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ABSTRACT

Metastable states in N_2O^+ and NO_2^+ have been observed, the production of the metastable dissociation being NO^+ in each case. In $N_2O^+(m)$, with a half life of $<0.2 \times 10^{-6}$ sec, the total kinetic energy given to the fragments NO^+ and N was found to be 1.05 ± 0.05 eV. In $NO_2^+(m)$ two processes are found, one of half life $0.7 \pm 0.1 \times 10^{-6}$ sec which leads to a total kinetic energy release of 1.12 ± 0.10 eV, and a second of half life $2.5 \pm 0.5 \times 10^{-6}$ sec which leads to a total kinetic energy release of 0.51 ± 0.10 eV. The effect of pressure on peak height shows the metastable peak from N_2O^+ to possess a unimolecular component, which, under proper conditions of operation, can be made to predominate over a normally intense collision induced dissociation peak. The metastable peaks from NO_2^+ both arise from unimolecular dissociation processes.

I. INTRODUCTION

Begun and Landau¹ have reported the existence of a metastable peak at $M/q = 20.45$ in the mass spectrum of nitrous oxide which they ascribed to the metastable dissociation



They concluded that in addition to a collision induced reaction, at least part of the process they observed arose from a unimolecular dissociation and that there exists a metastable electronic excited state of N_2O^+ .

Friedman and Irsa² have questioned this data and presented results indicating that the observed metastable peak was due solely to a collision induced transition. Their conclusions were based on the observation that a plot of the peak height ratio of $(M/q = 20.45)/(M/q = 14)$ against the peak height of $M/q = 14$ extrapolated to zero at zero $M/q = 14$ peak height. Begun and Landau³ questioned this latter conclusion and showed their plot of the ratio of the metastable peak height to the NO^+ peak height did not extrapolate to zero at zero NO^+ peak height, indicating the existence of a unimolecular dissociation.

It has recently been shown that a metastable excited state exists in the CO_2^{+2} ion,^{4,5} and Dibeler and Rosenstock have studied three metastable ions in the mass spectrum of H_2S .⁶ It was therefore of interest to re-examine the mass spectrum of N_2O and to examine the mass spectra of other triatomic molecules to determine if electronic excited states of small polyatomic molecules are

rare as suggested by Friedman and Irsa.² In the present paper, evidence is presented to show that the metastable dissociation in N_2O^+ occurs by a unimolecular process, and that a similar unimolecular process occurs in NO_2^+ . With NO_2^+ there are two contributing metastable states which yield different kinetic energy fragments and have different half lives for dissociation.

II. EXPERIMENTAL

The mass spectrometer used in this work was a modified Consolidated Electroynamics Corporation Model 21-103B. For these experiments the modifications of interest are as follows. The analyzer pumping system has been changed to an all metal system with pumping on both the ion source and collector ends of the analyzer tube. The residual pressure in this system as measured by nude ion gauges of the Alpert type located in the pumping lines just outside the magnetic field is less than 5×10^{-8} torr. This increased pumping speed has resulted in drastically reduced scattering of the ion beam and increased the linearity of peak height vs inlet system pressure to greater than 200 microns inlet pressure.

The metastable suppressor voltage system was modified by replacing the 47 megohm resistor string with a 0.1% precision, 50 megohm multiple decade potential divider so the fraction of the ion accelerating voltage applied to the metastable suppressor could be accurately measured.

In the Isatron control circuit, the potential divider in the inner focus control was increased in sensitivity by a factor of 10 in order that the metastable peaks and normal peaks could be brought to maximum focus at easily

reproducible settings. It has been mentioned previously that the ion source focus settings are different for maximum intensity on normal and most metastable peaks.⁷ In the repeller circuits, provision was made to increase the range of the repeller voltages by use of batteries.

The gases N_2O and NO_2 were obtained from the Matheson Company. The NO_2 was purified by trap to trap distillation, then further treated with O_2 gas to oxidize the N_2O_3 present and again subjected to trap to trap distillation. The final product was white when condensed as a solid, and traces of N_2O_3 were readily detectable by the blue color it imparted to the solid. The N_2O was purified by simple trap to trap distillation.

III. RESULTS

The peaks from ions resulting from metastable dissociations in the mass spectra of N_2O and NO_2 respectively are shown in Fig. 1. The calculated apparent masses of the



NO^+ from these dissociations shown in Eqs. (1) and (2) are 20.45 from N_2O and 19.57 from NO_2 . As shown in Fig. 1, these metastable peaks are centered about these respective masses, but the peaks have a broad mass distribution owing to kinetic energy given to the fragments in the dissociation process.

1) N₂O Studies—From the variation of peak height with repeller voltage based on only a few points we estimate the half life of the metastable N₂O⁺ to be less than 0.2 X 10⁻⁶ sec. (Begun and Landau¹ reported a value of ~2 X 10⁻⁶ sec.) Such a short half life is also compatible with the rapid disappearance of this peak as the accelerating voltage (V_A) is lowered using the normal operating conditions with repellers at 1% of V_A. All studies were thus made at either a) high V_A with normal repeller voltages or b) high repeller voltages at lower V_A values.

In Fig. 2, the peak heights of M/q = 20.45, 30 and 44 are plotted against inlet system pressure. The NO⁺ peak height increases linearly with pressure while the N₂O⁺ peak height falls off at higher pressures. The metastable peak height increases at a rate greater than linear with pressure, but certainly does not rise as the square of the pressure. The ratio of the metastable peak height to either the NO⁺ or N₂O⁺ peak height are also shown in Fig. 2. Each ratio shows a slow linear rise with pressure. These lines extrapolate to real values at zero pressure and the increase in the zero pressure ratio to the ratio at 400 μ inlet pressure is only 20 and 36% respectively. There is no doubt that these zero pressure ratios represent a unimolecular dissociation. The numerical values are not significant as they are dependent on such experimental parameters as V_A, V_R, and collector slit width.

The kinetic energy released to the fragments in the metastable dissociation of N₂O has been studied in three ways. 1) The width of the metastable peak at a given accelerating voltage, 2) the difference in width of the metastable peak at low and high accelerating voltages, and 3) the spread in voltage of the metastable cutoff curve.

In method (1), it has been shown that for the metastable dissociation



the spread in width of the peak, d , in mass units, is given by the equation⁸:

$$d = 4 \frac{M_1^2}{M_0} \sqrt{\frac{M_2}{M_1} \frac{T}{eV_A}} , \quad (4)$$

in which T is the total kinetic energy given the fragments M_1 and M_2 in the dissociation and V_A is the accelerating voltage. In the use of this equation with voltage scanning, where V_A may differ by many volts in focusing the high and low mass sides of the peak, it can be shown that use of the V_A required to focus the zero kinetic energy peak, e.g., M_1^2/M_0 , gives a result not significantly different than that found when V_A is constant and magnetic scanning is used.

The problem in applying Eq. (4) arises in deciding how the peak width, d , is to be measured. Beynon⁸ used the top of the peak at each end of the distribution and claimed these results to agree with results from measurement of the metastable cutoff curve (method 3). Fuchs and Taubert⁵ studied the kinetic energy of fragments from the dissociation of CO_2^{+2} and measured both the width at the tops of the peak and also the width at 50% peak height. These kinetic energies were compared to the kinetic energy found by the deflection method, and it was observed that the top peak width gave too low an energy and the 50% peak height width too high an energy. As suggested by the results of Fuchs and Taubert and as found in the results presented here, a measurement of

the peak width at 70% peak height gives results consistent with the other methods of determining the energy. This empirical result can be rationalized by the assumption that there is a Gaussian distribution of kinetic energies about some mean value and hence measurement at 67.5% of peak height would yield the mean value of the energy. (Obviously such an argument does not apply to dissociations in which quite small amounts of kinetic energy are released, for in these cases the effect of slit width and, in Dempster type mass spectrometers, change in the apparent mass with distance beyond the ion source exit slit at which dissociation occurs is a significant factor in determining the overall peak width.)⁷

In method (2), the difference in spread at two accelerating voltages should be independent of how the peak widths are measured as long as the measurements are consistent, though second order effects which change the peak shape at high and low voltages may affect the results. The equation relating to the difference in peak width at two accelerating voltages is:

$$\Delta d = 4 \frac{M_1^2}{M_0} \sqrt{\frac{M_2 T}{M_1}} \left(\frac{1}{\sqrt{eV_{A_1}}} - \frac{1}{\sqrt{eV_{A_2}}} \right) \quad (5)$$

In Table I are presented the results of measurements of peak widths at high and low voltages as measured by the top widths of the extrapolated sides of the peak and the width at 70% peak height. Also shown are the results calculated from the change in width with voltage. It is seen that the energy calculated at 70% peak height agrees fairly well with the energy calculated from the difference in peak width as measured at either point.

In Fig. 3 is shown the metastable cutoff curve of the $M/q = 20.45$ peak in N_2O where the peak area is plotted against the fraction of V_A applied to the metastable suppressor. With peaks of this type, increasing the voltage applied to the metastable suppressor does not gradually change the peak height over the whole curve, but first cuts off the low mass side of the peak. As the voltage applied to the metastable suppressor is increased, the peak simply becomes narrower until finally the high mass side is cut off. The height of the residual peak does not change over most of this progressive narrowing of the peak. Peak areas were determined by weighing the actual peak cut out of the chart paper.

The equation relating spread in the metastable suppressor cutoff voltage (V_{mss}) to the kinetic energy given the fragments in a metastable dissociation is given by⁸:

$$\Delta V_{(mss)} = \frac{4M_1 V_A}{M_0} \sqrt{\frac{M_2}{M_1} \frac{T}{eV_A}} \quad (6)$$

From the results in Fig. 3, T is calculated to be 1.09 eV, and this together with the results from the peak width difference method yields an estimated best value of $T = 1.05 \pm 0.05$ eV for the kinetic energy imparted to the fragments in the metastable dissociation of N_2O^+ .

2) NO_2 Studies—The $M/q = 19.57$ peak in NO_2 , shown in Fig. 1, is clearly composed of two components. When this peak is investigated as a function of accelerating voltage the relative widths of the shoulders with respect to the main peak decrease with increasing accelerating voltage, showing the two components to have different kinetic energies.

The half life of the state from which each component of this metastable peak arises has been estimated by the same method as used by Hipple⁹ and

Coggeshall.¹⁰ The high kinetic energy component (shoulders) arises from a metastable state with a half life of $0.7 \pm 0.1 \times 10^{-6}$ sec, and the low kinetic energy component from a metastable state with a half life of $\sim 2.5 \pm 0.5 \times 10^{-6}$ sec.¹¹

In studying the effect of pressure on the peak height of the $M/q = 19.57$ peak, it is to be noted that when all operating conditions except pressure were constant the pattern of the peak as measured on each shoulder, the maximum at each side of the main peak, and the center of the valley is, within reading error of the peak height, independent of pressure from 25 to 400 μ inlet pressure. In Fig. 4 only the height of the point on the high mass side is plotted, but since the pattern is constant, any other measure of peak height would yield a similar curve. It is seen that the peak heights of the metastable peak, $M/q = 30$ and $M/q = 46$ are each almost linear with pressure and the ratio of the metastable peak height to either NO^+ peak height or the NO_2^+ peak height is almost flat and extrapolates to values of 3.2×10^{-4} and 8.8×10^{-4} respectively at zero pressure. Again the extrapolated values are dependent on operating parameters. There is thus no doubt of the unimolecular character of this metastable dissociation. The fact that the pattern of the metastable peak is constant over the whole pressure range shows both components to be unimolecular.

The kinetic energies of the two components of the $M/q = 19.57$ peak have been evaluated by the same three methods as described for the N_2O metastable peak. The results are shown in Table II. The metastable suppressor cutoff curve, Fig. 5, shows the presence of two energy components, fairly clearly on the low energy end where the transition from cutting off the shoulder to cutting off the main peak is quite evident, but less clearly at the high energy end

where there seems to be a gradual merging of the peaks from one to the other. It is realized that the center portion represents the cutoff of both the central peak and that portion of the higher energy peak lying under it. A fair extrapolation of the high energy component cutoff can thus be made, but it is not at all clear how to obtain the low energy component from this curve. The high energy component yields $T_1 = 1.16$ eV, while if extrapolation of the low energy component is estimated to be at the top break in the curve and a similar point on the high mass end, a value of $T_2 \leq 0.65$ eV is obtained for the low energy component. From the results in Table II the best values for the T of metastable NO_2^+ are estimated to be 1.12 ± 0.10 and 0.51 ± 0.10 for the high and low energy components respectively.

IV. DISCUSSION

The evidence presented here shows that for both N_2O and NO_2 there exist excited states of the singly charged molecule ion which dissociate by unimolecular processes. This conclusion in regard to N_2O supports the position of Begun and Landau.¹ Friedman and Irsa² observed only the collision induced process, probably because they operated their ion source with "no repeller". Because of the very short half life of this metastable state, the residence time of the ions in their ion source was probably too long for the unimolecular process to be observed. In N_2O , the collision induced dissociation is predominant under normal operating conditions. By use of high repeller voltage, high accelerating voltage and fast pumping of the analyzer tube, the collision induced dissociation can be minimized and the unimolecular process made to be the major contributor to the observed peak. In NO_2 , the shape of the curves in Fig. 4 indicate that collision induced

processes contribute little to the metastable peak even at high inlet system pressures.

There is a real difference in the shapes of the metastable peaks for these two compounds. The metastable peak from N_2O is almost flat on top, while at least the low kinetic energy component of the NO_2 metastable peak has a definite maximum at each side of the peak. Because the center portion of the high energy component peak is hidden under the low energy peak, it is impossible to give a shape for that peak. Flowers¹² has analyzed the shape of metastable peaks in which kinetic energy is given to the fragments and shows that in a high resolution mass spectrometer the peak should appear with maxima on both the low and high mass sides of the peak. The same type peak should appear in Dempster type instruments as there is a cosine θ distribution of added velocities parallel to the beam direction and all angles are equally probable (θ is the angle between the direction of the dissociating fragment and the beam direction). It is thus not apparent why the peak in N_2O is flat while that in NO_2 is doubly peaked. It would appear to be a remarkable coincidence were the N_2O peak to be the sum of several doubly peaked curves which add up to a flat topped peak. That instrumental factors are involved is known, for we⁴ observed a flat topped peak at $M/q = 35.6$ from CO_2^{+2} , while Fuchs and Taubert⁵ observed a doubly peaked distribution of this metastable ion in their instrument. The problem of peak shape for this type peak will require more study before it is completely understood.

Table I. Kinetic energy of fragments in the metastable dissociation of N_2O^+ .

V_A	d (top)	$T_{(eV)}^a$	d (70% peak height)	$T_{(eV)}^a$
1010	1.67	(0.90)	1.80	(1.05)
3850	0.81	(0.86)	0.94	(1.09)
	Δd		Δd	
$\Delta V_A (1010-3850)$	0.86	1.03	0.86	1.03
Metastable suppressor cutoff				1.09
			T (average)	1.05 ± 0.05

^aFigures in parentheses not included in the average.

Table II. Kinetic energy give to fragments in the metastable dissociation of NO_2^+ .

Main Peak V_A	d (top)	$T(\text{eV})^a$	d (70% peak height)	$T(\text{eV})^a$
581 V	1.61	(0.46)	1.69	(0.51)
2328 V	0.77	(0.42)	0.85	(0.51)
	Δd		Δd	
$\Delta V_A(581-2328)$	0.84	0.51	0.84	0.51
Metastable suppressor cutoff				(≤ 0.65)
			T (average)	0.51 ± 0.10

<u>Base Peak</u>				
581	2.44	(1.06)	2.56	(1.17)
2328	1.22	(1.05)	1.20	(1.19)
	Δd		Δd	
$\Delta V_A(581-2328)$	1.22	1.07	1.26	1.14
Metastable suppressor cutoff				1.16
			T (average)	1.12 ± 0.10

^a Figures in parentheses not included in the average.

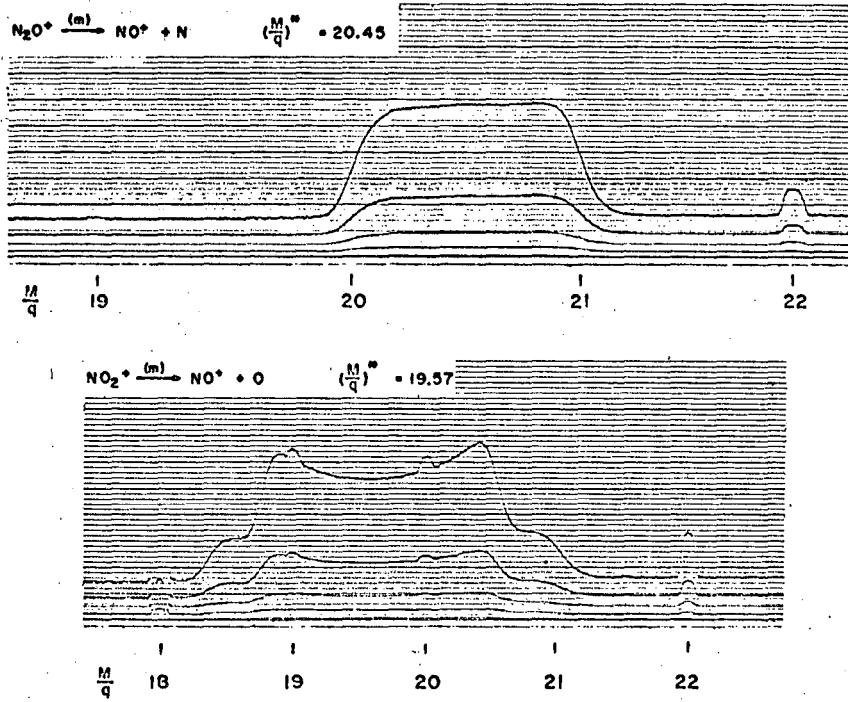
FOOTNOTES AND REFERENCES

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

1. G. M. Begun and L. Landau, J. Chem. Phys. 35, 547 (1961).
2. L. Friedman and A. P. Irsa, J. Chem. Phys. 36, 1082 (1962).
3. G. M. Begun and L. Landau, J. Chem. Phys. 36, 1083 (1962).
4. A. S. Newton and A. F. Sciamanna, J. Chem. Phys. 40, 718 (1964).
5. R. Fuchs and R. Taubert, Z. Naturforsch. 20a, 823 (1965).
6. V. H. Dibeler and H. M. Rosenstock, J. Chem. Phys. 39, 3106 (1963).
7. A. S. Newton, University of California Lawrence Radiation Laboratory Report UCRL-16483, "Metastable Peak Shapes in Dempster Type Mass Spectrometers," J. Chem. Phys. in press.
8. J. H. Beynon, R. A. Saunders, and A. E. Williams, Z. Naturforsch. 20a, 180 (1965).
9. J. A. Hipple, Phys. Rev. 71, 594 (1947)..
10. N. D. Coggeshall, J. Chem. Phys. 37, 2167 (1962).
11. This longer half life assumes that the two components are additive. The observed half-life of the combined peaks at the low mass maximum was $\sim 1.6 \times 10^{-6}$ sec over most of the time range. At each time point we have subtracted the shoulder from the total peak to arrive at the figure of 2.5×10^{-6} sec as given above. The shape of the peak comprising the shoulders is not known in the region under the peak of the low energy component.
12. M. C. Flowers, Chem. Communications 11, 235 (1965).

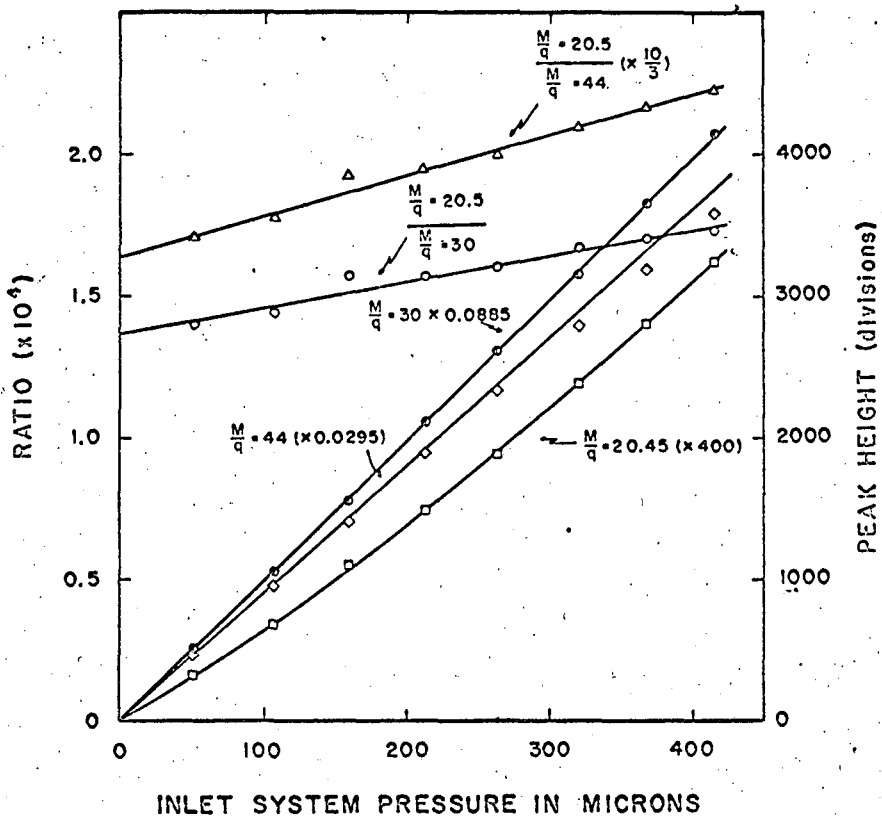
FIGURE CAPTIONS

- Fig. 1. Metastable peaks in the mass spectrum of N_2O and NO_2 . N_2O peak—Magnetic scan, $V_A = 3838$ V, Average repellers = 75 V, $V_I = 95$ V, Inlet pressure = 400 μ .
- NO_2 peak—Voltage scan, $MV_A = 11336$, repellers—1% V_A , $V_I = 70$ V, Inlet pressure = 300 μ .
- Fig. 2. Variation with inlet system pressure of peak heights and ratios of $M/q = 20.45$ to $M/q = 30$ and $M/q = 44$ peaks in N_2O . $MV_A = 45,100$, $V_R = 1.2\% V_A$.
- Fig. 3. Metastable suppressor cutoff curve of $M/q = 20.45$ in N_2O . $MV_A = 69,700$, $V_R = 1.8\% V_A$, inlet pressure = 400 μ .
- Fig. 4. Variation with inlet system pressure of peak heights and ratios of $M/q = 19.57$ and $M/q = 30$ and $M/q = 46$ in NO_2 . $M/q = 19.57$ scanned at $MV_A = 11,300$, $V_R = 1.2\% V_A$, $M/q = 30$ and 46 scanned at $MV_A = 45,200$, $V_R = 1.2\% V_A$.
- Fig. 5. Metastable suppressor cutoff curve for $M/q = 19.57$ in NO_2 . $MV_A = 11,300$, $V_R = 1.2\% V_A$, Inlet pressure = 300 μ .



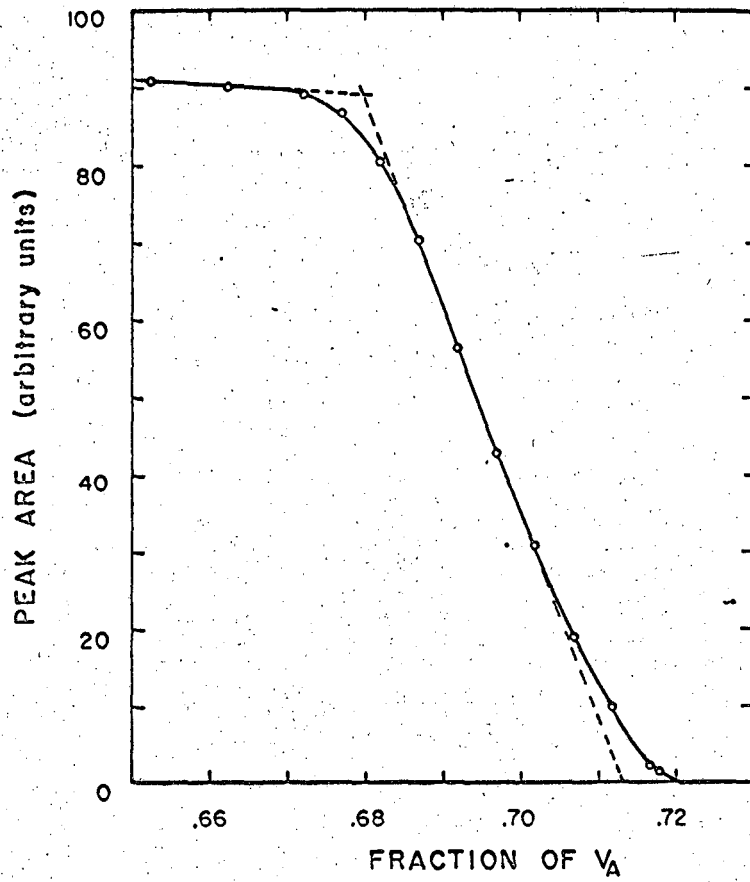
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Fig. 1



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Fig. 2



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Fig. 3

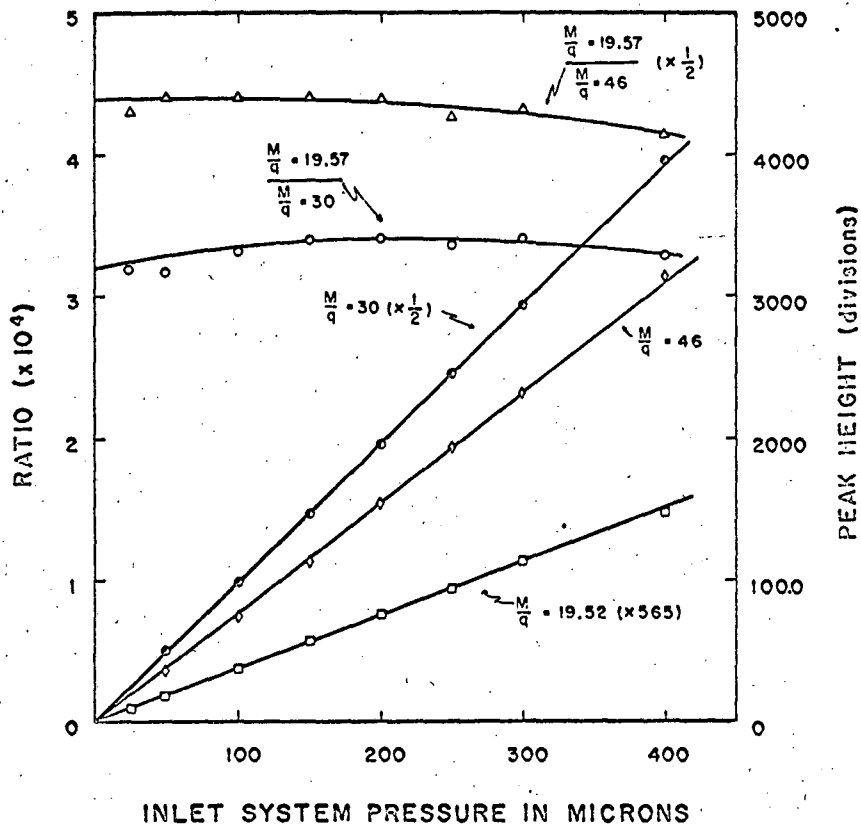


Fig. 4

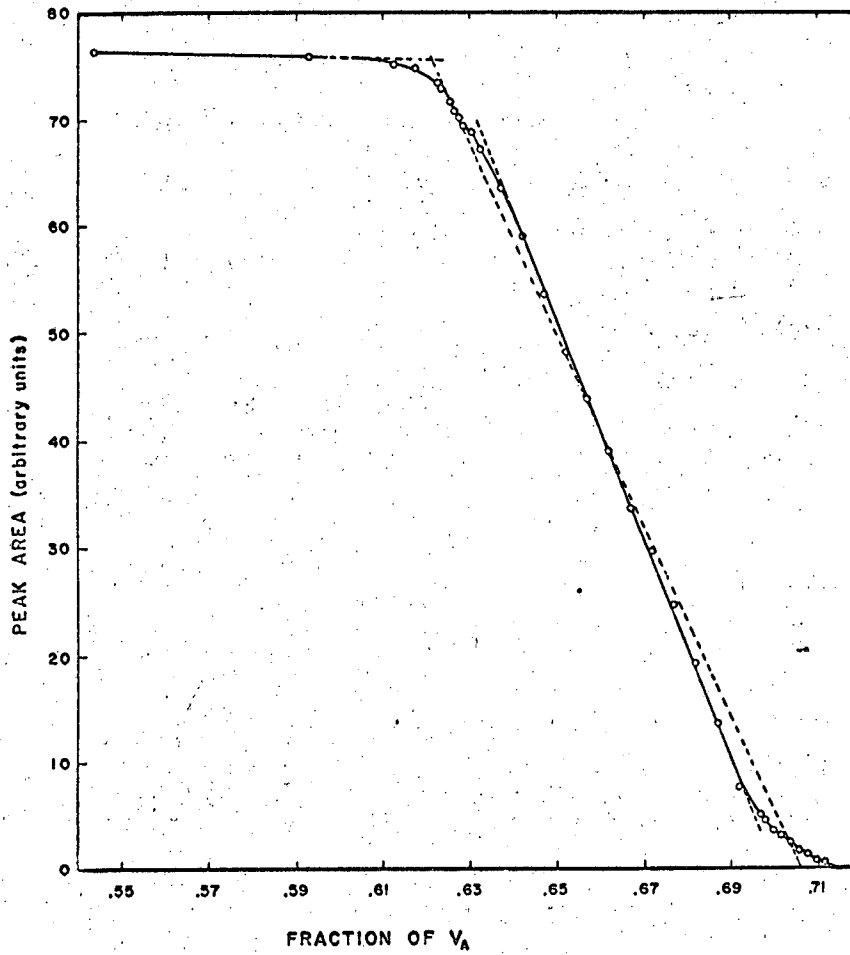


Fig. 5

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