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Amos S. Newton and A. F. Sciamanna

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METASTABLE PEAKS IN THE MASS SPECTRA OF N_2O AND NO_2 . II*Amos S. Newton[†] and A. F. Sciamanna[†]Lawrence Radiation Laboratory
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ABSTRACT

Metastable peaks arising from the delayed unimolecular dissociation of NO^+ to $O^+ + N$ in the mass spectra of both N_2O and NO_2 , and from the dissociation of N_2^+ to $N^+ + N$ in the mass spectrum of N_2O have been investigated. A new metastable dissociation of N_2O^{++} to $NO^+ + N^+$ was also studied. Further studies were made on the previously known metastable transitions of N_2O^+ to $NO^+ + N$ and of NO_2^+ to $NO^+ + O$.

The appearance potential, the kinetic energy release in fragmentation, and the half-life were determined for each metastable transition. Comparisons were made of the energetic and half-life characteristics of the metastable NO^+ ion as produced from the sources NO , N_2O , and NO_2 , and of the metastable N_2^+ ion from the sources N_2 and N_2O . The results are consistent with the unimolecular dissociation of these diatomic ions, N_2^+ and NO^+ , proceeding by predissociation mechanisms.

I. INTRODUCTION

Begun and Landau^{1,2} reported the metastable dissociation of N_2O^+ to NO^+ . This observation was later confirmed by Newton and Sciamanna,³ and an analogous metastable dissociation of NO_2^+ to NO^+ was observed. It was further established³ that the metastable dissociation of NO_2^+ to NO^+ proceeded from at least two excited states of NO_2^+ with the product NO^+ ions having different kinetic energies and being formed from states of different half-lives for dissociation.

Recently metastable ions in the mass spectra of N_2 and NO were observed.⁴ Since N_2^+ and NO^+ are prominent fragmentation peaks in the mass spectrum of N_2O , and NO^+ is prominent in the mass spectrum of NO_2 , it was of interest to examine the mass spectra of N_2O and NO_2 for the same metastable transitions previously observed in the mass spectra of N_2 and NO . The present paper presents results showing that metastable transitions of N_2^+ and NO^+ formed from N_2O , and of NO^+ formed from NO_2 , do indeed occur, but with different kinetic energy release than when formed from N_2 and NO . In addition, the metastable dissociation of N_2O^{++} to $NO^+ + N^+$ was observed. Information on the half-lives and energetics of formation of these metastable peaks has been obtained.

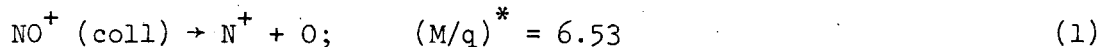
II. EXPERIMENTAL

The experimental work described herein was performed using a Consolidated Electrodynamics Corporation Model 21-103B Mass Spectrometer. Modifications on this instrument to increase the pumping speed and ion detector sensitivity have already been described, together with the experimental methods used to investigate metastable peaks.^{4,5} The present experiments were made with a collector slitwidth of 1.5 mm.

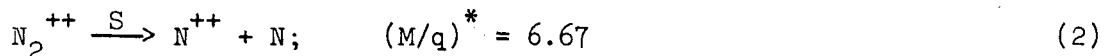
The N_2O and NO_2 gases were obtained from the Matheson Company and purified as described previously.³ With N_2O gas, the CO_2 content was a factor for evaluating the doubly charged ion peak at $M/q = 22$. Analysis of the gas (as received from the supplier) using gas chromatography (Porapak Q column, $25^\circ C$), showed the CO_2 content to be less than 7 ppm. Further scrubbing of the gas with KOH produced no change in the intensity or the behavior with instrumental parameters of the $M/q = 22$ peak when compared with the behavior of that peak from the unscrubbed gas. It was concluded that the CO_2 content of the gas was below any value that would influence the results described in this paper.

III. EXPERIMENTAL RESULTS

In Fig. 1 is shown the mass spectrum of N_2O in the mass range of 6 to 10 amu. Curve A is the spectrum at an ionizing electron energy above the AP of N^{++} and O^{++} , while curve B is at lower ionizing electron energies where N^{++} and O^{++} do not appear. The interpretations given below are consistent with the evidence to be presented later. The apparent masses given are those calculated for the transition as written. Observed values agree with these within the experimental error of ± 0.02 amu. The small broad peak at $(M/q)^* \cong 6.5$ is due to the collision-induced dissociation of NO^+ .



In curve A, the small peak at $(M/q)^* \cong 6.7$ is due to the surface-induced dissociation of N_2^{++} at the ion source focus slit.⁴



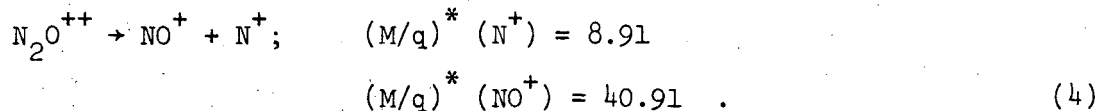
These peaks were not investigated further.

The broad metastable peak at $(M/q)^* = 7.00$ is due to the transition:



At electron energies above about 60 eV (curve A), the N^{++} peak is superimposed on this metastable peak.

Between $M/q = 8$ and $M/q = 10$ there is a very broad metastable peak with a double maximum centered about $(M/q)^* = 8.9$. This is due to the transition:

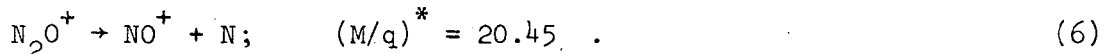


In Fig. 1, only the peak arising from N^+ appears. Superimposed on this broad metastable peak is a second peak centered around $(M/q)^* = 8.53$ which arises from the transition:



In Fig. 2 is shown the effect of application of the metastable suppressor to the broad peak from $M/q = 8$ to 10. At a voltage applied to the metastable suppressor, $V_{mss} = 0.50 V_A$, no apparent change in the peak occurs. At $V_{mss} = 0.55 V_A$, the peak at $(M/q)^* = 8.53$ disappears. The calculated cut-off of the O^+ ion from the metastable dissociation of NO^+ is at $V_{mss} = 0.533 V_A$.⁶ The broad peak from 8 to 10 is scarcely affected. At $V_{mss} = 0.62 V_A$, this broad peak is approximately one-half cut off. The calculated cutoff for N^+ from N_2O^{++} is at $V_{mss} = 0.636 V_A$. The small peak at $M/q = 9$ is an artifact of the instrument and gradually disappeared with time. Its source was not identified.

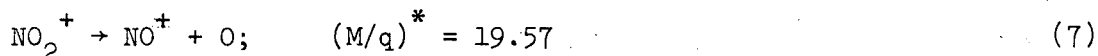
In Fig. 3 is shown the mass spectrum of N_2O in the mass range $M/q = 17$ to 26. Peaks at $M/q = 17, 18,$ and 19 are due to water background in the instrument (plus the isotopes of the O^+ peak at $M/q = 16$). The broad peak centered about $(M/q)^* = 20.45$ is due to the transition:



This peak was observed previously.^{1,3} The peak at $M/q = 22$ is N_2O^{++} plus CO_2^{++} background. The background of CO_2^{++} is linear with pressure of N_2O , and, under any given set of operational parameters, is quite reproducible after the instrument has been stabilized for operation with N_2O gas. The peak at $M/q = 23$ is an artifact of the instrument, and is due to Na^+ ions formed from two sources. One is by electron bombardment of sodium on the repeller (scattered electrons) and the other is ion bombardment of sodium on the first slit. When this peak is scanned using a narrow collector slitwidth, it can be resolved into two peaks at the apparent masses of 22.9 and 23.1, consistent with this mechanism of formation. With a wide slit only a shoulder appears at $M/q = 23.1$ to show this double source. The peaks from $M/q = 24$ to $M/q = 27$ are due to hydrocarbon background in the instrument. There is a definite rise in baseline between $M/q = 21$ and $M/q = 27$ which can tentatively be attributed to the dissociation of N_2O^+ (Eq. (6)) in the accelerating region of the ion source. This rise in baseline was shown to be linear with pressure. The possible metastable peak occurring at $M/q \cong 17.9$ has not been identified. The dip at $M/q = 26$ is normal in this instrument and is due to negatively charged secondary particles formed when $M/q = 28$ (a large peak) strikes the collector slitplate at the proper place.⁷

The mass peak of NO^+ from the metastable dissociation of N_2O^{++} according to Eq. (4), which should appear as a broad peak centered about $(M/q)^* = 40.9$, is not shown. The low resolution using a 1.5 mm collector slit, plus the small background of hydrocarbon peaks in the mass range from 36 to 43, are sufficient to make meaningful studies on the metastable peak impossible. In addition, a fairly intense peak at $M/q = 39$ due to NaO^+ increases the interference considerably.

In Fig. 4 is shown the mass spectrum of NO_2 in the mass range of 6.5 to 9.5 amu. The peaks at $M/q = 7$ and $M/q = 8$ are due to N^{++} and O^{++} respectively. The small peak at $(M/q)^* = 6.5$ is due to the collision-induced dissociation of NO^+ according to Eq. (1). The peak at $(M/q)^* = 8.53$ is due to the unimolecular dissociation of NO^+ according to Eq. (2). The peaks in the mass region near $(M/q)^* = 19.57$ in the mass spectrum of NO_2 differed in no appreciable respect from those previously determined.³ There is however, a definite rise in baseline in the mass region 21-27 after the metastable peak at $(M/q)^* = 19.57$. This rise is proportionately less than was the case in the mass spectrum of N_2O . This rise in baseline was linear with pressure of NO_2 .



In Figs. 5 and 6 is shown the dependence on inlet system pressure of the peak sensitivity (peak intensity/pressure) of various peaks in the mass spectrum of N_2O and NO_2 respectively. In Fig. 5, the peak at $(M/q)^* = 20.45$ in the mass spectrum of N_2O shows approximately the same rate of increase in sensitivity with pressure as determined previously.³ The zero pressure intercept shows >90% of the peak to be of unimolecular origin at 200 μ inlet

pressure. The metastable peaks at $(M/q)^* = 7.00$, $(M/q)^* = 8.53$, and $(M/q)^* = 8.91$ show little dependence of sensitivity on pressure. The dependence of $M/q = 22$ with pressure is of interest since N_2O^{++} is the parent of the metastable ion at $(M/q)^* = 8.91$. This determination was made at high ion accelerating voltage under which condition the N_2O^{++} constitutes $>85\%$ of the peak intensity, and the CO_2^{++} background makes only a minor contribution. (CO_2^{++} background is also linear with pressure of N_2O at low ion accelerating voltages.) It was expected that if N_2O^{++} was dissociated by collisional processes, the sensitivity of the $M/q = 22$ peak would decrease with pressure. No such decrease was observed.

The $(M/q)^* = 19.57$ peak in NO_2 shows little dependence of sensitivity with pressure confirming previous observations on this point.³ Similarly, the sensitivity of the $(M/q)^* = 8.53$ peak shows little dependence on pressure. The $(M/q)^* = 6.53$ peak, while its intensity is low, shows a zero intercept of sensitivity with pressure indicating it to be entirely of collision-induced origin. $M/q = 23$ consists of Na^+ background (linear with pressure with any gas) plus any NO_2^{++} ions which might exist. The total peak is linear with pressure. The existence of NO_2^{++} was not established. No metastable ions characteristic of O^+ from the metastable dissociation of NO_2^{++} were observed in the mass region $(M/q)^* = 11.13$.

The non-zero intercepts at zero pressure of the sensitivity of all the peaks arising through Eqs. (3), (4), (5), (6), and (7) in the mass spectrum of N_2O and NO_2 show these peaks to be of unimolecular origin. $(M/q)^* = 20.45$ in N_2O (Eq. (6)) is the only dissociation in the group which shows a measurable collision-induced contribution to the peak intensity.

All of these metastable peaks were shown to be linear with ionizing electron current from 10 to 75 μ amps ionizing current. Therefore they are not formed by second order electron processes in the ion source and ion trapping in the source was not observed.

Tests were also made on each of these metastable peaks to assure that these were not surface-induced dissociations at the last ion source slit. The method used, as has been previously described,⁸ consists of scanning the ion beam across the last ion source slit by varying the inner-focus potential. For each peak, only a single maximum in the curve of inner focus potential vs peak intensity was observed, and no double peak contribution characteristic of a surface-induced reaction was detectable. We estimate from previous results on argon⁸ that a 5% contribution of surface-induced dissociation would have been detectable.

Appearance potentials and excitation curves for the formation of these metastable ions were determined by methods previously described.⁴ In addition, the appearance potentials of other ions of interest, N^{++} and O^{++} , were determined. None of the excitation functions of these metastable ions showed any appearance of resonant behavior. These curves are not shown, but each rose to a broad flat maximum and showed no indication of structure except that some showed breaks on the rising curve. The appearance potentials observed together with the potentials at which significant breaks were observed are shown in Table I. The appearance potential of $(M/q)^* = 8.91$ from N_2O was compared to the appearance potential of $M/q = 22$ (N_2O^{++}) and the values were identical within experimental error at 36.5 ± 0.5 and 36.4 ± 0.5 eV. The measurement at $M/q = 22$ was made at a high ion accelerating voltage, under which condition

the contribution of CO_2^{++} was estimated to be only about 15% of the total peak intensity. The agreement between these values is far better than that indicated by the probable errors given. A difference of $<\pm 0.2$ eV is indicated by the comparison.

The kinetic energy release, T, in the metastable dissociation of N_2^+ and NO^+ and N_2O and NO^+ from NO_2 , were determined from the width of the metastable suppressor cutoff curves of these product metastable ions as described previously.³ Peak areas were plotted against the fraction of V_A applied to the metastable suppressor. The resulting curves are shown in Fig. 7. Owing to the wide collector slit used in this work, the cutoff width was corrected for the cutoff width of a normal peak in evaluating the kinetic energy release. Values found are shown in Table I.

In the case of the highly energetic fragmentation of N_2O^{++} where the metastable peak due to N^+ possesses a distinct double maximum, the use of peak areas gives a distorted metastable suppressor cutoff curve since few ions are found in the region of the peak between the maxima. The use of peak width in amu at half maximum as a measure of the amount of the peak remaining at a given fraction of V_A applied to the metastable suppressor yields a straight line cutoff curve as shown in Fig. 8. The value of T derived by this method was compared to the value derived from the peak width observed at a given value of V_A and also that value derived from the change in peak width with V_A .³ All values agreed within experimental error and the mean value of 10 determinations is $6.5^{+0.2}_{-0.5}$ eV. No value was found below 6.0 eV, but the probable error is larger on the low energy side because of a possible inherent bias in all methods owing to the use of a wide collector slit.

The determination of the half-lives of metastable ions using Dempster type mass spectrometers has usually been by the method devised by Hipple⁹ and extended by Coggeshall.¹⁰ In this method the intensity of the metastable ion is measured as a function of the residence time of the parent ion in the ion source, the residence time being varied by variation of the repeller potential. This method was used to estimate the half-lives of the two metastable states of NO_2^+ leading to $(M/q)^* = 19.57$ in the mass spectrum of NO_2 .³ The method is not easily applied to the measurement of the low intensity metastable peaks with which we are here concerned since variation of the repellers from optimum settings results in loss of signal on these peaks to the point where accurate measurements of peak intensity are difficult. Therefore other methods have been applied.

In the case of the metastable dissociation of N_2O^{++} , since it was apparent that most, if not all, of the N_2O^{++} observed at high ion accelerating voltages was metastable, the method used for the estimation of the half-life of metastable CO_2^{++} was applied.¹¹ In this method, the intensity of $M/q = 22$, the parent peak, was measured as a function of accelerating voltage. It is assumed that any dissociation between the time of formation in the ion source and time the ion passes through the collector slit results in loss of signal at $M/q = 22$. The accelerating voltage can be converted to total transit time between formation in the ion source and the passage through the collector slit. In Fig. 9 is shown the intensity of $M/q = 22$ as a function of transit time. The tail might consist of a CO_2^{++} background or a longer lived state of N_2O^{++} . Experiments in an AEI-MS-9 high resolution mass spectrometer showed no N_2O^{++} to be present after a transit time of ~ 6.7 μsec , with a limit of 0.0001% of

the N_2O^+ peak at $M/q = 44$.¹² It is therefore concluded that no stable state of N_2O^{++} exists and the tail on the experimental curve of Fig. 9 is due to background CO_2^{++} . Subtraction of the solid line from the observed curve yields a straight line decay of 0.46 μ sec half-life for N_2O^{++} . Also shown in Fig. 9 is an accelerating voltage discrimination curve of CO_2^{++} obtained when a trace of O_2 gas was admitted to the mass spectrometer. While the normalized CO_2^{++} curve is not identical to the subtracted background, it is nearly so, and use of the CO_2^{++} curve for subtraction yields a decay curve of N_2O^{++} which does not differ significantly from that shown. We conclude that the half-life for the metastable dissociation of N_2O^{++} is 0.46 ± 0.05 μ sec.

For the other metastable ions, one can obtain an approximate value of the half-life as measured over a limited time range by simply determining the accelerating voltage discrimination curve of the peak. In this method, both the time of arrival of the parent ions at the exit slit of the ion source and the time spent in the region of the analyzer tube where the decay product ions are formed in collectible orbits, vary (see Ref. 10).

If one assumes N_0 parent ions to be formed at $t = 0$ in the ion source, then N_1 arrive at the ion-source exit slit at the time t_1 and N_2 arrive at that point in the analyzer tube orbit beyond which the daughter ions are no longer collected, at the time t_2 . One can then write the following relations for an ion dissociating with the decay constant λ .

$$N_1 = N_0 \exp(-\lambda t_1) \quad (8)$$

$$N_2 = N_0 \exp(-\lambda t_2) \quad (9)$$

$$\Delta N = N_0 [\exp(-\lambda t_1) - \exp(-\lambda t_2)] \quad (10)$$

In Eq. (10), ΔN represents the number of daughter ions formed in the region from which they can be collected. Inasmuch as t_1 and t_2 are each proportional to $V_A^{-1/2}$, one may plot the log of the intensity of the metastable ion peak (proportional to ΔN) vs $V_A^{-1/2}$. The relation between t_1 and t_2 is constant for a given dissociation and can be evaluated by methods described by Coggeshall¹⁰ and Newton.¹³ In evaluating Eq. (10), it was convenient to calculate for each transition studied, the relation between t_1 and t_2 , and a set of curves for ΔN as a function of $V_A^{-1/2}$ at various half-lives from 0.05 to 10 μ sec. The slopes of these computed curves were readily compared to the slopes of the observed curves to evaluate the half-life. The range of accelerating voltages covered was from 3600 to 800 V, which represents approximately a factor of two on a time scale. The discrimination at the collector slit of a normal peak (i.e., one with no initial kinetic energy) is less than 3% over this range, so no correction was made for such discrimination.

Berry has derived an equation for calculating discrimination due to initial kinetic energy.¹⁴ Separate dimensionless parameters apply to the ion source region and the analyzer tube. The discrimination in each is calculated separately. Computer calculations of discrimination in the ion source as a function of accelerating voltage divided by initial kinetic energy (V_A/T_i) were used to estimate corrections which might be made. For the analyzer section, at $V_A/T_i > 4000$, i.e., for $T_i < 0.2$ eV, there is less than 10% loss by discrimination.

For those metastable transitions in which the initial ion is derived from a fast fragmentation process in the ion source which might be accompanied by initial kinetic energy discrimination between the electron beam and the

ion source exit slit, the situation is more complicated. Using the calculations from Berry's equations, corrections can be made for such initial kinetic energy if the energy release in the initial fast fragmentation is known.

In Fig. 10 is shown the voltage discrimination curve of the $(M/q)^* = 20.45$ peak in N_2O . The curve can be analyzed into two components of $t_{1/2} \geq 0.3 \mu\text{sec}$ and $t_{1/2} = 0.09 \mu\text{sec}$. Previously published values of this half-life were $< 0.2 \mu\text{sec}$ ³ and $\sim 2 \mu\text{sec}$.¹ Discrimination can have little effect on the short half-life value, i.e., a correction of 10 to 20% in the low voltage points will not affect the initial fast drop in intensity as V_A is decreased. The 0.3 μsec figure for the longer lifetime portion could suffer considerable correction and hence 0.3 μsec represents a minimum half-life for this portion of the curve. It is apparent however, that this metastable transition involves two processes decaying with different half-lives.

In Fig. 11, the voltage discrimination curve of $(M/q)^* = 7.00$ is shown with N_2 gas as a source and with N_2O gas as a source. Uncorrected (for initial kinetic energy of $(N_2^+)^*$ from N_2O) minimum values of 0.15 and $\sim 0.12 \mu\text{sec}$ from the two sources are indicated. When it is assumed that the initial fragmentation of N_2O^+ to $(N_2^+)^*$ involves $(N_2^+)^*$ being formed with $\sim 0.5 \text{ eV}$ of initial kinetic energy, and a correction is made for this initial discrimination, the slopes of the curves become essentially equal. We conclude the half-life of $(N_2^+)^*$ to be $\geq 0.15 \mu\text{sec}$ and to be independent of source.

In Fig. 12 accelerating voltage discrimination curves for $(M/q)^* = 8.53$ are shown with NO gas as a source, with N_2O gas as a source and with NO_2 gas as a source. The uncorrected curves indicate that from the NO source, the dissociation exhibits a half-life of $\sim 0.18 \mu\text{sec}$, while from N_2O to NO_2 sources, the half-life is $\sim 0.11 \mu\text{sec}$. If it is assumed that from N_2O and NO_2 , the $(NO^+)^*$

is formed in the ion source with initial kinetic energies of ~ 0.4 and ~ 0.8 eV respectively from two sources, the corrected points fall on a line closely parallel to the line from an NO source. We conclude the half-life to be ≥ 0.18 μ sec. Thus in the time range studied, no appreciable difference in half-life of $(NO^+)^*$ from any of these three sources is detectable with the method used to evaluate the half-lives.

In the analysis of the half-lives by any of the methods described herein, it is not possible to categorize the resultant values as being unique half-life values. We measure a change over a limited time interval, and the half-life derived is an average over this time interval. A mixture of half-lives with a limited range of values cannot be resolved by these methods. Wide differences such as observed for the $(M/q)^* = 20.45$ peak in N_2O do show up as two half-lives but each of these may be itself a distribution of values about the average observed. Furthermore, the method of using voltage discrimination curves yields a minimum average half-life since no correction for discrimination in the analyzer tube has been applied to these results. All such effects would result in the measured apparent half-life being shorter than the true half-life. Fortunately, the half-lives observed are all in a region of values where the curves are sensitive functions of half-life so the comparative values are significant.

IV. DISCUSSION

In Table I are summarized those data found on the energetics and half-lives of these peaks. Published data on the dissociation of N_2O^+ to NO^+ , NO_2^+ to NO^+ , N_2^+ to N^+ and NO^+ to O^+ are included for comparison.

In Table I, the observed appearance potentials of these metastable ions are compared to minimum values calculated from bond energies and spectroscopic ionization potentials. Included in these figures are the kinetic energies of dissociation found in this work. This calculation for the dissociation of N_2O^{++} is shown below to illustrate the method.



$$\begin{array}{r} \text{Kinetic Energy} \quad T = 6.5^{+0.2}_{-0.5} \\ \hline \text{Total} = 35.24^{+0.2}_{-0.5} \end{array}$$

The observed total of 35.2 eV is compared to the observed AP of 36.5 eV. The difference is 1.3 eV. In this case it is possible that 1) NO^+ is formed in a vibrationally excited state, 2) N^+ is formed in the 1D state ($\Delta = 1.898$ eV) or, more likely, 3) N_2O^{++} is formed in a state which radiates to the dissociative ground state of N_2O^{++} emitting radiation in the red or near infra red. If such radiation is an allowed transition, the half-life for radiation of this wavelength may be estimated to be of the same order of magnitude as the half-life of the observed dissociation, i.e., ~ 0.5 μsec . The equality of appearance potential of peaks at $M/q = 22$ and $(M/q)^* = 8.91$ and the lack of

any "stable" N_2O^{++} are all consistent with the conclusion that the lowest state of N_2O^{++} is a dissociative state and that metastability arises from an allowed radiative transition from a higher state only 1 to 2 eV above the dissociative level.

The value of $T = 6.5$ eV for this dissociation appears to be excessively high. It corresponds to the repulsion of unit charges with only 2.22 Å separation. The sum of the N-N and N-O bond distances in N_2O is 2.312 Å and it is reasonable to expect that in the doubly charged ion some expansion of these bonds will occur. We offer no explanation of this apparent anomaly, nor conversely can we explain why the experimental value of T for this transition might be from 0.5 to 1.0 eV too high using three different sets of measurements. These different measurements are admittedly not independent of each other in the sense that all are influenced in the same direction by any instrumental artifact which increases the apparent width of the metastable peak. The wide collector slit is one such factor, but we estimate its contribution to add less than 0.2 eV in excess kinetic energy to the true value.

The energy balance of the metastable NO^+ from both N_2O and NO_2 shows a discrepancy of observed minus calculated appearance potentials of 2.3 and 1.3 eV respectively from the two sources. In the case of metastable N_2^+ from N_2O , a discrepancy of 1.3 eV was observed. In none of these cases can this energy difference be ascribed to the emission of radiation by the excited molecule ion before fast fragmentation in the ion source to yield the metastable species. If that were the case, the metastability would be in the parent molecule rather than in the fragment. Nor can the excess energy be in vibrational excitation of the fragment, since such excitation would later appear as kinetic energy in the metastable dissociation of the fragment ion.

It is concluded that the extra energy is due to initial kinetic energy release during the fast fragmentation of the molecule ion in the ion source. On this basis the initial kinetic energy given $(\text{NO}^+)^*$ from N_2O and NO_2 , and $(\text{N}_2^+)^*$ from N_2O was estimated and used to correct the ion accelerating voltage discrimination curves used to estimate half-lives (Figs. 11 and 12).

With the present equipment there is no method of evaluating initial kinetic energy in a fast fragmentation process which yields a metastable fragment ion. The particular excited state of the fragment ion can be studied with the product ion of its metastable dissociation.

The half-lives for the metastable dissociation of NO^+ produced from NO , N_2O , or NO_2 are equal (or very close to equal). Similarly the half-life for metastable dissociation of N_2^+ is the same whether produced from N_2 or N_2O as the source. The kinetic energy release is different from different sources however, this difference being particularly striking in comparing the 0.20 eV release in the N_2^+ produced from N_2O as compared to the 0.55 eV release when the N_2^+ is prepared from N_2 . In the metastable dissociation of NO^+ , with NO as a source, $T = 0.04$ eV, but with N_2O or NO_2 as sources, $T = 0.13$ eV. If the metastability of these excited species arose because the dissociation process was one of tunneling through a low potential barrier,¹⁵ then the differences in T between N_2^+ from N_2 compared to N_2^+ from N_2O would correspond to a difference of a factor of 20 to 100 in half-lives of the respective metastable ions. The kinetic energy difference in NO would correspond to a difference in half-life of a factor of 5 to 10. No such difference in half-life for either of these species can be derived from the present data.

The equality of half-lives with different sources is compatible with the previously postulated predissociation mechanism as the source of the metastability.⁴ The crossing states of N_2^+ and NO^+ respectively are postulated to be the same respective states regardless of the source. Possible metastable states in N_2^+ and NO^+ have been discussed previously.⁴

While the data on the formation of N^{++} and O^{++} are of importance only to show that the AP's of these species are well above those of the metastable ions which were investigated, examination of their measured and calculated AP's in Table I does disclose an interesting anomaly concerning their formation. The observed AP's of both N^{++} and O^{++} from N_2O are above the values calculated for the dissociation limit with the co-products being the other separated atoms of the molecule. If the molecules NO and N_2 respectively were the co-products of this fragmentation, they would perforce be formed in quite highly excited states (8 and 10 eV respectively) or large amounts of kinetic energy would accompany the fragmentation. No evidence was found for the latter from the metastable suppressor cutoff curves of N^{++} and O^{++} . Less than 1 eV of initial kinetic energy could have been detected; none was observed.

On the other hand, the AP's of N^{++} and O^{++} from NO_2 are well below the limiting AP's calculated for separated atom co-products. With NO_2 , the co-products of N^{++} and O^{++} formation must be O_2 and NO respectively.

FOOTNOTES AND REFERENCES

- * Work performed under the auspices of the U. S. Atomic Energy Commission.
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Table I. Energetics of formation of various ionic species and half-lives of metastable transitions in the mass spectra of N₂O, NO₂, NO, and N₂.

Molecule	(M/q)*	Transition	AP (eV)	Breaks (eV)	Standard	T (eV)	t _{1/2} (μsec)	Calculated ^b AP (eV)	ΔAP (eV) (obs-calc)
N ₂ O	20.45	N ₂ O ⁺ → NO ⁺ + N	15.7±0.5	19.5	H ₂ ⁺	1.05±0.05 ^a	~0.09 ≥0.3	15.23	0.5
	8.53	NO ⁺ → O ⁺ + N	27.5±0.5		He ⁺	0.13±0.03	≥0.18	25.16 ^c	2.3
	7.00	N ₂ ⁺ → N ⁺ + N	27.5±0.5	32±1 37±1	He ⁺	0.20±0.05	≥0.15	26.18 ^c	1.3
	8.91	N ₂ O ⁺⁺ → NO ⁺ + N ⁺	36.5±0.5		Ar ⁺⁺	6.5 ^{+0.2} -0.5	0.46±0.05	35.20	1.3
	22.00	N ₂ O ⁺⁺	36.4±0.5		Ar ⁺⁺				
	7.00	N ⁺⁺	57.1±1.0	64.4 72.6	Ne ⁺⁺			49.08(+NO) 55.56(+N+O)	
	8.00	O ⁺⁺	60.5±1.0	74.8	Ne ⁺⁺			50.44(+N ₂) 60.19(+N+N)	
NO ₂	19.57	NO ₂ ⁺ → NO ⁺ + O	12.6±0.3(w)	14.1±0.3(s) 15.6±0.3	H ₂ ⁺	(1.1) ^a (0.5) ^a	(0.7) ^a (2.5) ^a	12.86 (T=0.5)	
	8.53	NO ⁺ → O ⁺ + N	24.6±0.5	30±1	He ⁺	0.13±0.5	≥0.18	23.35 ^c	1.3
	7.00	N ⁺⁺	51.5±1(w)	65.0 71.0	Ne ⁺⁺			48.65(+O ₂) 53.73(+O+O)	
	8.00	O ⁺⁺	52.1±1(w)	69.3 75.5	Ne ⁺⁺			51.88(+NO) 58.35(+N+O)	
N ₂	7.00	N ₂ ⁺ → N ⁺ + N	(24.9±0.3) ^d		He ⁺	(0.55±0.10) ^d	≥0.15	24.85	0.0
NO	8.35	NO ⁺ → O ⁺ + N	(20.2±0.2) ^d		He ⁺	(0.04±0.10) ^d	≥0.18	20.14	0.0

(continued)

Table I. Footnotes.

^aData taken from Reference 8.

^bAP calculated to the lowest dissociation limit. Figure includes measured kinetic energy release of the metastable transition.

^cFigure does not include any initial kinetic energy of the fast fragmentation process.

^dData taken from Reference 4.

^wWeak onset.

^sStrong onset.

FIGURE CAPTIONS

Fig. 1. Mass spectrum of N_2O in the mass range of $M/q = 6$ to $M/q = 10.5$.

$MV_A = 22,200$, Inlet pressure = 400μ .

Curve A - $V_{e^-} = 100 + 0.0058 V_A$

Curve B - $M/q = 6$ to 7.7 , $V_{e^-} = 31 + 0.0058 V_A$

$M/q = 7.7$ to 10.5 , $V_{e^-} = 51 + 0.0058 V_A$

Fig. 2. Behavior of peaks in the mass spectrum of N_2O in the mass range $M/q = 8$ to $M/q = 10$ with voltage applied to the metastable suppressor

(V_{mss}). The small peak at $M/q = 9$ is unidentified. $MV_A = 26,000$,

$V_{e^-} = 100 + 0.0058 V_A$, Inlet pressure = 200μ .

Fig. 3. Mass spectrum of N_2O in the mass range $M/q = 17$ to $M/q = 27$.

$MV_A = 63,000$, $V_{e^-} = 80 + 0.0058 V_A$, Inlet pressure = 200μ . Focus adjusted to maximize the metastable peak at $(M/q)^* = 20.5$.

Fig. 4. Mass spectrum of NO_2 in the mass range $M/q = 6.5$ to $M/q = 9.5$.

$MV_A = 22,620$, $V_{e^-} = 100 + 0.0058 V_A$, Inlet pressure = 100μ .

Fig. 5. Variation of peak sensitivity with inlet system pressure for various peaks in the mass spectrum of N_2O .

▲ $(M/q)^* = 20.45$, $MV_A = 63,000$, $V_{e^-} = 100$ eV

○ $M/q = 22$

△ $(M/q)^* = 7.00$, $MV_A = 21,000$, $V_{e^-} = 46.7$ eV

□ $(M/q)^* = 8.53$, $MV_A = 25,600$, $V_{e^-} = 100$ eV

● $(M/q)^* = 8.91$, (Measured at $(M/q)^* = 8.10$), $MV_A = 25,600$, $V_{e^-} = 100$ eV.

Fig. 6. Variation of peak sensitivity with inlet system pressure for various peaks in the mass spectrum of NO_2 . $MV_A = 22,600$, $V_{e^-} = 100$ eV.

● $(M/q)^* = 19.57$

△ $M/q = 23$

■ $(M/q)^* = 8.53$

○ $(M/q)^* = 6.53$

Fig. 7. Metastable suppressor cutoff curves for metastable peaks at $(M/q)^* = 7$ in N_2O (open circles), $(M/q)^* = 8.53$ in N_2O (closed circles), $MV_A = 17,500$; and $(M/q)^* = 8.53$ in NO_2 (triangles), $MV_A = 12,860$.

Fig. 8. Metastable suppressor cutoff curve of peak at $(M/q)^* = 8.91$ in mass spectrum of N_2O . $MV_A = 17,500$; $V_{e^-} = 100 + 0.0058 V_A$.

Fig. 9. Dependence of intensity of peak at $M/q = 22$ in the mass spectrum of N_2O with total transit time from formation in the ion source to the collector.

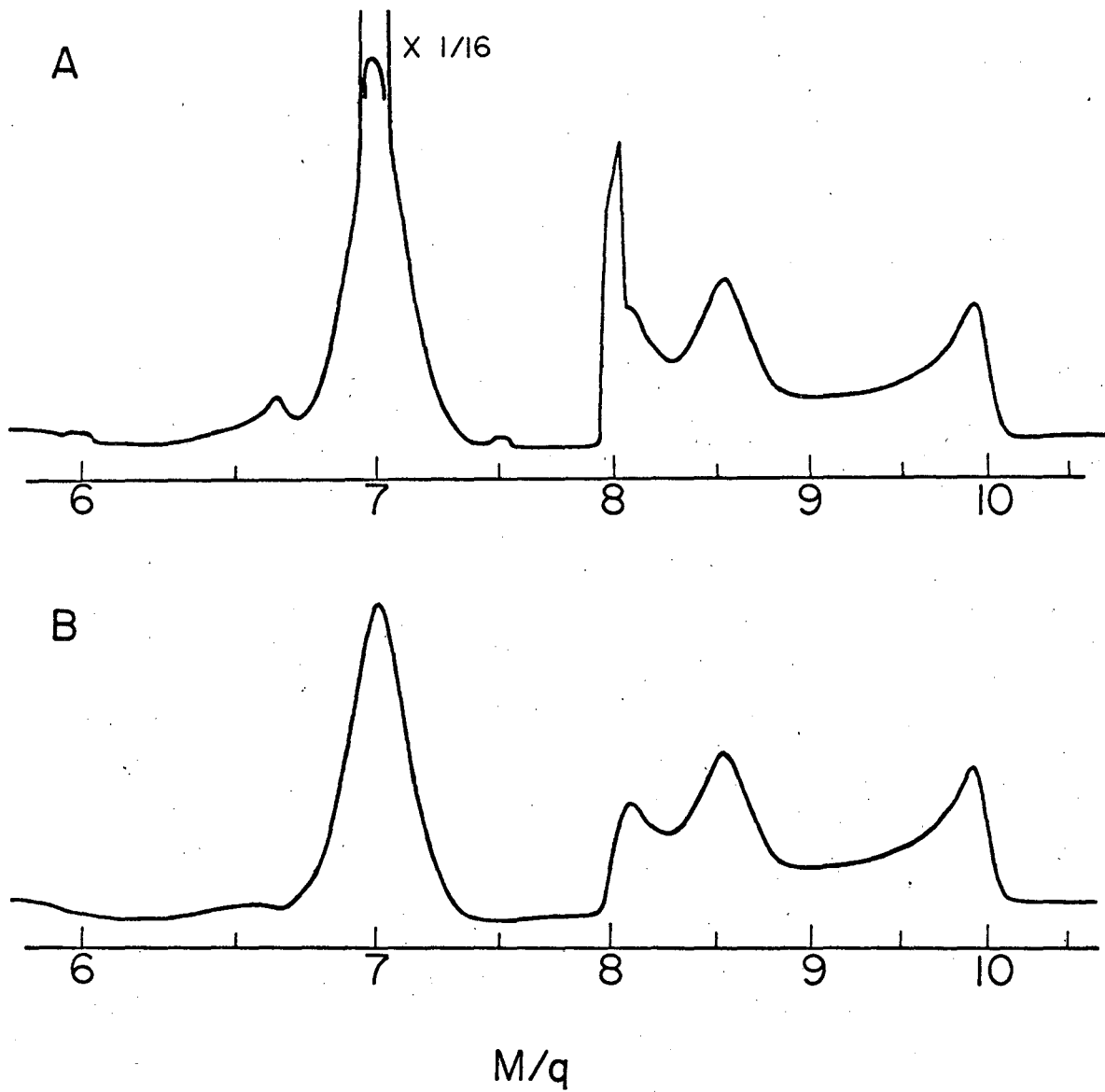
Open circles, dashed line--observed intensity of $M/q = 22$ in N_2O ;
 solid line, no points--line subtracted to yield an exponential decay;
 open circles, solid line--resolved decay of N_2O^{++} ; closed circles, dotted
 line-- $M/q = 22$ peak of CO_2^{++} (from O_2) normalized to N_2O curve at long
 transit times.

Fig. 10. Accelerating voltage discrimination curve of $(M/q)^* = 20.45$ peak in mass spectrum of N_2O . Open circles, no line--experimental points. Lines are of slope calculated for the transition, $\text{N}_2\text{O}^+ \rightarrow \text{NO}^+ + \text{N}$, for half-lives of 0.3, 0.10, and 0.09 μsec respectively. Lower points are subtraction of the 0.3 μsec line from the observed points.

Fig. 11. Accelerating voltage discrimination curves of $(M/q)^* = 7.00$ peak from various sources. Points are experimental. Lines are calculated for the transition $N_2^+ \rightarrow N^+ + N$, with the assumed half-lives shown. Peak intensity expressed as product of peak height and half width in amu. Closed circles-- N_2 source, open circles-- N_2O source, triangles-- N_2O source corrected for initial kinetic energy of N_2^+ .

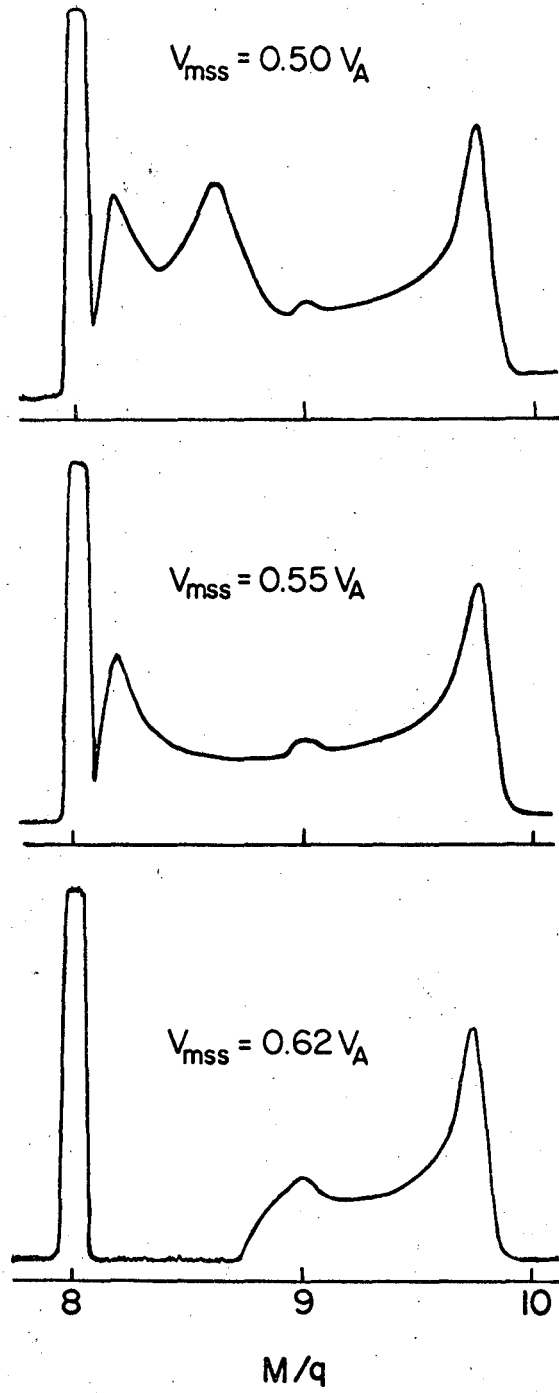
Fig. 12. Accelerating voltage discrimination curves of $(M/q)^* = 8.53$ from various sources. Points are experimental; lines are calculated for the transition $NO^+ \rightarrow O^+ + N$ at the assumed half-lives shown.

Open circles--NO source, closed circles--NO source corrected for collision-induced component. Open squares-- N_2O source, open triangles-- NO_2 source, closed squares-- N_2O source corrected for initial kinetic energy of NO^+ , closed triangles-- NO_2 source corrected for initial kinetic energy of NO^+ .



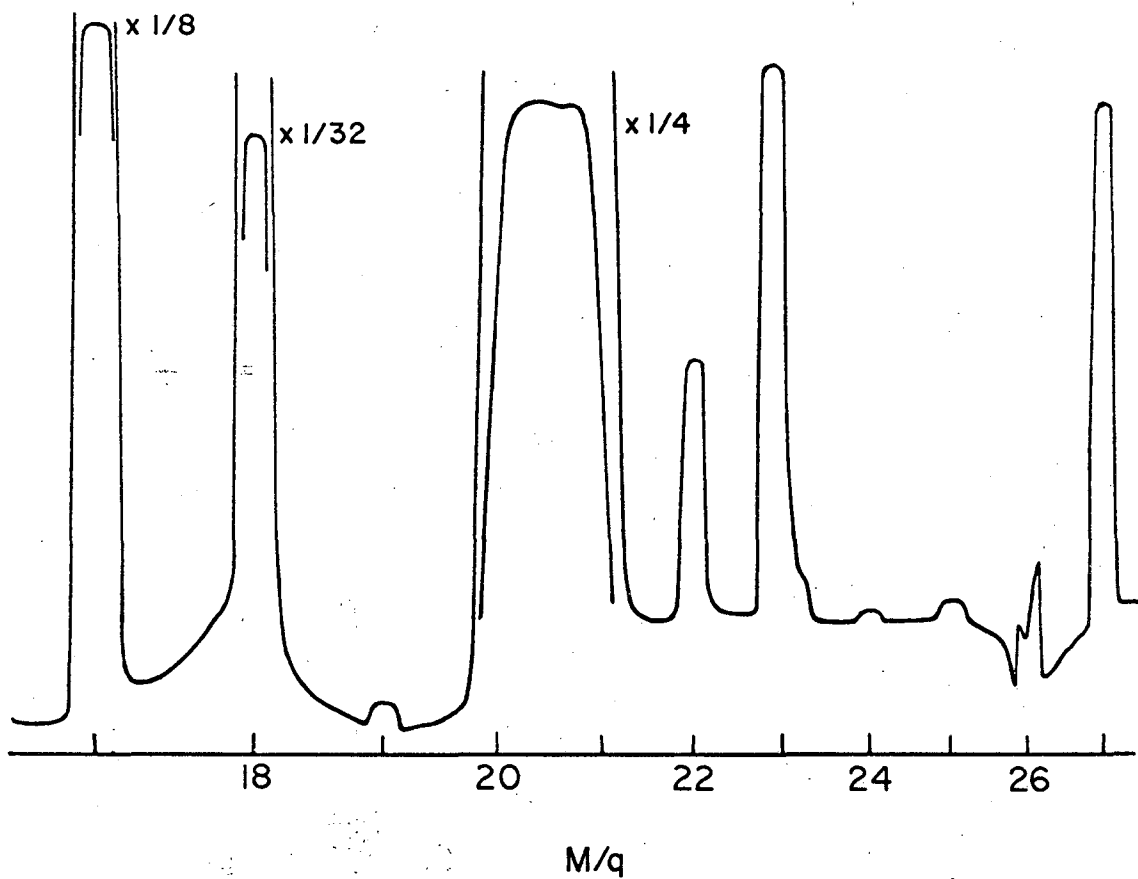
XBL 695-522

Fig. 1



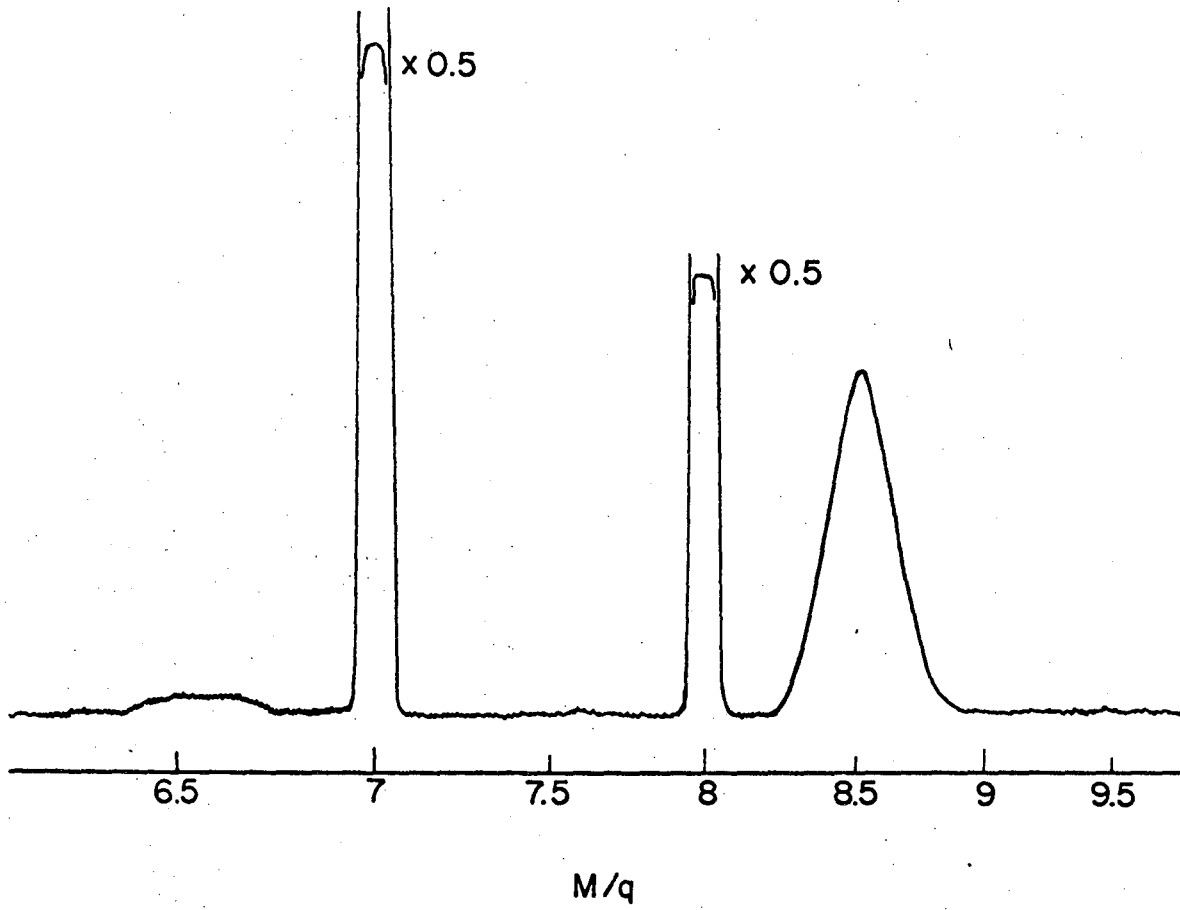
XBL 695-515

Fig. 2



XBL 695-516

Fig. 3



XBL 695-517

Fig. 4

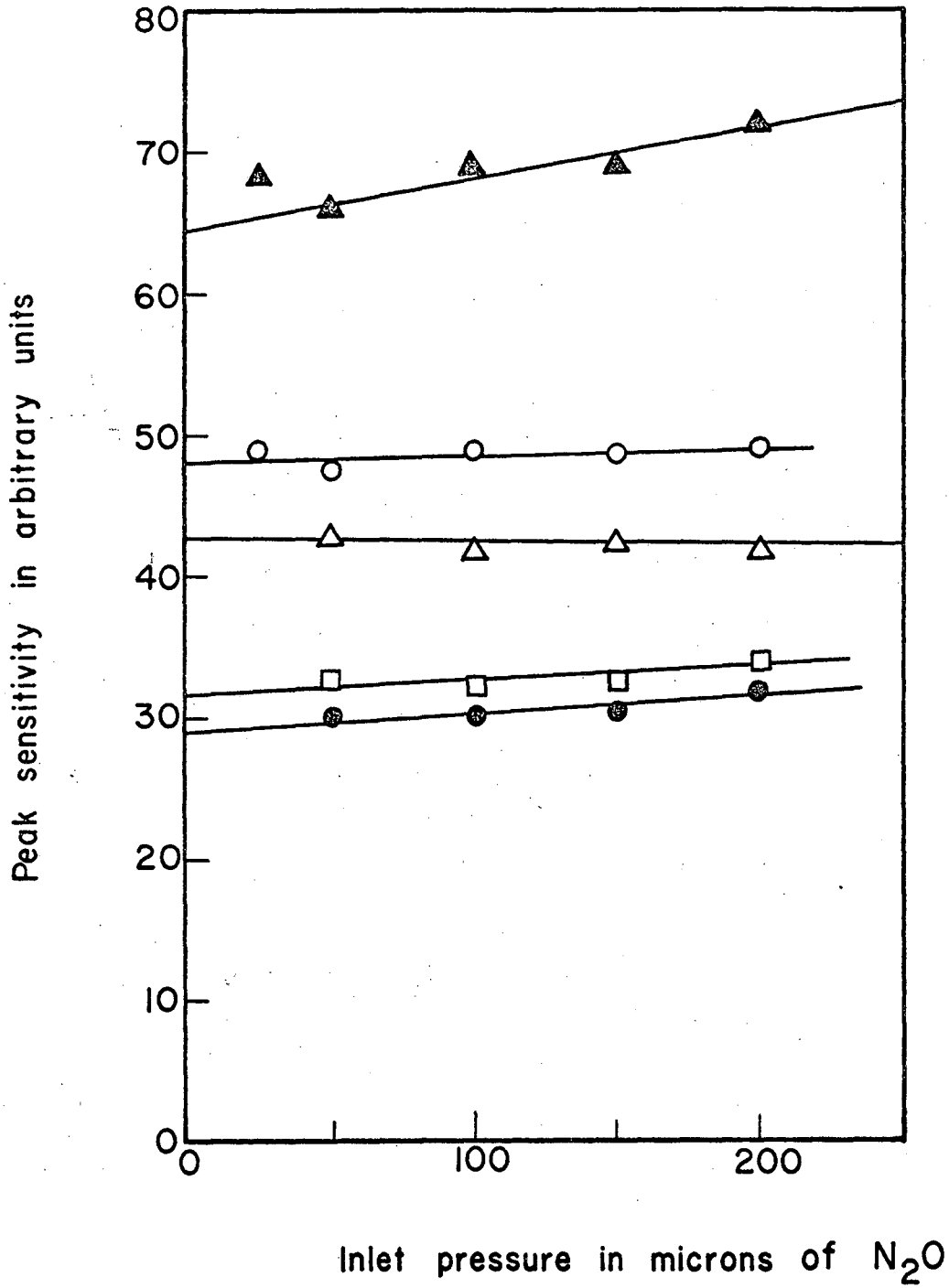
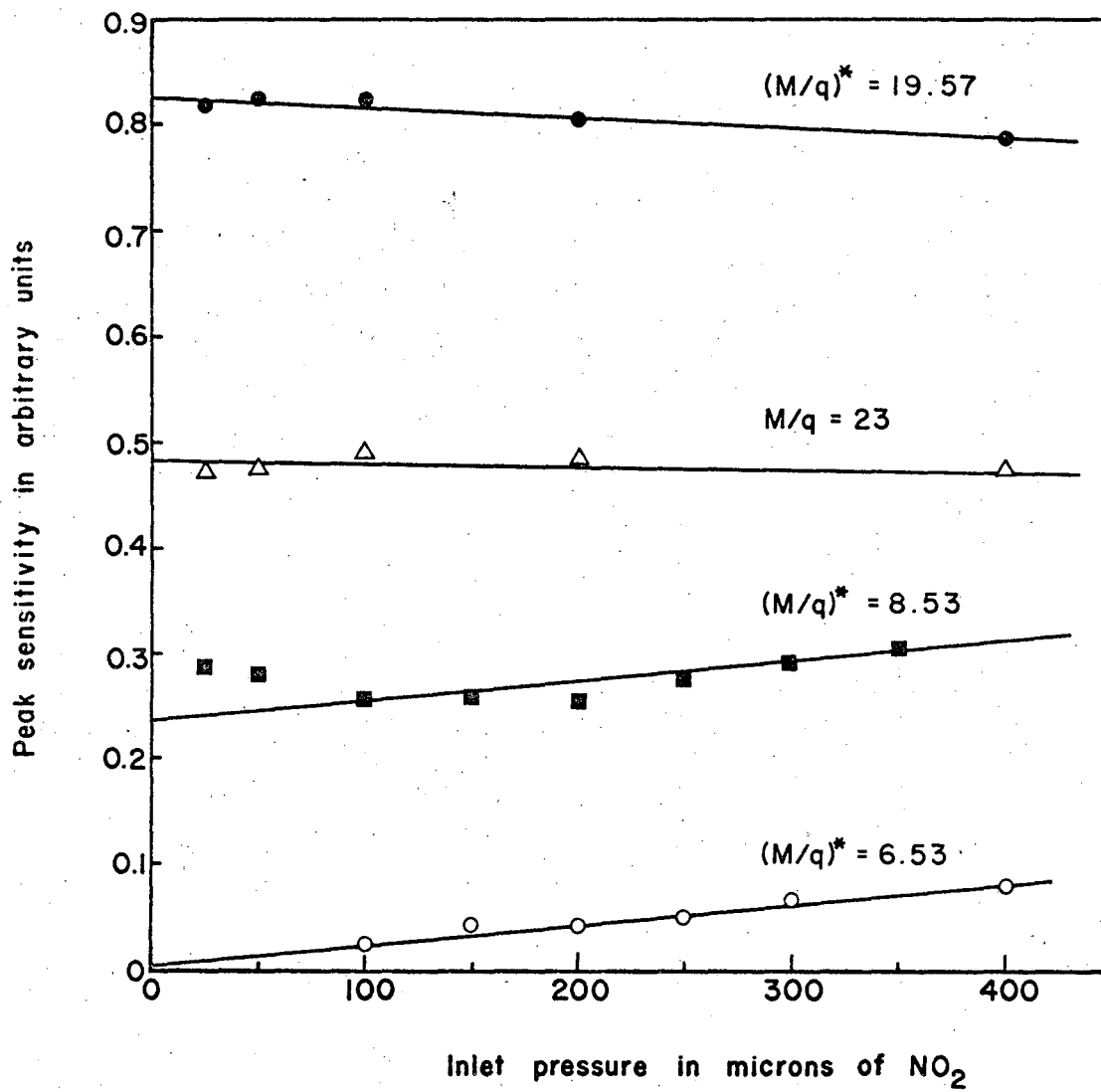


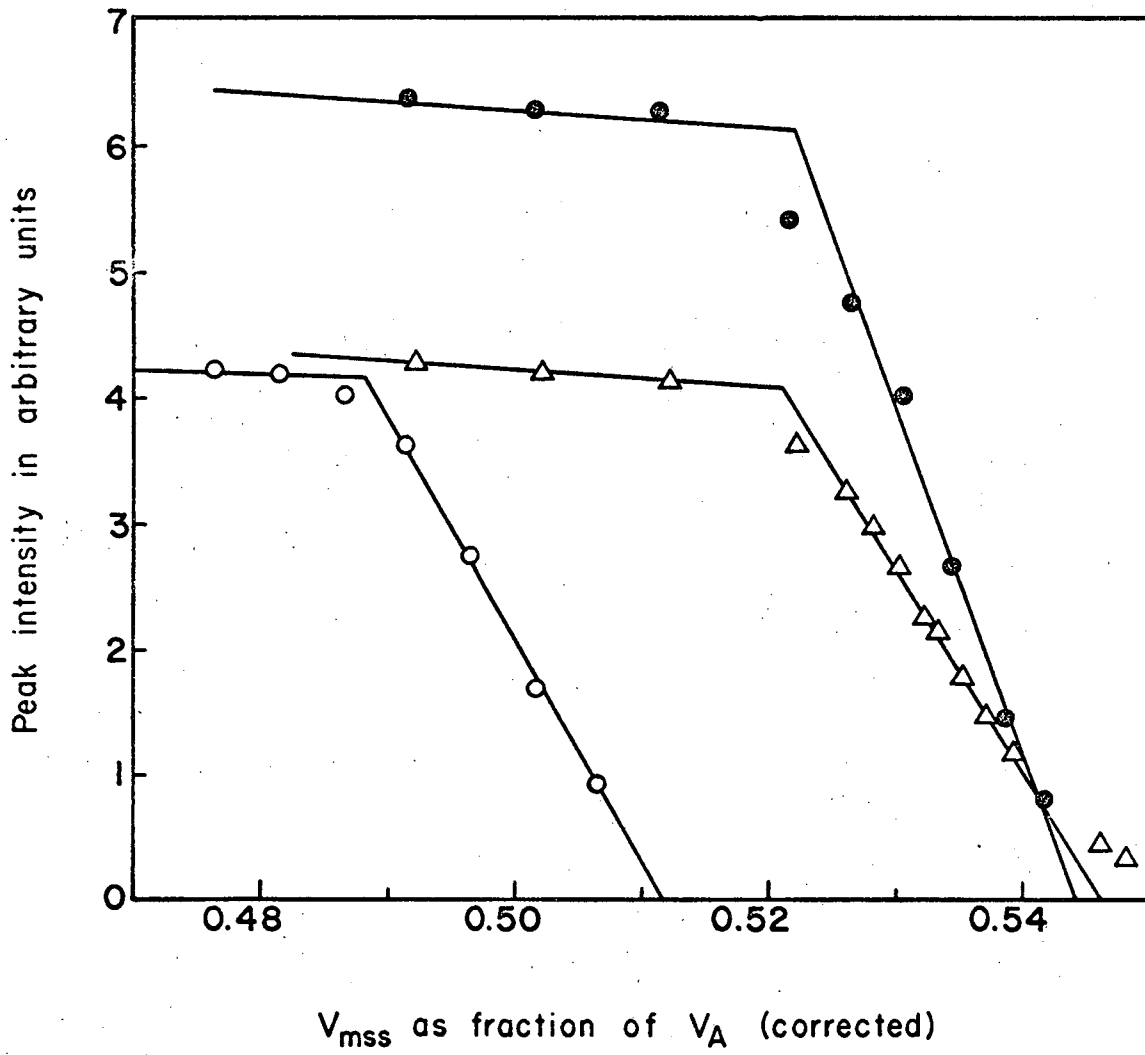
Fig. 5

XBL 695-518



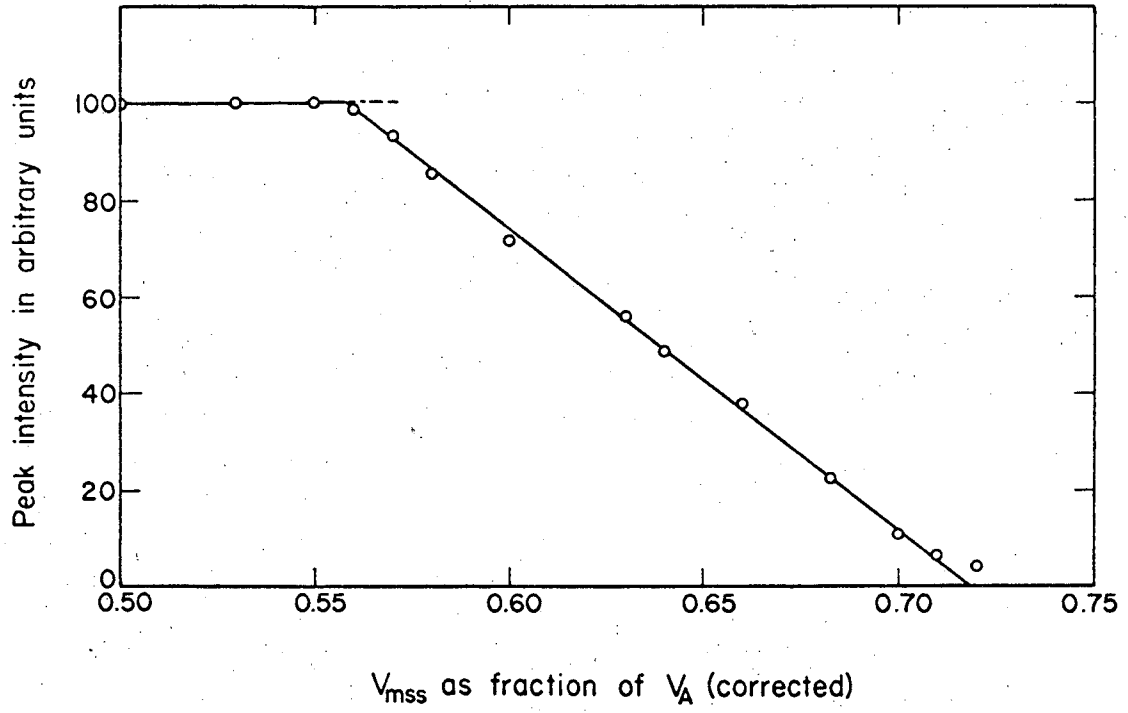
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Fig. 6



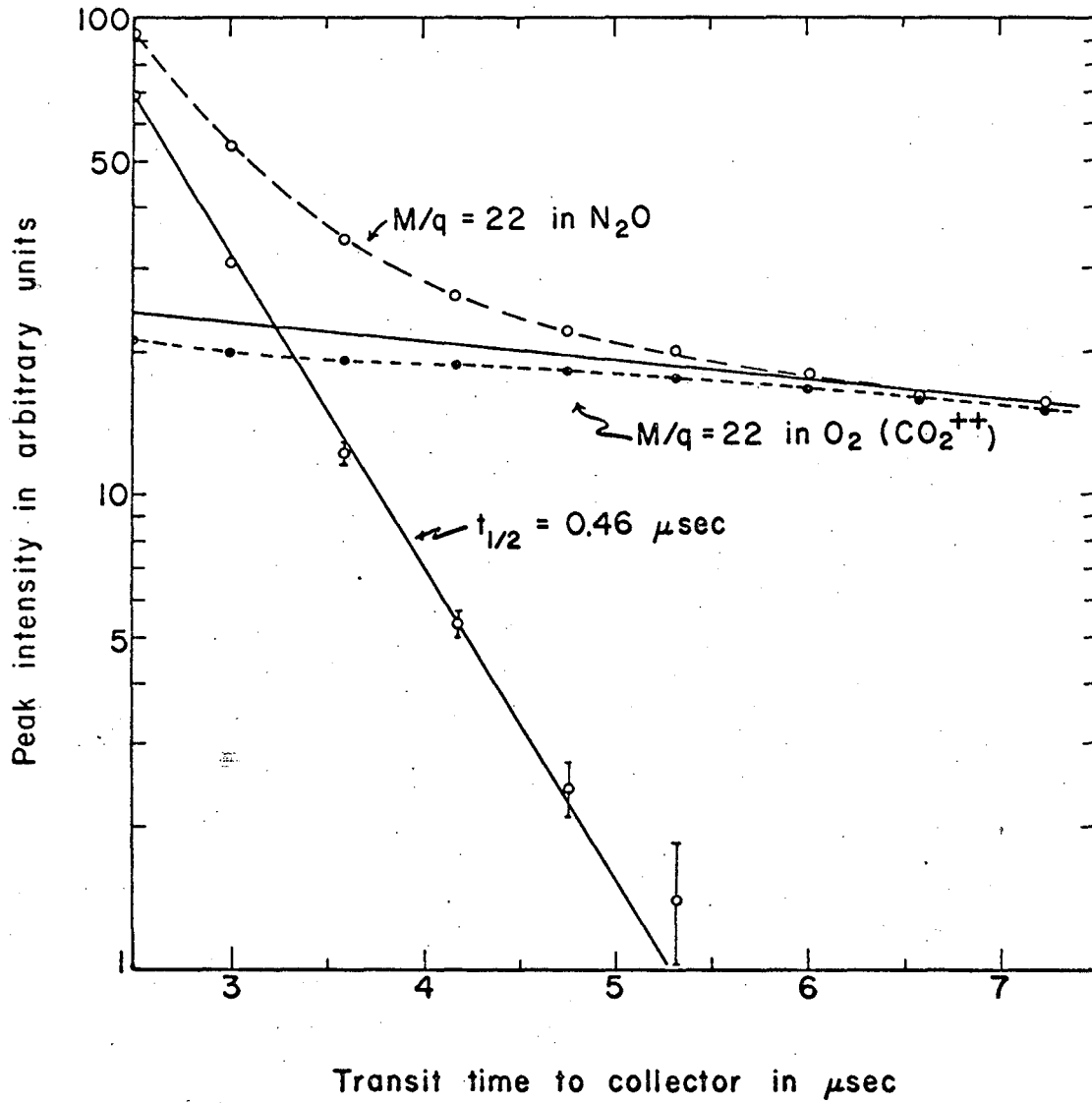
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Fig. 7



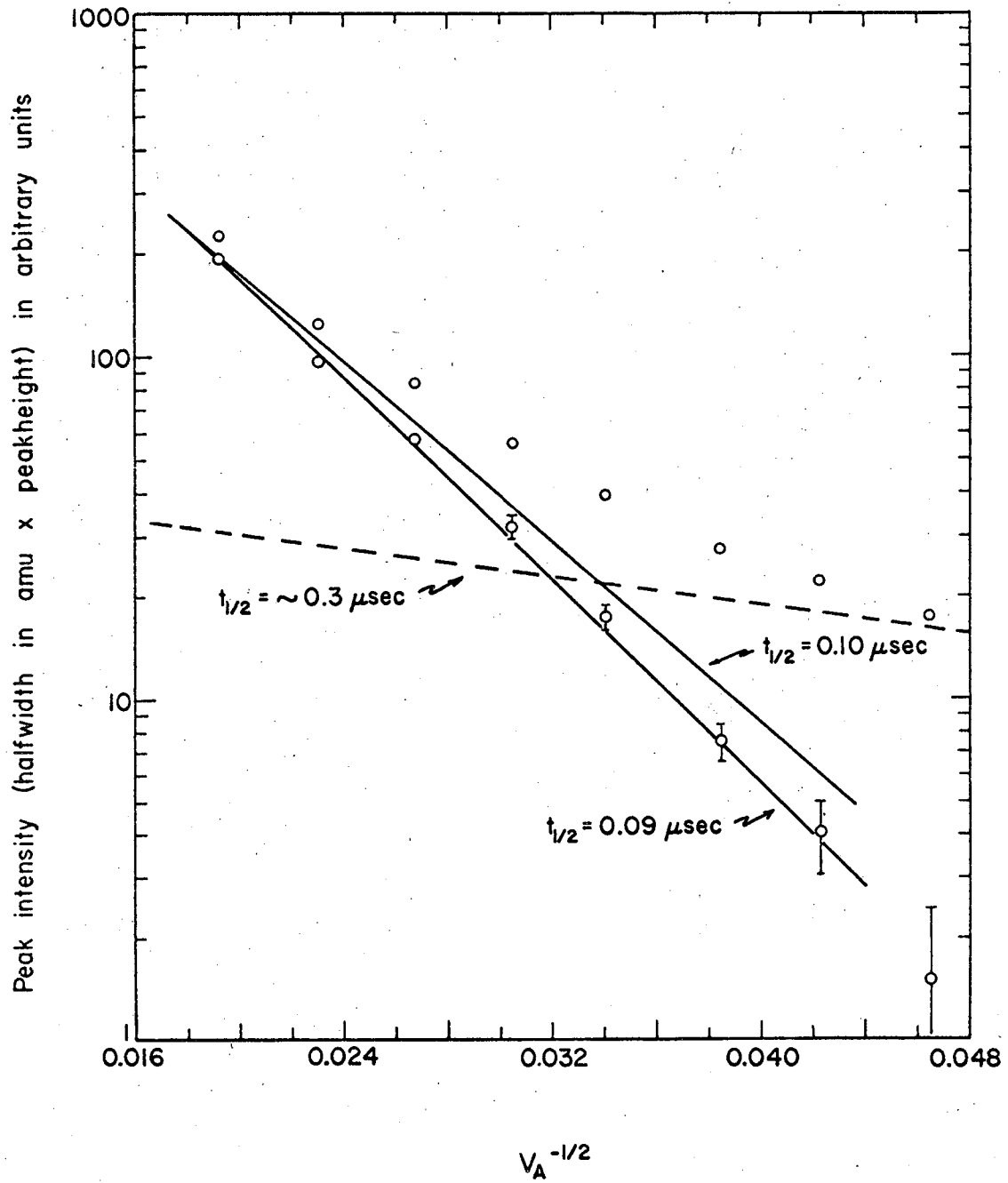
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Fig. 8



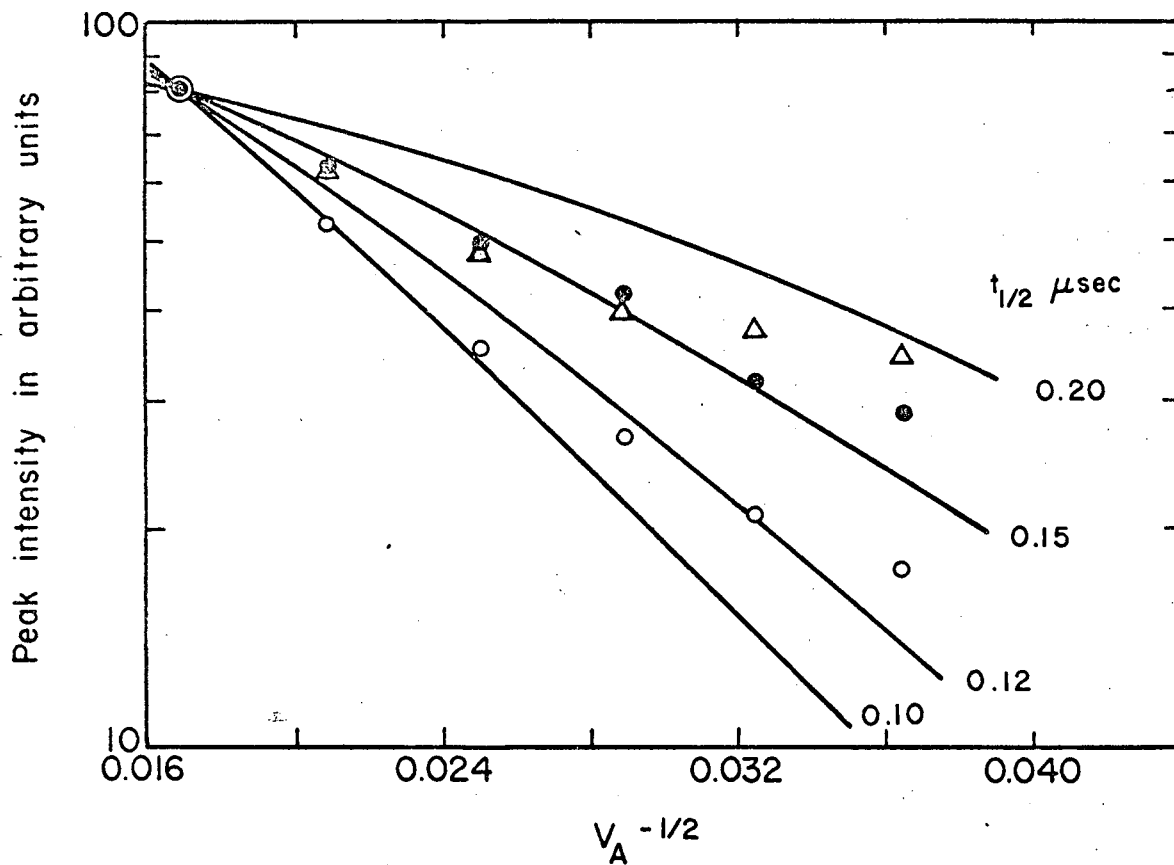
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Fig. 9



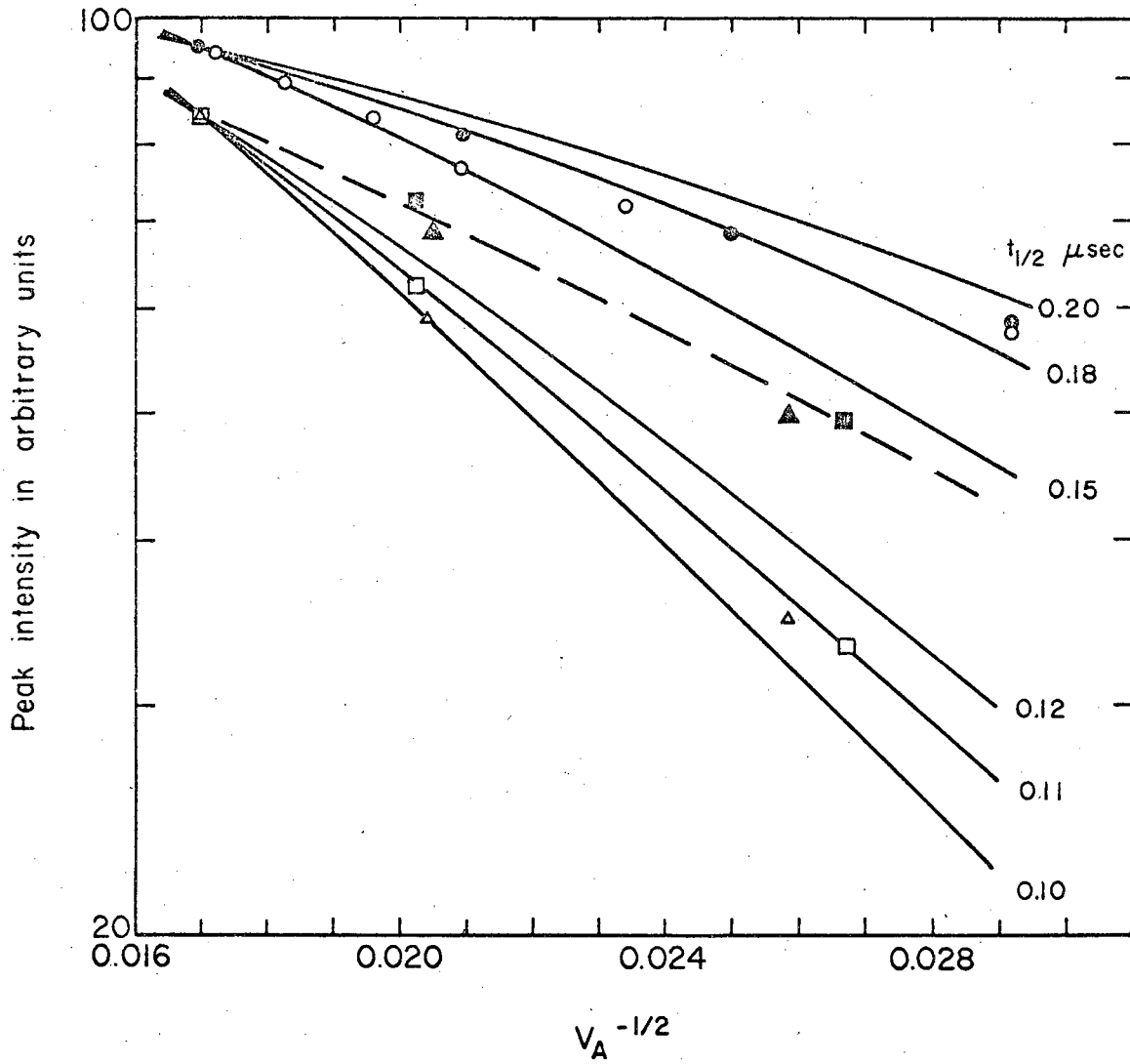
XBL 695-513

Fig. 10



XBL 695-514

Fig. 11



XBL 695-519

Fig. 12

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