17]

However, in attempting to apply this mechanism to the neon levels, some difficulties arise. The neon metastable levels are ^3P in character, according to L-S coupling; hence they cannot, by this coupling scheme, be

excited through the direct interaction mechanism. This difficulty can be surmounted if it is assumed, as is indicated by the strong mixing of the $^3P_1$ and $^1P_1$ states to remove metastability of the $^3P_1$ level, that L-S coupling is not adequate to describe the states. According to the J_c-j coupling scheme, the direct interaction process is not forbidden.

A further difficulty arises, however, in J_c-j coupling notation, in that the transitions are not of the s-s type for which exchange is predicted to be important[18] and which are the only type for which doubly peaked excitation functions have previously been observed. In particular, neither Smit et al. nor Thieme, in investigating several transitions to ^1P levels of helium and mercury, observed any indications of doubly peaked excitation functions.

It may be that the existence of two roughly equivalent maxima for excitation of the neon metastables reflects the intermediate character of the coupling, such that both excitation mechanisms make significant contributions. Such intermediate character is also indicated by, on the one hand, the short lifetime of the $^3P_1$ level where L-S coupling predicts long life and, on the other, the distinct grouping of the four $2p^5 3s$ levels into a low-lying triplet and a slightly higher singlet where J_c-j coupling predicts doublet-doublet spacing.

Final determination, which of the alternatives is correct, must await experiments, perhaps done by the optical absorption technique reported by Smit et al., to measure the individual excitation functions of the $^3P_2$ and $^3P_0$ states.

B. Argon and Krypton

Excitation function curves obtained for argon and krypton are shown in Figs. 4 and 5. These curves display the same general characteristics that are shown by the neon curve, except that the ratio of the first resonance peak height to subsequent cross section decreases significantly in the order Ne-Ar-Kr. In each case there are definite resonant peaks corresponding to excitation of the lowest and next lowest excited configurations. Further analysis of the curves obtained is even more difficult than for neon as a result of the closer spacing of higher excited states to the lowest metastable states. However, it is probable that the same considerations are applicable to argon and krypton as were given for neon. In that case, the reduction in resonance to non-resonance ratio in going to higher atomic weight lends some additional support to the explanation of the curve shapes that involves mixing of L-S and j-j coupling character, inasmuch as higher weight atoms approach j-j coupling more closely, and this in turn would be expected to enhance the direct interaction process while having little effect on the resonant exchange process.

C. Molecular Hydrogen

The excitation function for metastable molecular hydrogen is shown in Fig. 6. The curve shows just the character that might be expected for molecular triplet excitation: immediate, resonant-type rise of cross-section above threshold, but without the immediate peak and fall because of excitation of many successive vibrational levels of the triplet state. There is evidence of fine structural features on the curve, but the experimental scatter of points is too great to permit definite determination of such structure. The experiments of Lichten show a marked increase

in cross-section for metastable formation at about 14 V electron energy, presumably as a result of excitation of the numerous states above 13.9 eV that can radiate to the metastable level at 11.8 eV.[3] We do not see this rise, perhaps as a result of geometric factors: at energies as high as 14 V for molecules as light as hydrogen (and, indeed, to a large extent even for 11 and 12 V electrons), the momentum transferred to the molecule in the excitation process is generally sufficient to deflect the molecule out of the molecular beam. Thus, metastables formed as a result of excitation to levels above 13.9 eV followed by radiation are not capable of reaching the detector.

There are a large number of other triplet energy levels of hydrogen not indicated in Fig. 6, but these others all decay by radiation to the lowest triplet state, $b^3\Sigma_u^+$, which is a repulsive state that dissociates to give two "hot" hydrogen atoms. These states cannot give rise to any detector signal, since the kinetic energy imparted to the hydrogen atoms in the dissociation is more than sufficient to remove the atoms from the beam, except in the relatively improbable occurrence of breakup with one atom ejected along the beam axis. Examination of the electron energy region below 11.8 eV showed no evidence of signal arising from direct excitation of the $b^3\Sigma_u^+$ state.

Lichten has commented that the higher vibrational levels of the $c^3\pi_u$ state at 11.8 eV probably radiate to the $a^3\Sigma_g^+$ state, which in turn radiates to the repulsive $b^3\Sigma_u^+$ state.[3] However, the absence in this study as well as in Lichten's of a peak and fall in the excitation function implies that at least several of the vibrational levels must be excited, since excitation to any single level would be expected to be be sharply resonant in analogy to the resonant excitation to the ^3P neon level. The further possibility exists in our experiments that, owing to the great number of levels in this energy region from which optical transitions are allowed, there is sufficient contribution to the counting rate from photons

to obscure the peak and fall of the metastable state excitation curve. In Lichten's experiments, however, this possibility did not exist.

D. Molecular Nitrogen

The excitation function for nitrogen metastable states is shown in Fig. 7, along with the location of the known energy levels that might lead to metastable states.[19] The curve exhibits similar general features to that determined by Lichten;[2] the improved electron energy resolution of our work, however, shows quite distinctly the presence of a resonance type excitation process with an onset at 11.8 eV.

The excitation curve shown was taken with a detector-electron gun separation distance of 22 cm, which corresponds to a beam flight time of 0.46 msec. Some data were also taken with a detector-gun separation of 7 cm, corresponding to a flight time of 0.15 msec. With this separation, the character of the excitation function for electron energies above 8.5 eV was markedly different. There was a rather rapid, monotonic rise in signal from 8.5 eV up to electron energies above 17 eV; on this curve, the resonance at 11.8 eV was superimposed.

This change in character of the excitation curve clearly indicates the existence of two metastable states with independent lifetimes. This is in agreement with Lichten's determination of two separate metastable lifetimes in nitrogen;[2] his assignment of the shorter-lived state to the $a^1\pi_g$ state is verified, firstly by the singlet-type excitation function that is obtained at the shorter distance, and secondly by the onset energy at roughly 8.5 eV. From our data it is possible to estimate the lifetime of this state to be about $1.2 \pm 0.5 \times 10^{-4}$ sec., in excellent agreement with Lichten's determination of $1.7 \pm 0.3 \times 10^{-4}$ sec.

Failure to observe any signal from metastables in the electron energy region between 6.2 eV and 7.2 eV is not surprising, inasmuch as Franck-Condon transitions from the nitrogen molecule ground state to the lower vibrational levels of the $A^3\Sigma_u^+$ are not possible owing to the difference in equilibrium internuclear separation of these states. The linear rise in cross-section from about 7.2 eV up to about 10.8 eV can be attributed to excitation both of higher vibrational levels of the $A^3\Sigma_u^+$ state and of vibrational levels of the $B^3\pi_g$ state. The potential energy curves of these two states are virtually coincident in this region; hence only by observation of the $A^3\Sigma_u^+$ - $X^1\Sigma_g^+$ emission bands might the relative population of the two states be determined.

The resonance peak occurring at 11.8 eV has a shape strikingly similar to atomic resonance excitations. In fact, when the threshold-to-peak cross section rise is normalized to that for the first neon resonance, the two peaks can be exactly superimposed. This demonstrates that vibrational levels extending over at most a 0.1 eV energy spread are being excited; a wider spread in available vibrational levels would result in broadening of the resonance peak.

We assign this sharp resonance to excitation of the yet undesignated E triplet state at 11.8 eV. The assignment is made on the basis of several determinations of the location of the onset of the resonance, both by direct measurement using a clean electron gun which had not built up contact potentials (as determined by subsequent measurement of the neon resonance threshold) and by a measurement of the energy separation of the neon and nitrogen resonance onsets made by running a mixed beam of the two gases. These determinations gave for the onset energy the value 11.85 ± 0.05 eV.

Judging from the assignment of emission lines from the E state by Herman,[20] only the ground and first vibrational level of this state can be

excited by a Franck-Condon process; thus the state meets the requirement, imposed by the narrowness of the peak, of a narrow spread in energy of levels excited.

Schulz, in examining the scattering of electrons that were involved in inelastic collisions with nitrogen, has observed a similar resonance process whose onset he fixes at 11.2 eV.[6] On the basis of this onset energy, he attributes the resonance to excitation of the $C^3\pi_u$ state. Inasmuch as neither we nor he observed any further structure in this energy region, and inasmuch as both his and our resonances indicate excitation of at most two vibrational levels of the state involved, it is probable that the processes observed by each of us are the same.

Examination of the potential energy curves for the ground state ($X^1\Sigma_g^+$) and the $C^3\pi_u$ state indicate that the first four or five vibrational levels can be reached by Franck-Condon transitions. This is confirmed by the work of Tyte, who in a discharge study determined that all of the first five vibrational levels of the $C^3\pi_u$ state are significantly populated by electron impact.[21] Therefore, the $C^3\pi_u$ state cannot be the one giving the narrow resonance peak.

It is possible that the discrepancy in energy between Schulz' work and ours is due to the development of contact potentials during the course of measurements on nitrogen. A difference in the energy scales of roughly one-half volt is required to bring the results into agreement. We have observed contact potentials of this order of magnitude in our work, even at the very low residual pressures at which a molecular beam apparatus is operated, as a result of the presence of gases other than the noble gases. We have attempted to eliminate errors arising from such contact potentials in our work by measuring thresholds for neon and nitrogen while both gases were present in the apparatus.

E. Carbon Monoxide

The excitation function for metastable states of carbon monoxide is shown in Fig. 8. This curve was taken with the detector-gun distance 7 cm. With greater separation, no signal was obtained.

The lowest triplet state of CO, $a^3\pi$, is a metastable state but has a lifetime of about 10 microseconds, which renders it too short-lived to be observed in the present study even at 7 cm. detector-gun separation.[22] This explains the lack of signal in the energy region above the $a^3\pi$ threshold at 6.0 V. The low-level signal observed in the 7-10 eV energy region is probably due to light, although there may be a small metastable signal from the $a^3\pi$ state if the cross-section for formation in this energy region is sufficiently high.

The rather strongly rising cross section with an onset at 10.5 eV must be attributed to some higher metastable state of the CO molecule that possesses a lifetime of the order of 0.1 msec. This level probably is not a singlet level, inasmuch as all conceivable singlet levels that might lie in this region could decay by allowed transitions either to the ground state ($X^1\Sigma^+$) or to the first excited state ($A^1\pi$) at 8 volts. The $b^3\Sigma^+$ state lies at about the right energy. The transition from this state to the ground state is more strongly forbidden than is the $a^3\pi$ - $X^1\Sigma^+$ transition;[23] moreover, the equilibrium internuclear distance for this state is sufficiently different from those for the lower-lying triplet states that there could conceivably be a Franck-Condon prohibition on triplet transitions from the $b^3\Sigma^+$ state.[18] Experiments of Hansche show a peculiar dependence of the emission intensity of the $a^3\pi$ - $X^1\Sigma^+$ bands on pressure and power of the discharge that can be explained by assuming population of the $a^3\pi$ state by radiation from some higher, slightly longer-lived metastable state.[22]

Whether this is the same state whose excitation function we have observed, and whether this state is the $b^3\Sigma^+$ state or some other, cannot presently be ascertained.

FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. Block diagram of molecular beam apparatus for triplet state excitation studies.

Fig. 2. Excitation function for metastable states of neon. Energies of the first several excited levels are indicated.

Fig. 3. Low-lying electronic levels of the neon atom. Both L-S and J_c-j coupling designations are shown.

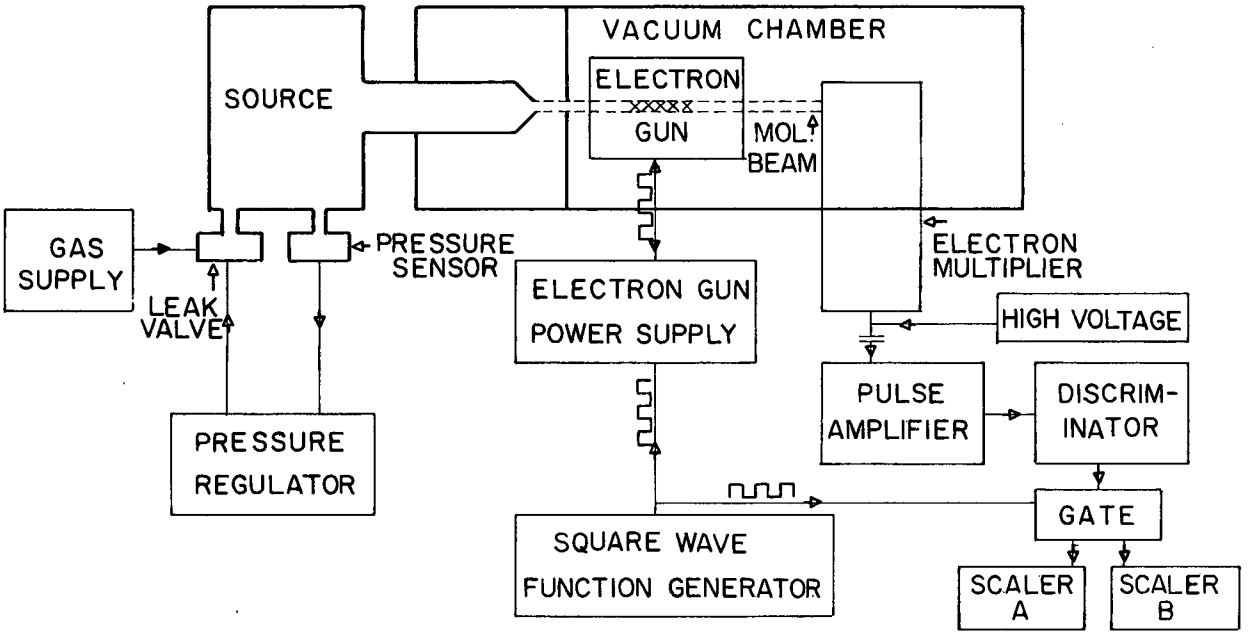
Fig. 4. Excitation function for metastable states of argon. Energies of levels that can contribute to formation of metastables are indicated.

Fig. 5. Excitation function for metastable states of krypton. Energies of levels that can contribute to formation of metastables are indicated.

Fig. 6. Excitation function for metastable states of molecular hydrogen. Energies of levels that can contribute to formation of metastables are indicated.

Fig. 7. Excitation function for metastable states of molecular nitrogen. Energies of levels that can contribute to formation of metastables are indicated.

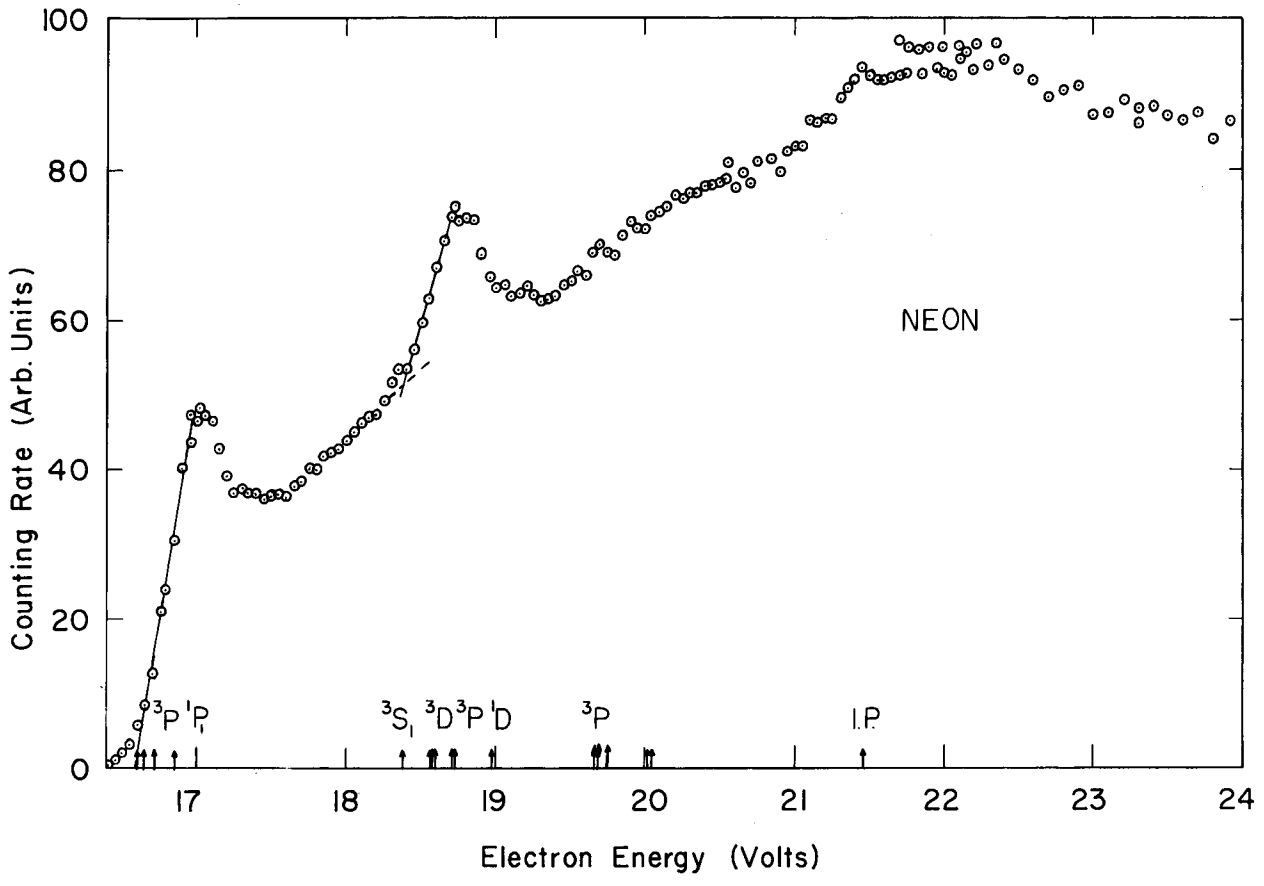
Fig. 8. Excitation function for metastable states of carbon monoxide. Energies of the excited triplet states of the molecule are indicated.



TRIPLET STATE EXCITATION APPARATUS

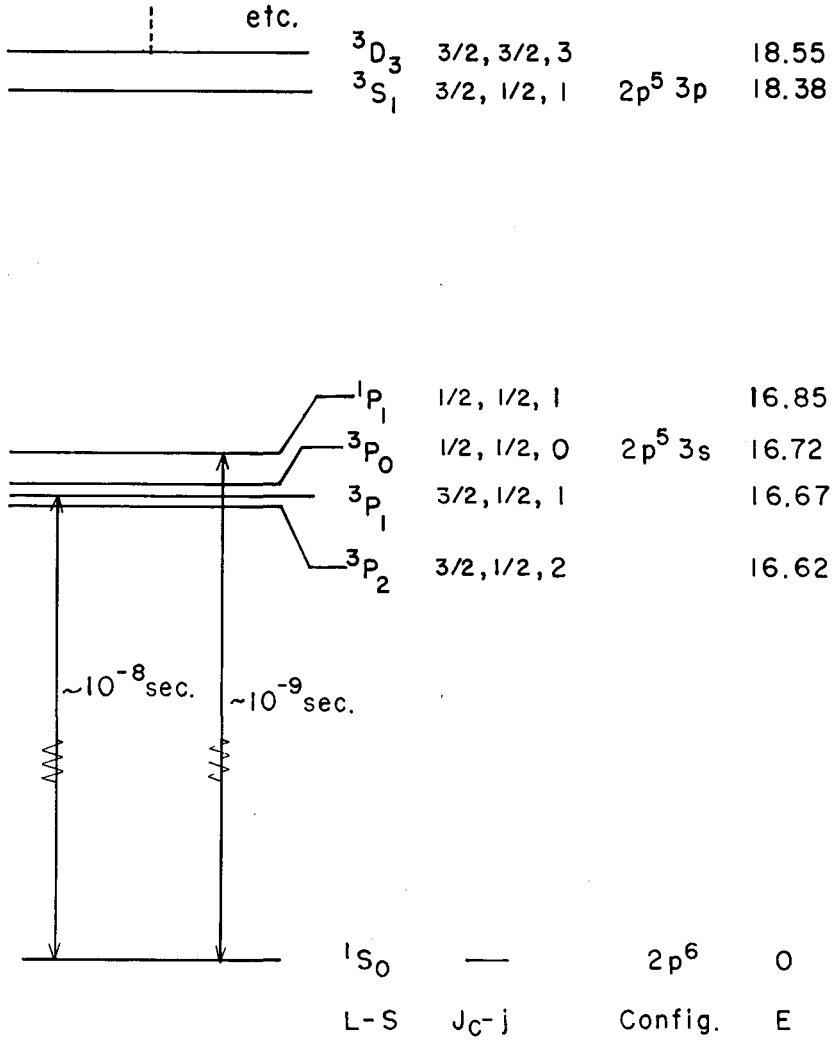
MUB-3933

Fig. 1



MUB-3934

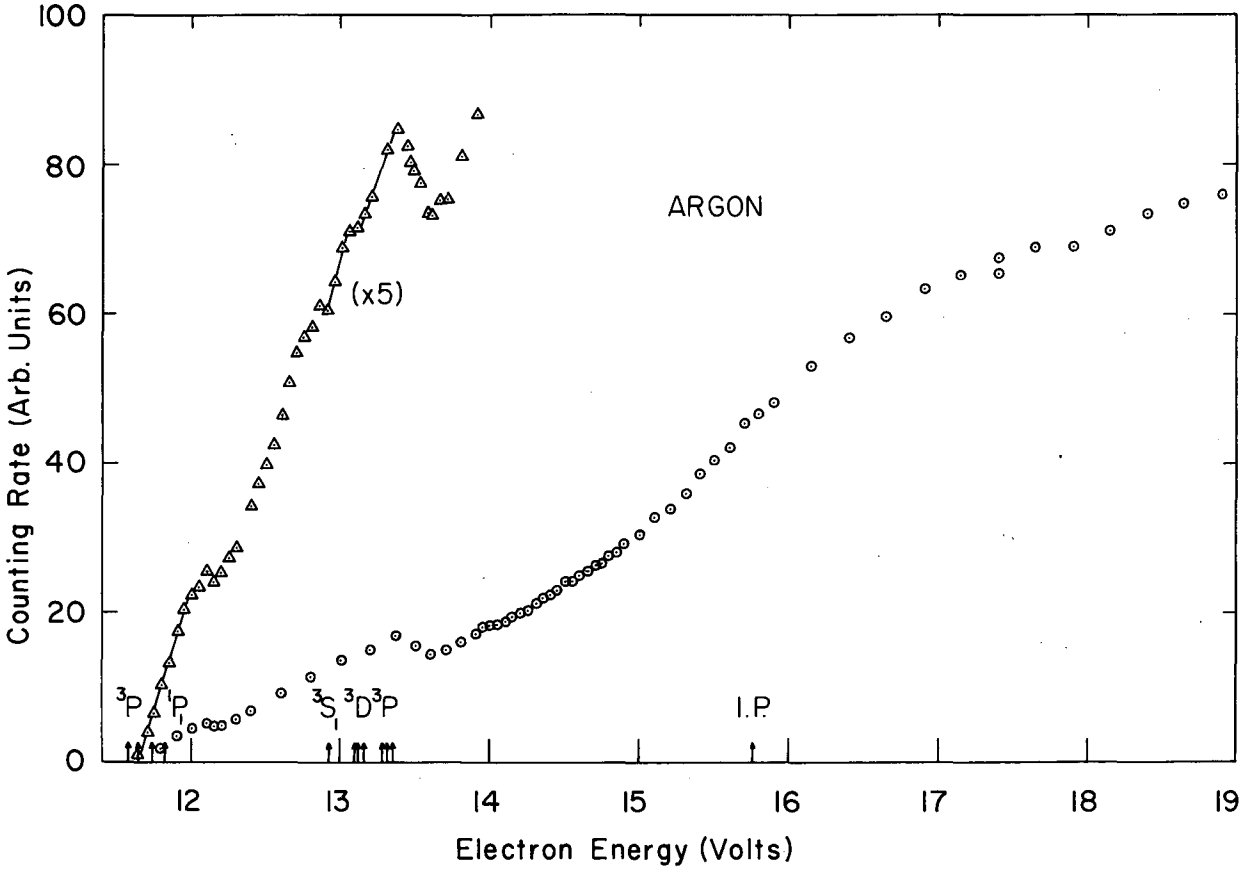
Fig. 2



Low-Lying Energy Levels of Neon

MUB-3935

Fig. 3



MUB-3936

Fig. 4

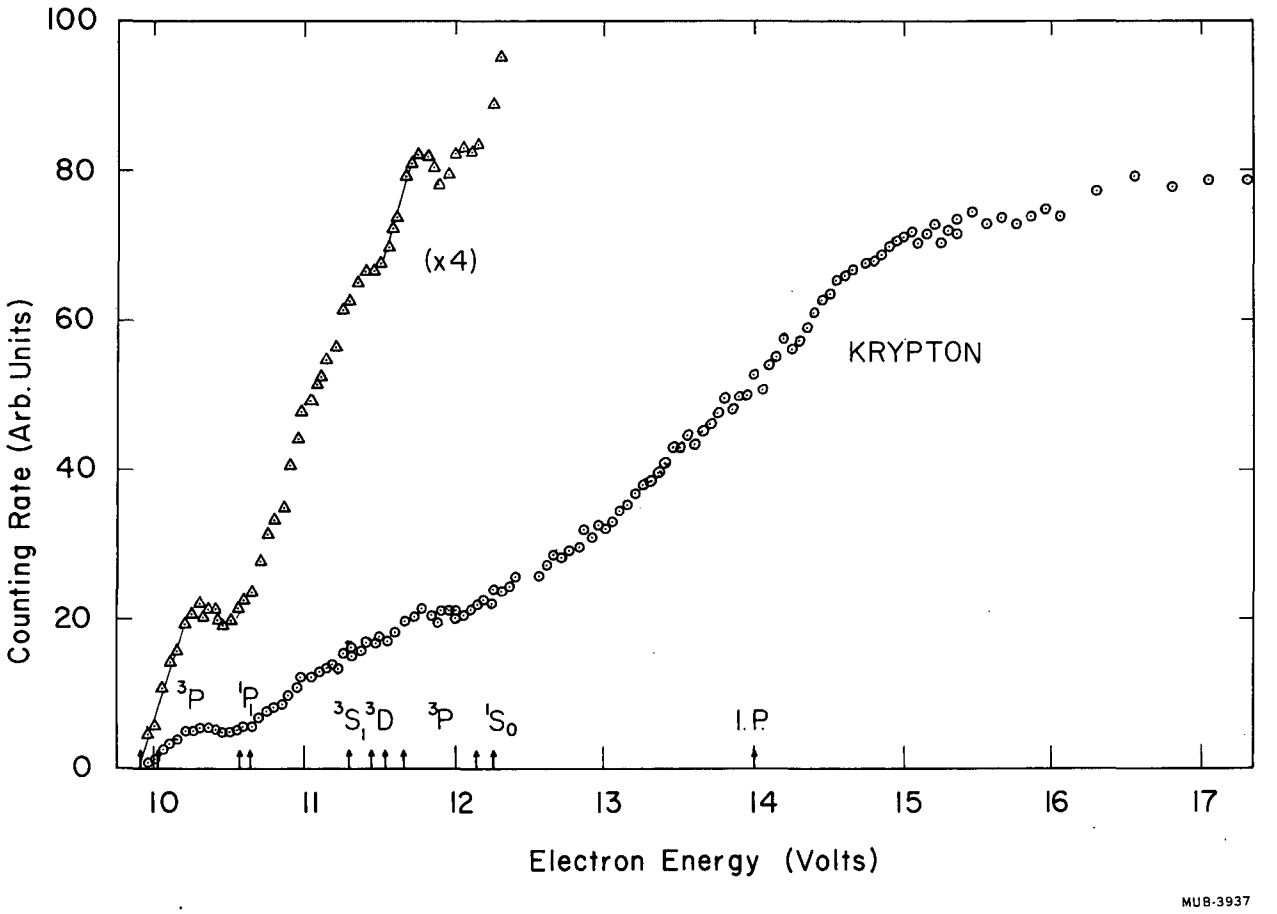

100
80
60
40
20
0
Counting Rate (Arb. Units)
(x4)
KRYPTON
^3P
$^1P_1$
$^3S_1$ ^3D
^3P
$^1S_0$
I.P.
10
11
12
13
14
15
16
17
Electron Energy (Volts)
MUB-3937

Fig. 5

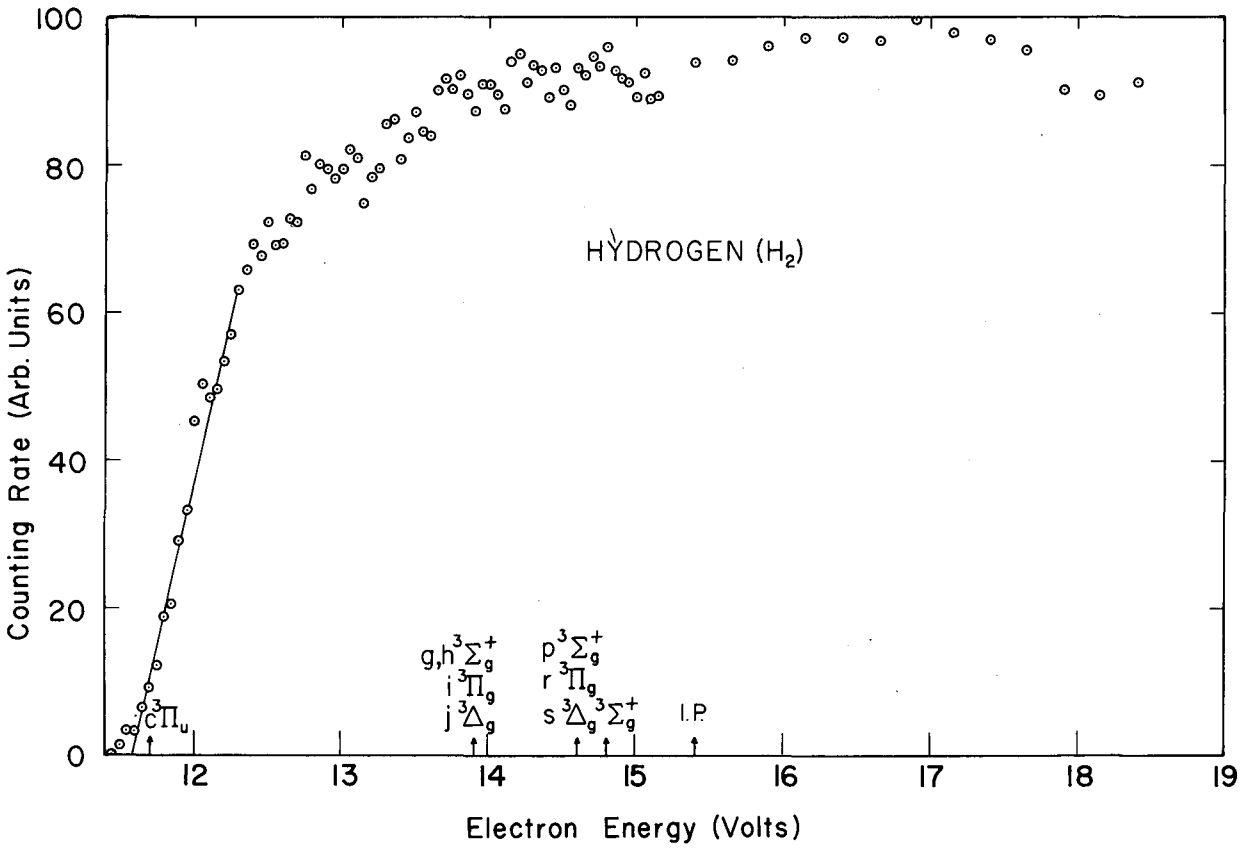


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Fig. 6

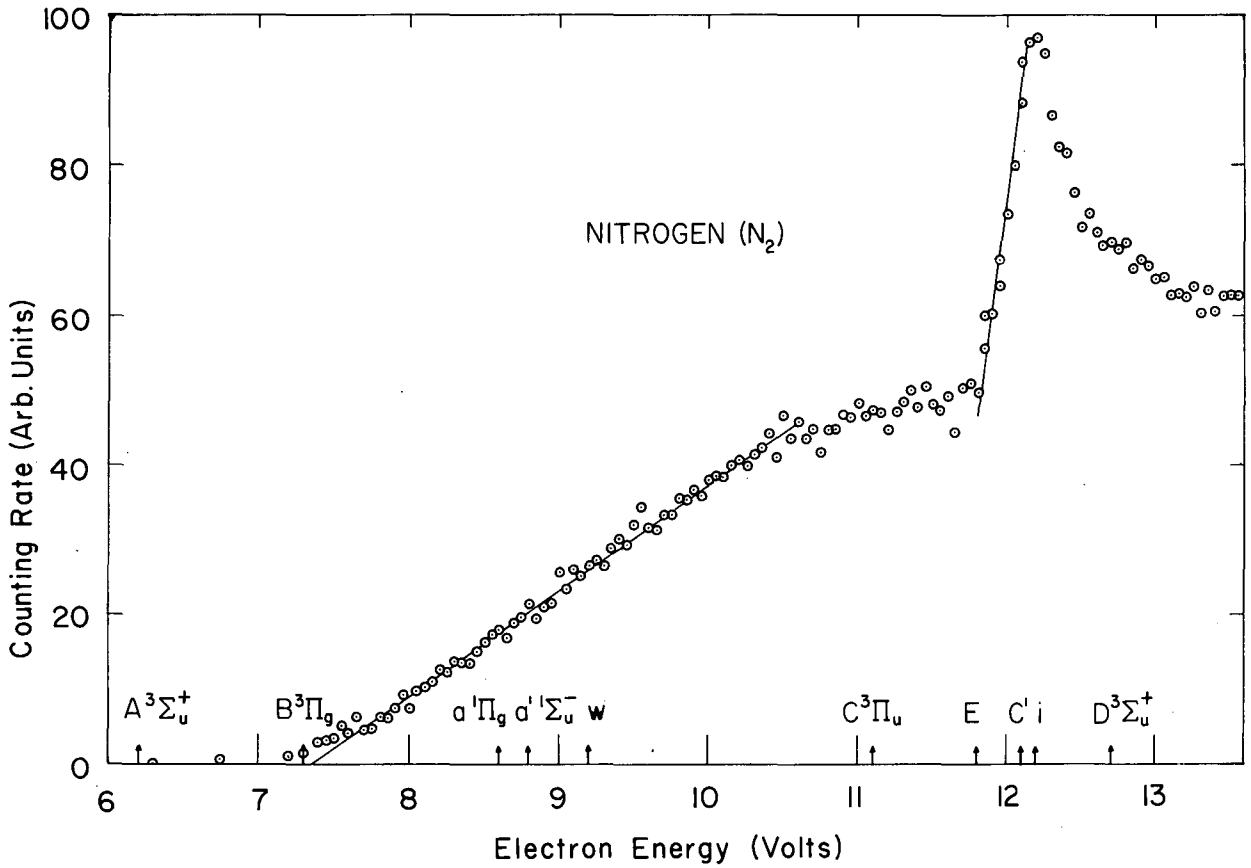

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Fig. 7

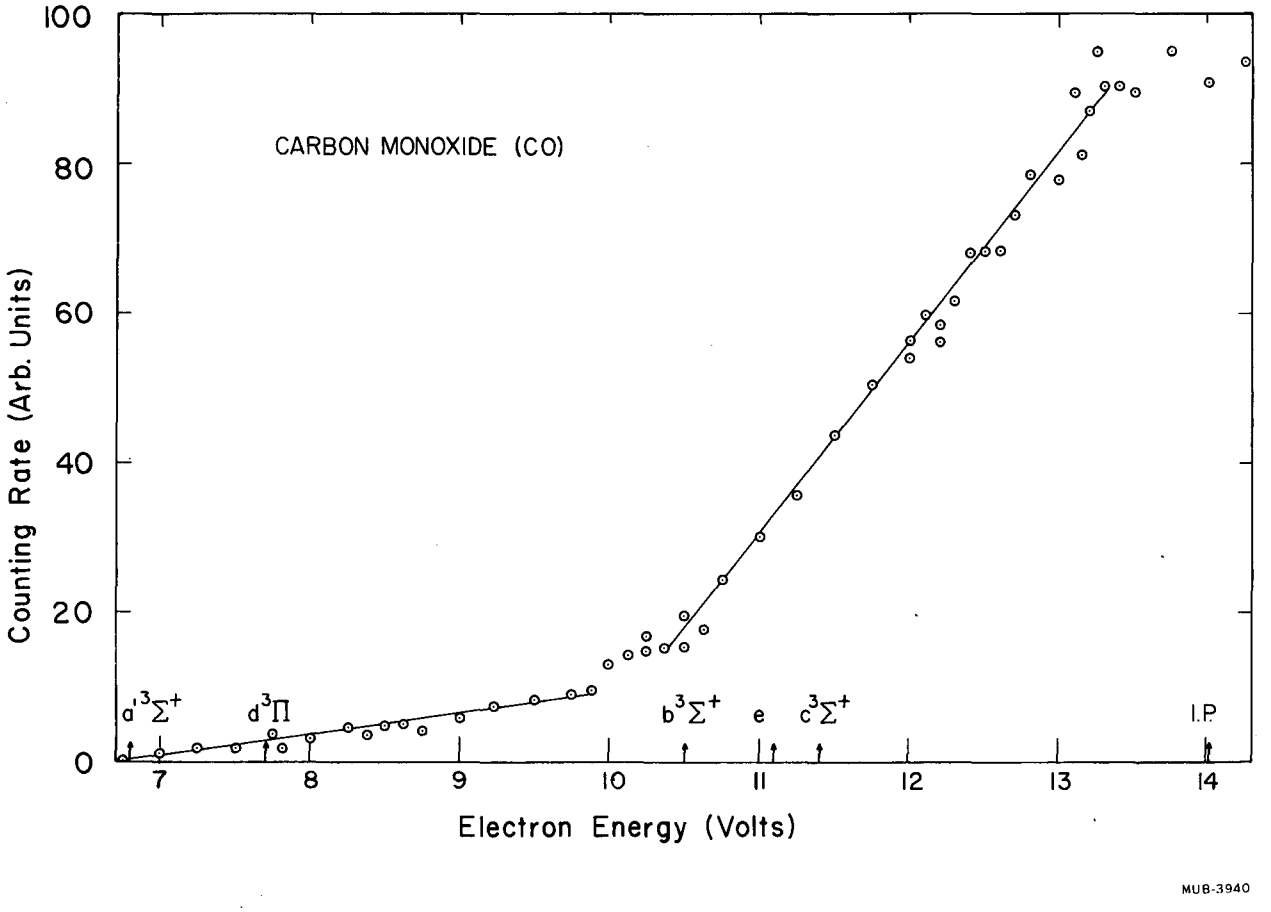
CARBON MONOXIDE (CO)
Counting Rate (Arb. Units)
Electron Energy (Volts)
0
20
40
60
80
100
7
8
9
10
11
12
13
14
a'³Σ⁺
d³Π
b³Σ⁺
e
c³Σ⁺
I.P.
MUB-3940

Fig. 8

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