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PRODUCED BY ELECTRON IMPACT

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ON THE METASTABLE DISSOCIATION OF THE CH⁺ ION PRODUCED BY ELECTRON IMPACT*

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ABSTRACT

The metastable dissociation of CH⁺ and CD⁺ ions have been investigated. CH⁺(m) from CH₄, C₂H₂, C₂H₄, CHCl₃, CH₂Cl₂ and CD⁺(m) from CD₄, C₂D₂, C₂D₄ and CDF₃ were studied. CH⁺(m) and CD⁺(m) dissociate with a half life of $0.4 \pm 0.2 \times 10^{-6}$ sec and with kinetic energy release in the dissociation of 1.1 ± 0.3 and 1.4 ± 0.3 respectively. Using 70 eV electrons, CD⁺(m) and CH⁺(m) are formed with initial kinetic energy, the value being dependent on the compound irradiated. Appearance potential measurements show that when formed from C₂H₂ and C₂D₂, the CH⁺(m) and CD⁺(m) must dissociate to the lowest dissociation limit of CH⁺, i.e., C⁺ (²P_{1/2}^o) and H (²S). It is postulated that the metastability arises from a predissociation of the b ³Σ⁻ state with the repulsive c ³Σ⁺ state of CH⁺.

INTRODUCTION

The existence of metastable states of CH_x^+ ions has been the subject of several studies. Most such studies have concentrated on methane as the source gas. Dibeler and Rosenstock observed no metastable ions in the mass region 12-16 from CH_4 but observed metastable ions from CD_4 .¹ Melton and Rosenstock² observed only collision-induced dissociation products in the mass region below mass 12. Ottinger³ and Hills, Vestal and Futrell⁴ restudied the metastable ions from CH_4 and CD_4 and observed several metastable ion peaks in the mass range 12-16. The mass region below 12 was not studied. Lorquet, Lorquet, Momigny and Wankenne⁵ recently observed the metastable dissociation of the CH^+ ion from C_2H_2 and HCHO and of the CD^+ ion from C_2D_2 . In a following theoretical paper, Lorquet, Lorquet, Momigny, Wankenne and Lefebvre-Brion⁶ discussed the calculated potential energy curves in the CH^+ system and possible states of CH^+ which might account for the metastable dissociation. They concluded the unimolecular metastable process to arise from the predissociation of the $5\Sigma^-$ state by the $c\ 3\Sigma^+$ (a weak process) and the predissociation of the 3Δ state by $3\Sigma^-$, 3π or 5π repulsive states. The AP of the metastable ion was reported to be 29 ± 1 eV for the weak process and 32.5 ± 0.7 eV for the strong process.

The results presented here confirm the existence of metastable CH^+ ions but are consistent with a simpler interpretation than that previously given. In view of the importance of CH^+ ions in astrophysics^{7,8,9,10} and the possible role of these ions as intermediates in the radiation chemistry of organic gaseous systems, it is important that the state or states responsible be identified and the energetics of the process be determined as exactly as possible. Inasmuch as the forbidden states of CH^+ have not been related to the ground state except theoretically,⁶ the energetics of the metastable ion should define one point

on the potential energy curves of the states involved which will either confirm or lead to a readjustment of the energy scale of the calculated curves.

EXPERIMENTAL

The experiments described here were performed with a Consolidated Electroynamics Corp. Model 21-103B mass spectrometer. Modifications to increase the vacuum capabilities of the instrument, to increase the sensitivity of the recording system, to make negative repeller studies of initial kinetic energy, to measure metastable suppressor cutoff potentials, and to record ionization-efficiency curves directly on an X-Y recorder have already been described.^{11,12,13}

The methane used was obtained from Pacific Oxygen Company and was > 99.993% pure. Acetylene was welding grade and purified by standard cryogenic vacuum techniques. No impurities were detectable in the purified product. The CD_4 , C_2D_2 , C_2D_4 , and CF_3 were products of Merck, Sharp and Dohme. The chloroform and dichloromethane used were reagent grade.

RESULTS

In the mass region below mass 12, the calculated apparent masses at which products of various dissociations in CH_x^+ and CD_x^+ will appear are shown in Table I. In this table the form in which multiple loss of H atoms appear in processes 4, 5 and 6 are not shown. Processes 4, 5 and 6 can be unimolecular only if, in each process, the parent ion is accelerated and a metastable dissociation releasing one fragment is followed by one or more fast dissociations releasing the other fragments.

The variation of peak sensitivity with pressure of peaks at $(M/q)^* = 11.077$ from various compounds containing the CH group and of $(M/q)^* = 10.286$ in various CD containing compounds was studied. The sensitivity of each of these respective peaks (peak intensity/pressure), while increasing slowly with pressure indicating some collision-induced contribution, extrapolates to a well defined non-zero intercept at zero pressure showing each to be the result of a unimolecular dissociation. The peak from CH_4 shows the largest collision-induced contribution, and this is true even when the contribution of the $(M/q)^* = 11.267$ peak is removed by the metastable suppressor set with a retarding potential equal to $0.900 V_A$ (cutoff = $0.866 V_A$, where V_A is the ion accelerating voltage) at which level the $(M/q)^* = 11.077$ peak is passed (cutoff = $0.923 V_A$).

The variation of peak sensitivity with pressure of some other peaks in deuterated compounds were also studied, using the peaks in the mass spectrum of C_2D_6 as an example. In this group of peaks, $(M/q)^* = 10.286$ at moderate pressures is formed almost entirely by a unimolecular dissociation process. $(M/q)^* = 9.000$ (process 2) shows a definite positive zero-pressure intercept of sensitivity, indicating a unimolecular component, but at moderate pressures the peak observed is nearly half collision-induced. $(M/q)^* = 10.889$ (process 3)

shows a probable non-zero intercept but the low intensity makes a definite conclusion on the real existence of a unimolecular process open to question. $(M/q)^* = 8.000$ (diffuse peak only, process 4) extrapolates to zero at zero pressure and, at this sensitivity level, the results show no indication of a unimolecular component in the dissociation.

It is concluded that CD^+ and CH^+ dissociate by unimolecular processes into $C^+ + D$ and $C^+ + H$ respectively. CD_2^+ probably dissociates by a unimolecular process into $C^+ + D_2$ and CD_3^+ possibly dissociates by a unimolecular process into $CD^+ + D_2$. The unimolecular component of each of these last two dissociation processes was found to be of too low intensity to investigate further.

The kinetic energy release in the metastable fragmentation of $CH^+(m)$ and $CD^+(m)$ was studied by the change in peak width with change in ion accelerating voltage.¹⁴ The equation relating T , the kinetic energy release in the metastable dissociation, to Δd , the change in peak width in amu when the ion accelerating voltage, V_A , is changed from V_1 to V_2 for the transition $M_0^+ \rightarrow M_1^+ + M_2$, is given by:

$$T = (\Delta d)^2 \left(\frac{M_0^2}{16M_1^4} \right) \left(\frac{M_1}{M_2} \right) \left(\frac{eV_1 eV_2}{(\sqrt{eV_1} - \sqrt{eV_2})^2} \right) \quad (1)$$

In those cases where the neutral fragment is the H atom, this light fragment carries most of the energy hence the change in peak width is a less sensitive function of T than is the case in those metastable fragmentations where the mass difference between M_1 and M_2 is less pronounced. The derived value of T is therefore less precise for fragmentations in which an H atom is the neutral product. Substitution of deuterium improves the accuracy to which T can be determined. The kinetic energy release on fragmentation of a metastable ion

can also be measured by the width of the metastable suppressor cutoff curve of the metastable peak,¹⁴ and this method was also used for some of the compounds with results similar to those found by the change in peak width with ion accelerating voltage. The results of measurements on the metastable dissociation of CH^+ and CD^+ as formed from various sources are shown in Table II. These results indicate the kinetic energy release in the metastable dissociation of CH^+ to be independent of the molecular source of the ion, but that the deuterated ion may dissociate with slightly greater kinetic energy release than does the protonated ion. Values of $T = 1.1 \pm 0.3$ eV for the dissociation of $\text{CH}^+(\text{m})$ and $T = 1.4 \pm 0.3$ eV for the dissociation of $\text{CD}^+(\text{m})$ were observed. It is not certain the difference in these values is real since the probable errors overlap and possible systematic errors may occur in the case of CH^+ where the proximity of $M/q = 12$ can influence the results.

In the fast fragmentation processes necessary to form the metastable state of CH^+ from various compounds, the $\text{CH}^+(\text{m})$ can be formed in the ion source with initial kinetic energy. This initial kinetic energy may be zero at the appearance potential of $\text{CH}^+(\text{m})$, but with the equipment used in these experiments, initial kinetic energy measurements cannot be made at or near the AP. Measurements can be made at ionizing electron energies of 70 eV by the negative repeller cutoff method.¹³ In the case of $\text{CH}^+(\text{m})$ which has a short half life, the negative repeller cutoff will be influenced by the increased residence time in the ion source chamber as the negative potential on the repellers is increased. The cutoff value obtained will therefore be a minimum value for the maximum initial kinetic energy. In those cases such as CH_4 and CHF_3 , where multiple fast fragmentations must occur in the formation of $\text{CH}^+(\text{m})$, the shape of the curve near the cutoff point may be influenced by the distribution of

velocities in each of the successive fragmentation steps. Negative repeller cutoff curves of $CD^+(m)$ from CD_4 , C_2D_2 , and CDF_3 are shown in Fig. 1. For comparison, the negative repeller cutoff curve of ${}^3He^+$ is shown. It is clear that $CD^+(m)$ from all sources has initial kinetic energy when formed by impact with 70 V electrons, and that in the case of CDF_3 , this initial kinetic energy is substantial. Initial kinetic energies of $CH^+(m)$ and $CD^+(m)$ derived from curves of this type are shown in Table III. The table shows a difference in initial kinetic energy between $CH^+(m)$ from C_2H_2 and $CD^+(m)$ from C_2D_2 . This difference is well outside the experimental error.

The initial kinetic energy with which $CH^+(m)$ or $CD^+(m)$ is formed in the ion source affects the first slit discrimination in the collection efficiency of these ions and hence will have an effect on voltage discrimination curves. This effect must be considered in utilizing this method of determining half lives of the metastable ions. The initial kinetic energy also affects the apparent shape of the metastable ion peak. This is illustrated in Fig. 2 in which the shapes of the 10.286 peak in various CD containing compounds is shown. There are almost no differences in shape of the respective peaks from CD_4 , C_2D_4 , and C_2D_2 from which the initial kinetic energy of $CD^+(m)$ is in the range 0.6 to 0.8 eV. But the peak from CDF_3 , where the $CD^+(m)$ initial kinetic energy is 3.2 eV, has a markedly different shape and much of the structure, i.e., the front shoulder, center peak, and back shoulder are less pronounced in the peak from CDF_3 compared to the peaks from the other compounds. The peak is also skewed to the high mass side so the apparent center of the peak is at an $(M/q)^*$ slightly greater than 10.286. The peak shapes shown in Fig. 2 were recorded at an ion accelerating voltage of 2000 V. They exhibit less structure

than those shown in Ref. 5 which were recorded at an ion accelerating voltage of 600 V. At low ion accelerating voltages, we obtain peak shapes which are quite similar to those shown in Ref. 5. Such low voltages were avoided in the present work owing to severe discrimination problems with low energy ions.

Methods of estimating half lives for the dissociation of metastable ions¹⁵ using a Dempster type mass spectrometer are: 1) variation of the intensity of the metastable peak with change in repeller potential,^{16,17} and 2) variation of the intensity of the metastable peak with change in ion accelerating voltage with the repeller potential a constant fraction of V_A .¹⁸ Each of these methods suffers from the short time interval over which the data can be evaluated. When the metastable ions are formed with initial kinetic energy, corrections are necessary because of discrimination at the ion source exit slit. Berry¹⁹ has discussed discrimination caused by initial kinetic energy and corrections for discrimination at the ion source exit slit can be made if the initial kinetic energy is known.

A second factor to be considered occurs when the ion beamwidth at the collector slit is wider than the collector slitwidth. If the beamwidth varies with the parameter changed to adjust the time scale, then a correction must be made for this factor since the peak height does not represent a constant fraction of the total beam intensity.

In Fig. 3 the discrimination curves are shown for the change in peak intensity vs. ion accelerating voltage for $(M/q)^* = 11.077$ from CH_4 and $(M/q)^* = 10.286$ from CD_4 . The lines are calculated for the half lives shown for each dissociation. The observed points (circles) indicate a half life of about 0.1 μ sec for these transitions. When corrections are made for the beamwidth being wider than the slitwidth (square points) a half life of about

0.17 μsec is indicated. Since the slitwidth is less than a third of the beamwidth even at $V_A = 3500$ V, the integrated peak intensity was approximated by multiplying the maximum peak height by the halfwidth in amu. All curves are normalized for the intensity at $V_A = 3500$ V equal to 100. A further correction for initial kinetic energies of the $\text{CH}^+(\text{m})$ and $\text{CD}^+(\text{m})$ respectively raise the apparent half lives to > 0.5 and < 0.8 μsec (triangles).

In Fig. 4 the data for $(M/q)^* = 11.077$ from C_2H_2 is plotted. The observed discrimination curve indicates a half life of less than 0.1 μsec (circles). Correction for beamwidth increases this to about 0.15 μsec (squares) and the further correction for initial kinetic energy of $\text{CH}^+(\text{m})$ leads to a half life of > 0.5 and < 0.8 μsec (triangles). Considering the differences in initial kinetic energy of the metastable ions from CH_4 , CD_4 and C_2H_2 shown in Table III, this agreement is satisfactory.

It is difficult to properly evaluate this data since the distribution of initial kinetic energies of $\text{CH}^+(\text{m})$ or $\text{CD}^+(\text{m})$ in each case is not known. The calculations were made assuming all ions of each respective type to possess the maximum initial kinetic energy shown in Table III. This assumption is almost certainly incorrect and the correction for initial kinetic energy should probably be less than indicated in Figs. 3 and 4. A half life of 0.4 ± 0.2 μsec certainly encompasses the possible errors in the correction terms and represents the best estimate of the half life derivable from the present data.

Using the method of variation of the repeller potential, Lorquet, Lorquet, Momigny, and Wankenne⁵ found a half life of 0.1 μsec for this metastable dissociation. This value agrees with the apparent half life indicated by the uncorrected data observed in the present work. Owing to the necessity of correcting for initial kinetic energy of the $\text{CH}^+(\text{m})$ and the change in peakwidth

with repeller variation, the reported value of 0.1 μ sec must be too low. In this case the use of stable CH^+ ions as a comparison standard does not negate the necessity for corrections for initial kinetic energy. It would be most improbable that $\text{CH}^+(\text{m})$ and stable CH^+ would each be formed with the same distribution of initial kinetic energies.

Ionization efficiency curves for the appearance of the $(\text{M}/\text{q})^* = 10.286$ peak in CD containing compounds and of $(\text{M}/\text{q})^* = 11.077$ peak in CH containing compounds were determined using the appearance of the He^+ ion as a standard with CH compounds and $^3\text{He}^+$ or $^{22}\text{Ne}^+$ as the standard with compounds containing CD. When using ^{22}Ne with CD_4 , the CD_5^+ peak was separated from the ^{22}Ne peak when using a 0.5 mm collector slitwidth. An example of these curves is shown in Fig. 5 (solid curve A) where the ionization efficiency curves of $\text{CD}^+(\text{m})$ from C_2D_2 and is shown. This curve was taken at an inlet pressure of 150 μ m and indicates the AP of $\text{CD}^+(\text{m})$ to be very close to 26 eV. Because of the importance of the AP of the unimolecular process for establishing the dissociation limit to which the metastable ion dissociates, an attempt has been made to determine the ionization-efficiency curve at zero pressure. In Fig. 6 are shown the variation of peak sensitivity with pressure as a function of ionizing voltage for $(\text{M}/\text{q})^* = 10.286$ from C_2D_2 . The voltage scale was established at each C_2D_2 pressure by measurement of the initial break in the $^{22}\text{Ne}^+$ ionization-efficiency curve. A small shift in voltage scale with pressure was observed and the scale was corrected for this shift. At each corrected ionizing voltage, the pressure-sensitivity curve was extrapolated to zero pressure. The zero pressure points are plotted as curve B of Fig. 5. At the same time the 150 μ pressure points have been superimposed in curve A. Because the points and curve A were taken with different (though equivalent) amplifiers, curve B and the points

on curve A were normalized at 34 eV. The agreement is quite satisfactory and both curves indicate the AP to be 26.0 ± 0.5 eV. The probable error encompasses the range of experimental values we have observed as well as possible systematic errors.²⁰

These results, depending as they do near the AP on the extrapolation of data of low intensity, must be considered in that frame of reference. Certainly from Fig. 6, it is clear that at 26.0 eV the response at high pressures is entirely due to a collision-induced dissociation. At 28 eV the results clearly show a positive zero-pressure intercept. From these two results the AP is certainly less than 28 eV and equal to or greater than 26 eV. The results at 27 eV indicate a positive zero-pressure intercept, but the value of the intercept is somewhat uncertain.

Wider range ionization-efficiency curves for the formation of CH^+ and CD^+ from various sources all exhibit a slow rise for the first few volts above the AP, followed by a faster rise to a maximum about 20 eV above the AP. The curves then gradually decrease as the ionizing voltage is increased.

DISCUSSION

In Table IV are shown the calculated dissociation limits to yield $C^+ + H$ from CH_4 , C_2H_2 and C_2H_4 and their deuterated analogues. The limits are those leading to the lowest energy of dissociation, $[C^+ (^2P_{1/2}^o) + H (^2S)]$ with all products in their lowest electronic and vibrational levels and no initial kinetic energy release in their formation at the appearance potential. This last assumption is difficult to verify for metastable species. If it is assumed that the kinetic energy release in the metastable fragmentation of CH^+ or CD^+ is independent of the energy of the impacting electron, this energy must be added to the calculated dissociation limit to obtain the calculated AP to be expected as shown in column 5 of Table IV. These calculated appearance potentials may be compared to the observed values given in column 6. For CH_4 and CD_4 , the calculated and observed values differ by about 5 eV. From C_2H_2 and C_2D_2 however, the calculated and observed values agree quite well and it is clear that from these compounds, the metastable dissociation proceeds to the lowest dissociation limit. If the dissociation were to proceed to the $C^+ (^4P)$ limit, the calculated AP from C_2H_2 and C_2D_2 would be 31.2 and 31.5 eV respectively. As shown in Fig. 5, the metastable ion intensity has already reached a respectable level at this energy.

In the case of C_2D_4 the AP of the metastable peak is again too low for the $CD^+(m)$ dissociation to be to the $C^+ (^4P)$ limit. The energy deficit to this limit is approximately 2.8 eV and this difference is well outside the experimental error of the determination.

The shapes of the metastable peaks arising from the dissociation of CH^+ and CD^+ were interpreted by Lorquet, Lorquet, Momigny, and Wankenne⁵ to be the sum of two components. The central peak was ascribed to a dissociation

in which little (~ 0.1 eV) kinetic energy was released and the broad shoulders to a dissociation in which 2.0 ± 0.5 eV of kinetic energy was released. The results reported here show values of 1.1 and 1.4 eV respectively for the kinetic energy release in the dissociation of these ions. These values include the shoulders in the measurement. No measurements were possible on the central portion of the peaks, since this portion could not be isolated from the shoulders. It is probable that the shape of the observed peak is the result of a distribution of kinetic energy release values possible in a diatomic ion which undergoes predissociation.^{21,22} The distribution will be determined by those vibronic levels of the crossing states which participate in the predissociation. Several experiments have shown that, with the equipment used in the experiments described in the present work, with a given compound as the source of $\text{CH}^+(\text{m})$, no discernable difference (< 1 eV) was apparent in the AP of the metastable peak measured at the center as compared to measurements made at either shoulder. Neither did the halfwidth of the peak or the ratio of shoulder height to central peakheight change appreciably as the ionizing electron energy was lowered. The limit of measurement of peak shape is several volts above the AP, so no firm conclusion can be made concerning changes in peak shape as the electron energy approaches the AP more closely.

Even if the assumption is made that the kinetic energy release in the metastable dissociation of $\text{CH}^+(\text{m})$ or $\text{CD}^+(\text{m})$ is zero at the AP, in the case of C_2H_2 and C_2D_2 , the dissociation cannot be to any dissociation limit other than the lowest one. This conclusion is contrary to that of Lorquet, Lorquet, Momigny, Wankenne and Lefebvre-Brion⁶ who postulated two metastable states of CH^+ , one with an AP of 29 ± 1 eV and the other with an AP of 32.5 ± 0.7 eV. These authors have also calculated potential energy curves for all predicted

states of CH^+ . Their curves have been reproduced in Fig. 7 with the addition of an energy scale relating the curves to the ground state of C_2H_2 . This scale was calculated on the assumption that the other product from C_2H_2 was CH in the $X^2\Pi$ ground state and $v = 0$ vibrational level, and that no kinetic energy release occurred in the initial fragmentation of C_2H_2^+ .

In interpreting the excitation function for the formation of $\text{CH}^+(m)$ from C_2H_2 it is important to remember that electron impact leads to the excitation of C_2H_2^+ to a number of possible excited states. It does not appear feasible to predict how $(\text{C}_2\text{H}_2^+)^*$ might fragment when C_2H_2 is excited by electrons of energy 26 eV or higher. Certainly various states of CH^+ and CH can result. The AP of $\text{CH}^+(m)$ can be related to a specific excited state of CH^+ in Fig. 7, only for that process in which $\text{CH}^+(m)$ is formed together with CH in the ground state and no kinetic energy release occurs. One might reasonably expect this to be a quite improbable process and the AP curve of $\text{CH}^+(m)$ to exhibit an indistinct threshold and to rise slowly from that threshold. As further degrees of freedom are allowed in terms of kinetic energy release in the fragmentation of $(\text{C}_2\text{H}_2^+)^*$ or in vibrational or electronic excitation in the CH fragment, the cross section for forming $\text{CH}^+(m)$ should increase. This behavior of the excitation function is just what is observed. One cannot, however, with this many degrees of freedom in the system and with no knowledge of the energy state of the CH fragment, draw any conclusions concerning the existence or non-existence of higher states of CH^+ which might also be metastable.

The data presented here are consistent with a metastable state of CH^+ which dissociates to the lowest dissociation limit $\text{C}(^2\text{P}_{1/2}^0) + \text{H}(^2\text{S})$ with the release of about 1.1 eV of kinetic energy. From the calculated curves of Lorquet et al.⁶ reproduced in Fig. 7, the $b^3\Sigma^-$ state of CH^+ , which is crossed

about 1.6 eV above the dissociation limit by the repulsive $c\ ^3\Sigma^+$ state, meets all the qualifications. The crossing is forbidden by the selection rule $\Sigma^+ \not\rightarrow \Sigma^-$ and the crossing level is approximately correct for the kinetic energy release observed. The $b\ ^3\Sigma^-$ state can radiate by an allowed transition to the $a\ ^3\Pi$ state. Two bands which have been ascribed to the $^3\Sigma^- \rightarrow ^3\Pi$ system have been reported by Carre,^{23,24} the 0-0 band at 349.9 nm and the 1-0 band at 327.7 nm. In order for the $c\ ^3\Sigma^-$ state to be metastable, the predissociation must compete with radiation to the $a\ ^3\Pi$ state, and the observed metastable half life would be determined by the combination of the partial half lives for depopulation of the $c\ ^3\Sigma^-$ state by each of these respective processes. No measurements have been reported on the radiative lifetime of the bands observed by Carre. In an attempt to decide whether a radiative lifetime of the order of 0.4 μ sec is reasonable for an allowed $\Sigma \rightarrow \Pi$ transition of this energy, data on all measured values of $\Sigma \rightarrow \Pi$ and $\Pi \rightarrow \Sigma$ radiative lifetimes of diatomic molecules in the recent compilation by Anderson²⁵ were correlated. It was assumed that the dipole matrix elements for these transitions all cancelled and the lifetimes reported by Anderson could be corrected only for the transition energy (the transition probability is proportional to ν^3). Allowed transitions of the $\Sigma \rightarrow \Pi$ type were found in NO, CH, OH, and N_2 , and $\Pi \rightarrow \Sigma$ transitions were found in CO^+ , NO^+ , N_2 , CN, NH, CH^+ , and BH^+ . All except the last two yielded half lives for radiation between 0.26 and 1.0 μ sec when corrected to the energy of the bands observed by Carre. The molecules CH^+ and BH^+ (each $A\ ^1\Pi \rightarrow X\ ^1\Sigma^+$) gave corrected half lives of $< 0.1\ \mu$ sec. Except for NO^+ ($A\ ^1\Pi \rightarrow X\ ^1\Sigma^+$) and for which the energy correction is large, these are the only singlet-singlet transitions in the list. All the others are doublet-doublet or triplet-triplet transitions. On the basis of the above correlation it is not unreasonable to

expect the radiative lifetime of the CH^+ ($b \ ^3\Sigma^- \rightarrow a \ ^3\Pi$) transition to be within the 0.4 ± 0.2 μsec limits observed for the metastable ion dissociation. Both processes would then compete for depopulating those levels of the $b \ ^3\Sigma^-$ state which are predissociated with the $c \ ^3\Sigma^+$ state.

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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15. The term 'metastable ion' is used to designate the parent ion, AB^+ in the slow dissociation process, $AB^+ \rightarrow A^+ + B$. The apparent mass, $(M/q)^*$, at which the daughter ion A^+ appears in the mass spectrum is designated as the 'metastable peak'. Note that AB^+ can be the result of one or a series of fast dissociation processes in the ion source.

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20. Prof. Momigny has kindly sent the authors data from his laboratory similar in form to some of that presented here. The interpretation of his data as given in Ref. (6) differs from the interpretation we have given our data.
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TABLE I. Dissociation Process of CH_x^+ Ions Leading to Apparent Metastable Ion Peaks Below $(M/q) = 12$.

Process	Type	$(M/q)^* \text{CH}_x$	$(M/q)^* \text{CD}_x$
1) $\text{CH}^+ \rightarrow \text{C}^+ + \text{H}$	(m)	11.077	10.286
2) $\text{CH}_2^+ \rightarrow \text{C}^+ + \text{H}_2$	(m)	10.286	9.000
3) $\text{CH}_3^+ \rightarrow \text{CH}^+ + \text{H}_2$	(m)?	11.267	10.889
4) $\text{CH}_3^+ \rightarrow \text{C}^+ + (3\text{H})$	(c)	9.600	8.000
5) $\text{CH}_4^+ \rightarrow \text{CH}^+ + (3\text{H})$	(c)	10.563	9.800
6) $\text{CH}_4^+ \rightarrow \text{C}^+ + (4\text{H})$	(c)	9.000	7.200

(m) = metastable ion plus collision-induced component observed.

(c) = only collision-induced dissociation observed.

TABLE II. Kinetic Energy Release in the Metastable Fragmentation of $\text{CH}^+(\text{m})$ and $\text{CD}^+(\text{m})$ from Various Sources.

Compound	$T^{\text{a})}$	$T^{\text{a})}$
	$\text{CH}^+ \rightarrow \text{C}^+ + \text{H}$	$\text{CD}^+ \rightarrow \text{C}^+ + \text{D}$
C_2H_2	1.1 ± 0.3	
C_2D_2		1.4 ± 0.2
C_2H_4	1.1 ± 0.2	
C_2D_4		1.1 ± 0.3
CH_4	(b)	
CD_4		1.4 ± 0.3
CHF_3	1.3 ± 0.5	
CDF_3		1.4 ± 0.3
CHCl_3	1.1 ± 0.3	
CH_2Cl_2	1.1 ± 0.3	

a) Probable errors include estimates of errors in measuring width of peaks as well as reproducibility with various voltage differences.

b) Value not recorded owing to interference from $(\text{M}/\text{q})^* = 11.267$.

TABLE III. Initial Kinetic Energy of $\text{CH}^+(\text{m})$ and $\text{CD}^+(\text{m})$ Formed by 70 eV Electron Impact with Various Source Molecules.

Source	Initial KE (eV) $\text{CH}^+(\text{m})$ or $\text{CD}^+(\text{m})$	T (init.)
CH_4	0.3 ± 0.1	Indeterminate
CD_4	0.6 ± 0.2	Indeterminate
C_2H_2	1.3 ± 0.2	2.6 ± 0.4
C_2D_2	0.7 ± 0.2	1.4 ± 0.4
CDF_3	$\sim 3.2 \pm 0.4$	Indeterminate

TABLE IV. Energetics of Formation of the Metastable Ions CH^+ and CD^+ from Various Sources.

Compound	Products ^{a)}	Diss. Limit (Calc) ^{b)} eV	T ^{c)} eV $\text{CH}^+(\text{m})$	AP eV (Calc)	AP ^{d)} eV (Obs)	Std.
CH_4	$[\text{C}^+ + \text{H}] + \text{H} + \text{H}_2$	23.99	~1.4	25.4	31.0 ± 1	He^+
CD_4	$[\text{C}^+ + \text{D}] + \text{D} + \text{D}_2$	23.99	1.4	25.4	30 ± 1	$^{22}\text{Ne}^+$
C_2H_2	$[\text{C}^+ + \text{H}] + \text{CH}$	24.78	1.1	25.9	26.9 ± 0.5	He^+
C_2D_2	$[\text{C}^+ + \text{D}] + \text{CD}$	24.78	1.4	26.2	26.0 ± 0.5	$^{22}\text{Ne}^+$ $^3\text{He}^+$
C_2D_4	$[\text{C}^+ + \text{D}] + \text{D} + \text{CD}_2$	26.74	1.1	27.8	30.3 ± 0.5	$^{22}\text{Ne}^+$

a) Bracketed species appear as the metastable ion.

b) Assuming C^+ in the $^2\text{P}_{1/2}^o$ ground state. For C^+ in the ^4P first excited state, add 5.33 eV.

c) This is the kinetic energy of fragmentation of the metastable ion. Other fragmentations are assumed to occur with zero kinetic energy release at the AP.

d) All AP's from the initial break compared to the initial break in the standard.

FIGURE CAPTIONS

Fig. 1. Negative repeller cutoff curves for the metastable peak at $(M/q)^* = 10.286$ in the mass spectra of CD_4 , C_2D_2 , and CDF_3 . Conditions: Magnetic scan, $V_A = 3000$ V, $V_e = 70$ V, $I_e = 38$ μ A. Inlet pressure: $CD_4 = 175$ μ m, $C_2D_2 = 120$ μ m, $CDF_3 = 300$ μ m. Zero intensities have been offset for clarity of presentation.

Fig. 2. Peak shapes of $(M/q)^* = 10.286$ peak from various sources of $CD^+(m)$. Conditions: voltage scan, $MV_A = 20,570$, $V_e = 70$ V, $I_e = 38$ μ A. Inlet pressures: $C_2D_2 = 120$ μ m, $C_2D_4 = 200$ μ m, $CDF_3 = 200$ μ m, $CD_4 = 130$ μ m. Focus adjusted for maximum metastable peak.

Fig. 3. Ion accelerating voltage discrimination curves for the metastable peak at $(M/q)^* = 11.077$ from CH_4 and $(M/q)^* = 10.286$ from CD_4 . Lines calculated for the half lives shown for the transitions $CH^+ \rightarrow C^+ + H$, solid lines, and $CD^+ \rightarrow C^+ + D$, dashed lines. Observed points: open circles CH_4 , filled circles CD_4 . Points corrected for peak width: open squares CH_4 , filled squares CD_4 . Points further corrected for initial kinetic energy: open triangles CH_4 , filled triangles CD_4 .

Fig. 4. Ion accelerating voltage discrimination curves for the metastable peak at $(M/q)^* = 11.077$ in the mass spectrum of C_2H_2 . Lines calculated for the half lives shown. Observed points - circles; corrected for metastable peak width - squares; corrected for peak width and initial kinetic energy of $CH^+(m)$ - triangles.

Fig. 5. Ionization efficiency curve of $(M/q)^* = 10.286$ in the mass spectrum of C_2D_2 .

Curve A - X-Y recording of ion intensity vs electron energy at an inlet pressure of 150 μ m. Points are from peak sensitivity vs pressure curves at 150 μ m inlet pressure from Fig. 6.

Curve B - Zero pressure intercepts of peak sensitivity pressure plots from Fig. 6.

Fig. 6. Peak sensitivity vs pressure of $M/q = 10.286$ in the mass spectrum of C_2D_2 at various ionizing electron voltages. Voltage standard, $^{22}Ne^+$.

Fig. 7. Potential energy curves of the CH^+ ion as calculated by Lorquet, Lorquet, Momigny, and Wankenne (Ref. 5). The energy scale on the right is added and refers to energy above the C_2H_2 ground state with CH formed in $v = 0$ of the $X^2\Pi$ ground state and with no initial kinetic energy release.

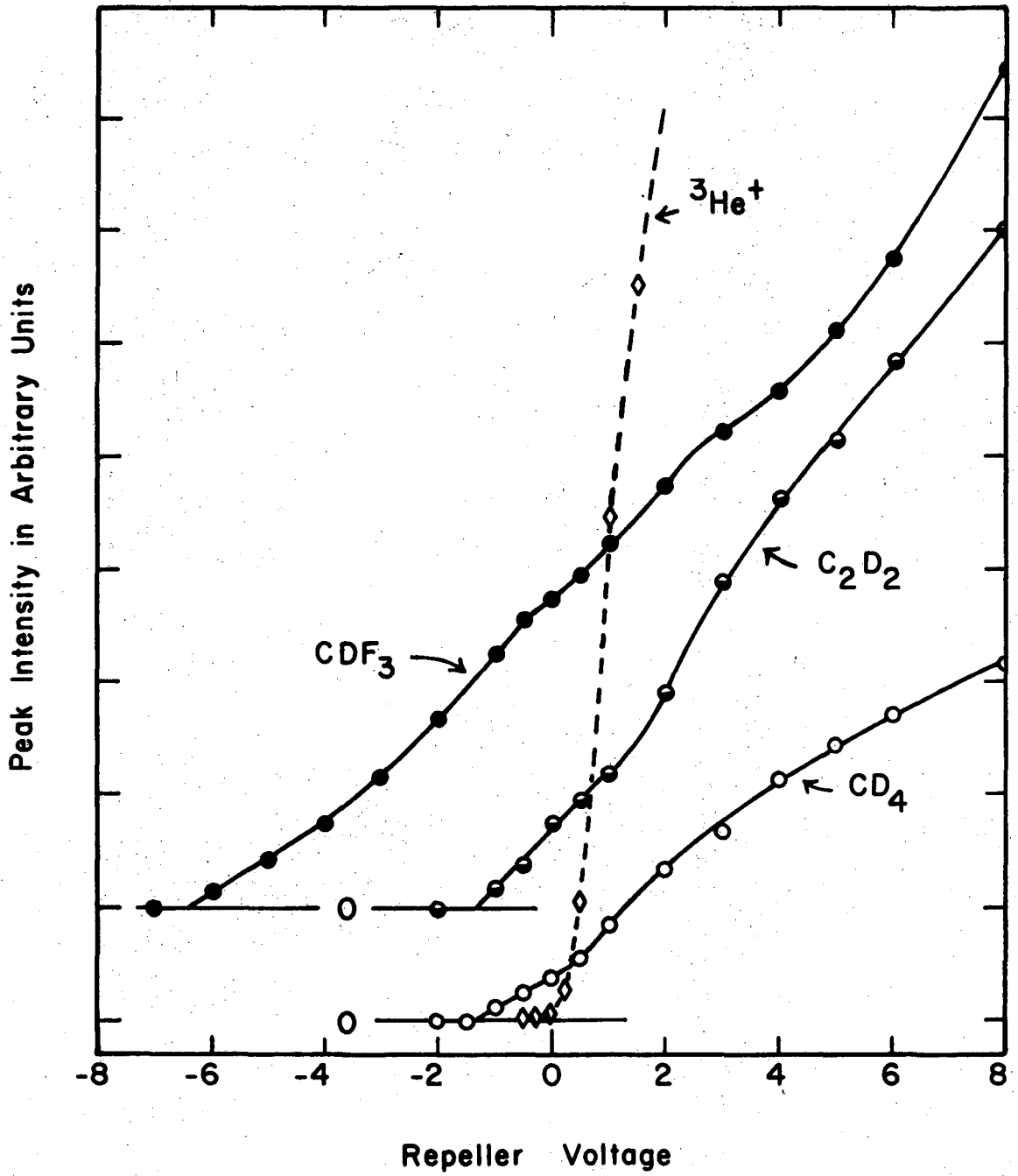
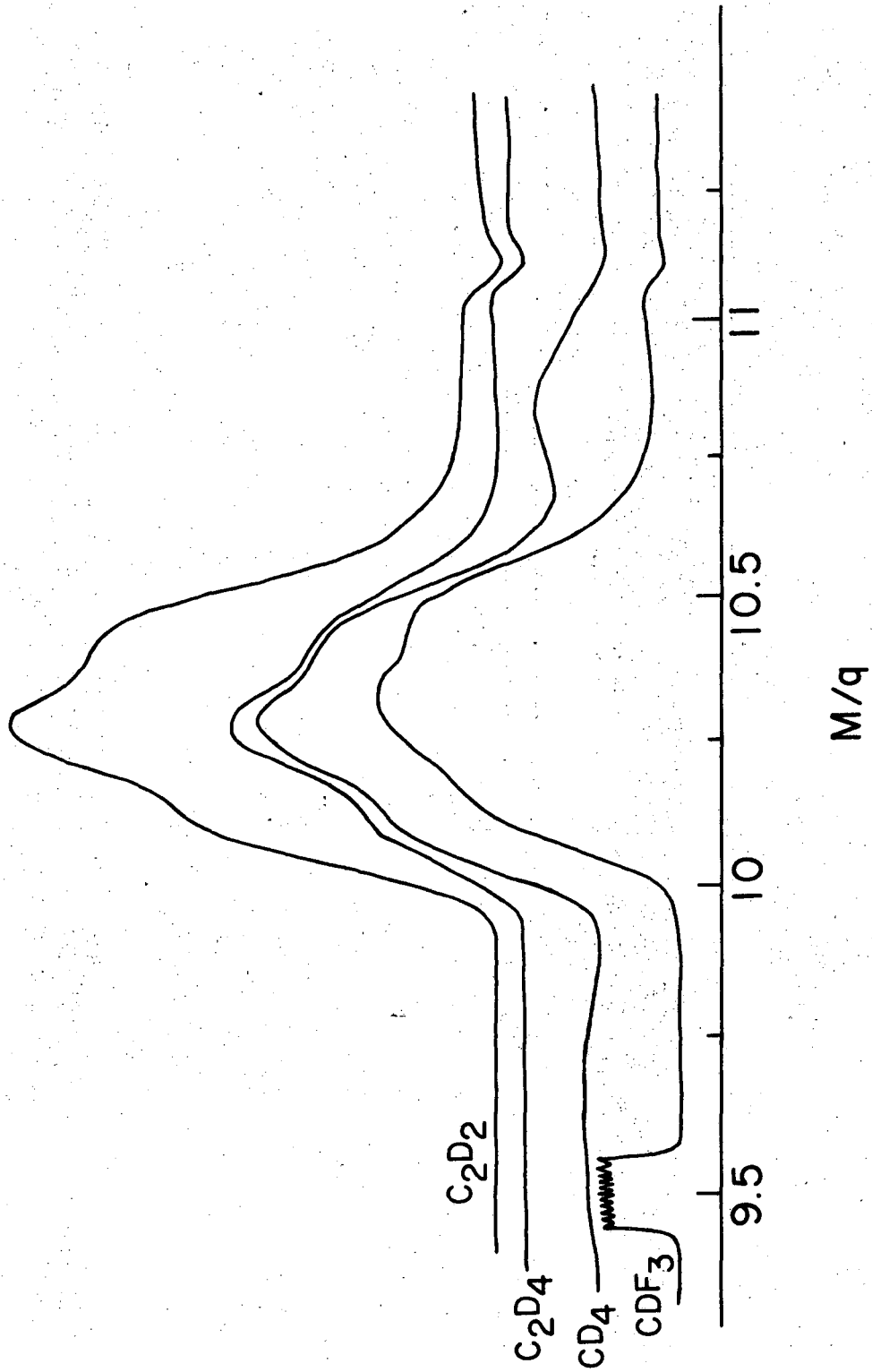
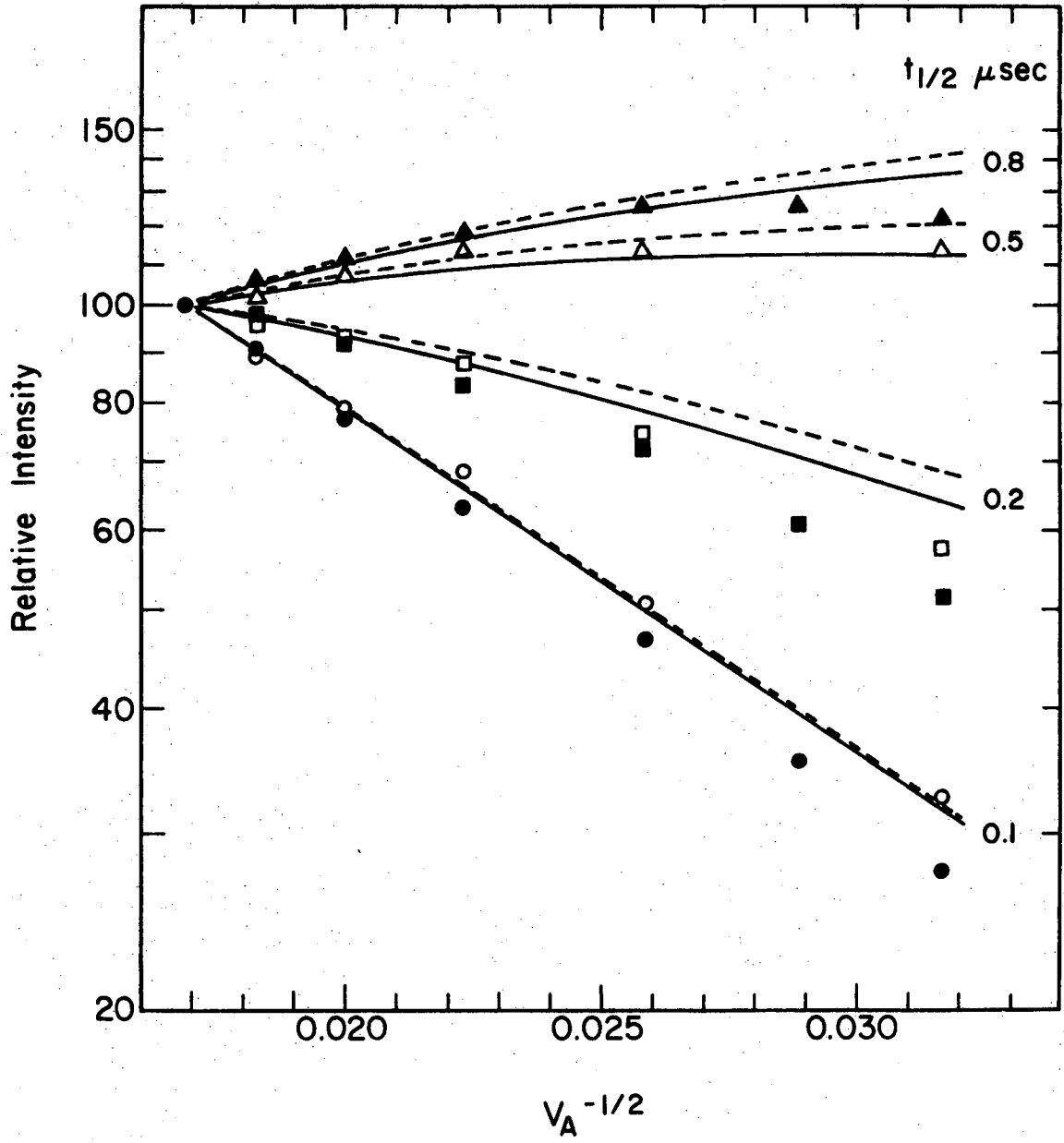


Fig. 1



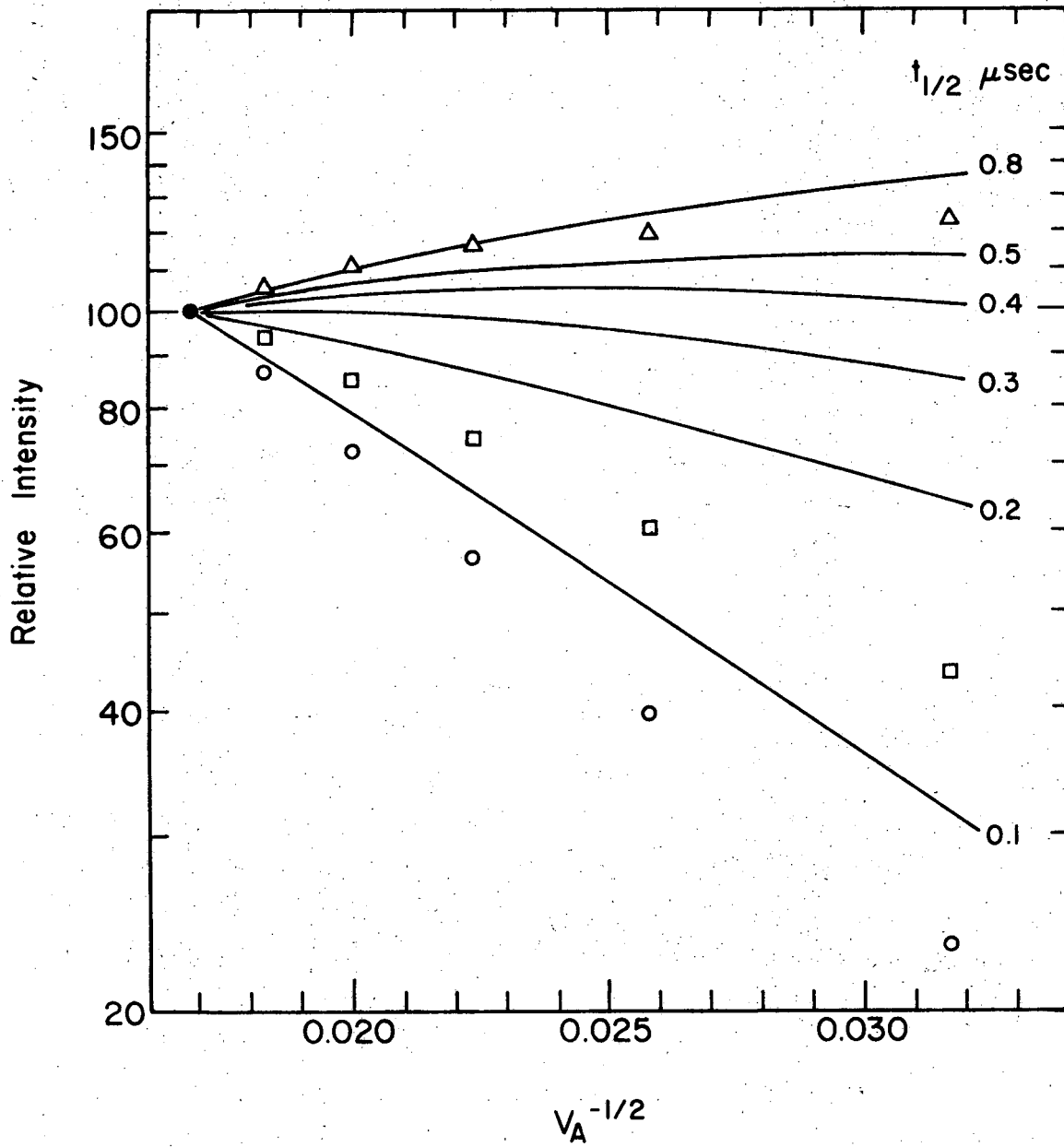
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Fig. 2



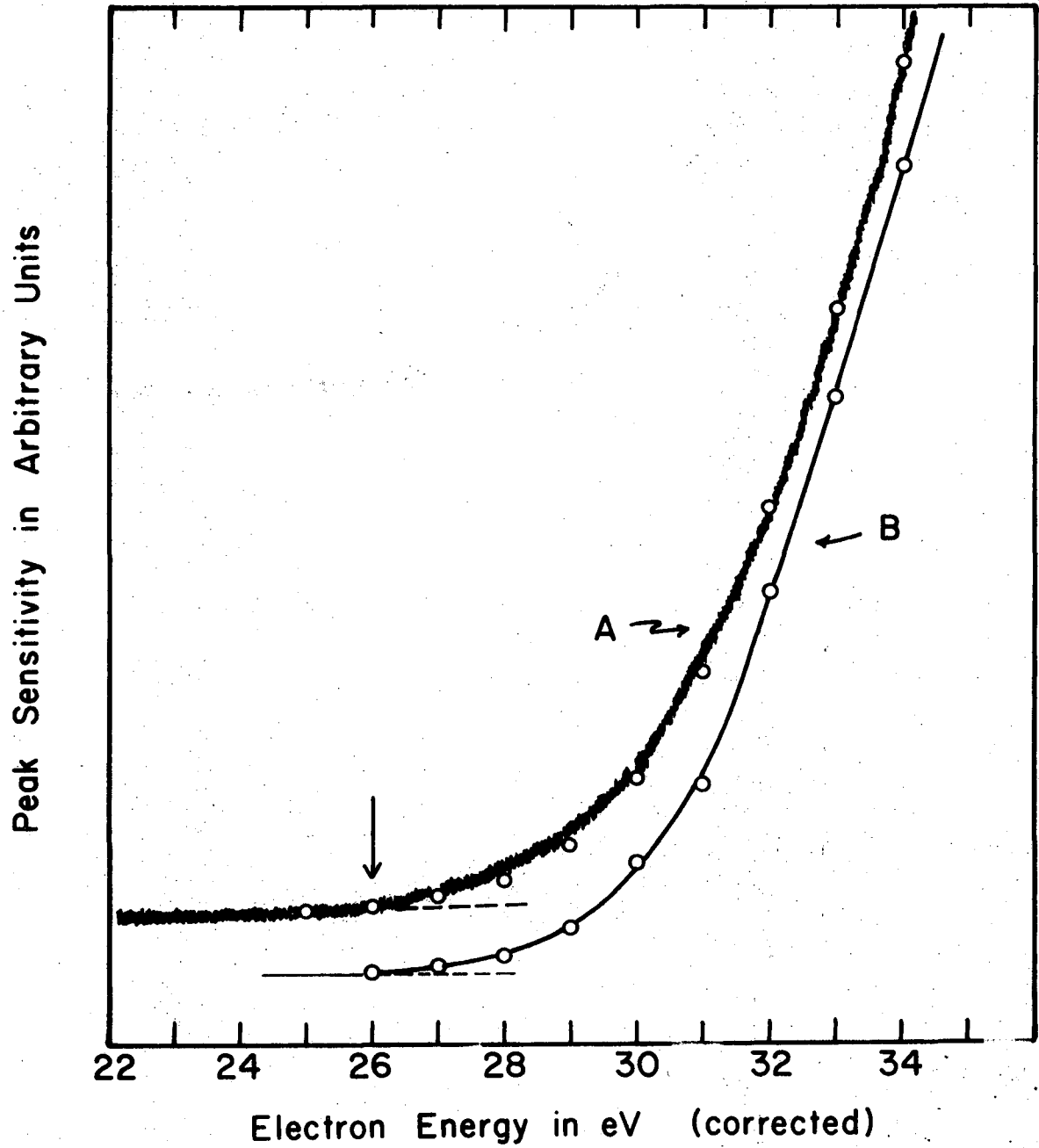
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Fig. 3



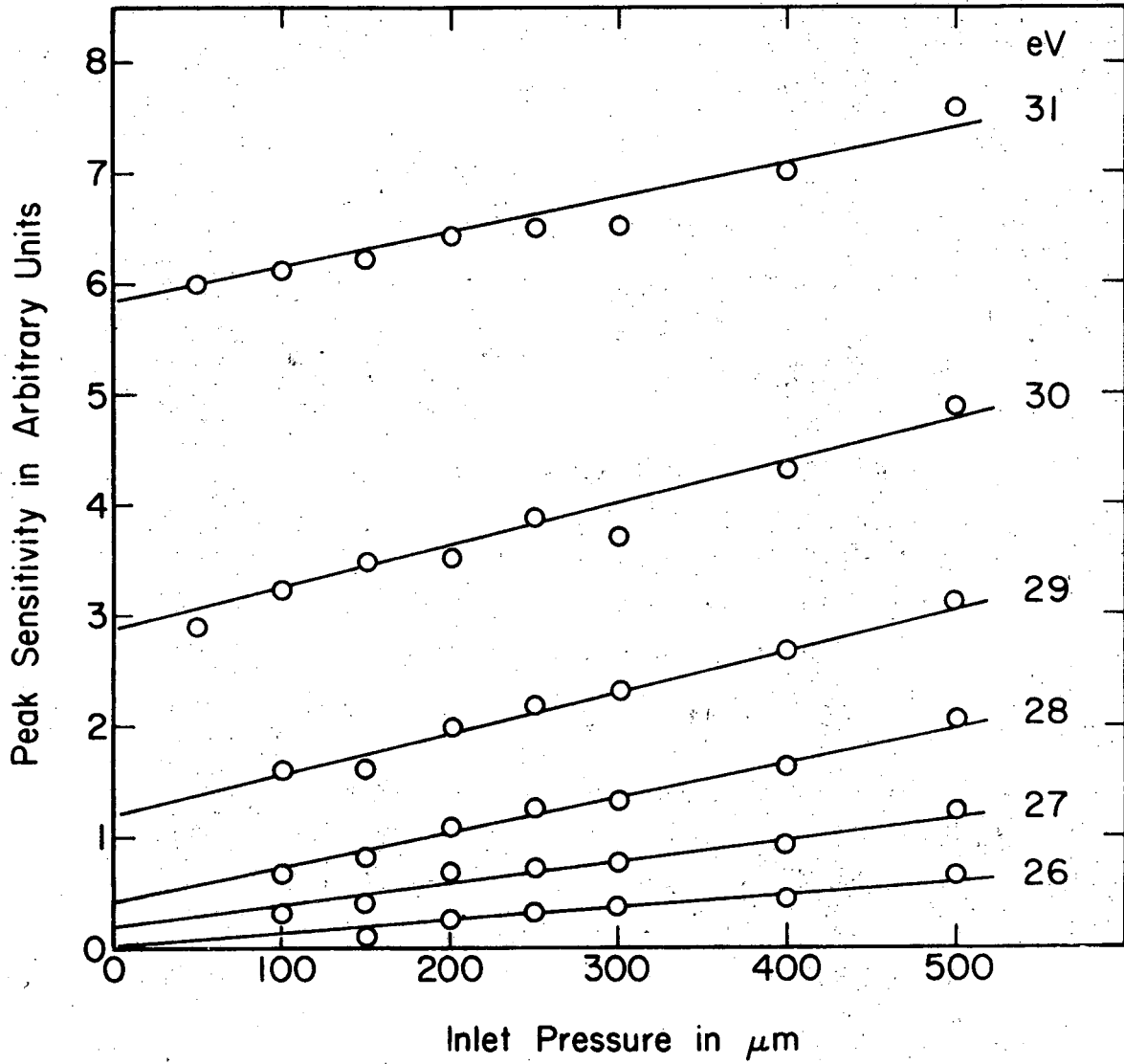
XBL 721-8

Fig. 4



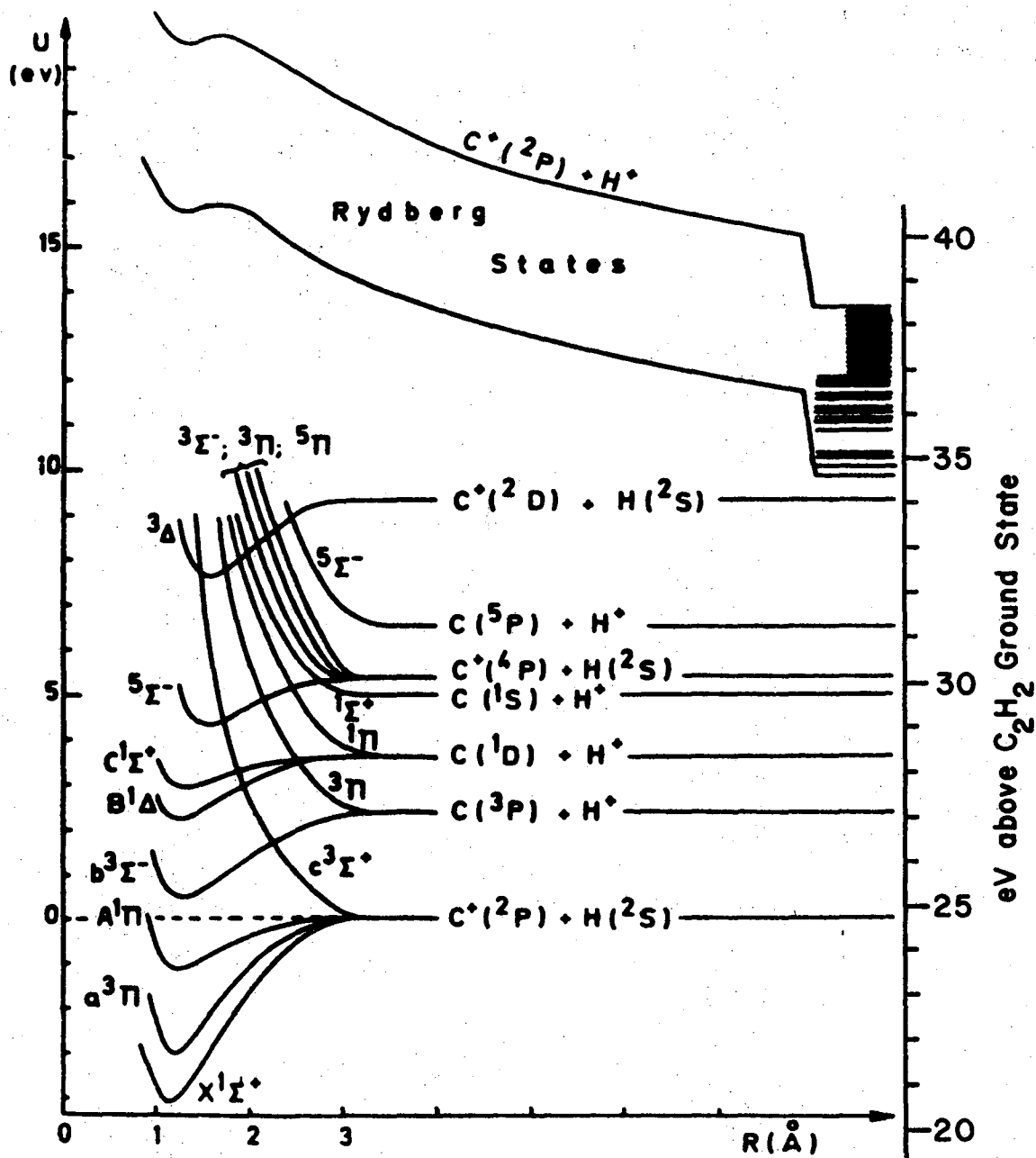
XBL 724-655

Fig. 5



XBL 724-656

Fig. 6



XBL 723-563

Fig. 7

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