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Jet expansions of ammonia readily induce condensation, so this phenomenon has long been used to make ammonia clusters for spectroscopic, thermochemical, and reactivity studies. (ny)

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CLUSTER PRODUCTION IN FREE-JET EXPANSIONS: CHLOROBENZENE  
SERDED IN AMMONIA

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(Abstract)

Molecular beams collimated from the free jet expansion of a 200:1 ammonia-chlorobenzene mixture were analyzed to obtain the relative intensities of the neutral clusters produced, and their dependences on nozzle pressure up to 1200 torr. A single-photon photoionization method was used. All species observed,  $(\text{NH}_3)_2$ ,  $(\text{NH}_3)_3$ ,  $(\text{NH}_3)_4$ ,  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ , and  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$ , rise rapidly from low pressure but decrease slowly to higher pressures, contrary to present understanding. Possible reasons for this behavior are discussed.

Jet expansions of ammonia readily induce condensation, so this phenomenon has long been used to make ammonia clusters for spectroscopic, thermochemical, and reactivity studies. These investigations have often encompassed mixed complexes of ammonia with other molecules, e.g. acetylene [1], benzene [2], carbon dioxide [3], chlorobenzene [4], phenol [5], pyrazine [2], pyrimidine [2], water [6], and many others [7]. However, none of this work, as far as we are aware, has addressed the very interesting problems of how specific clusters are produced in jet expansions, especially elucidation of the interdependence of their

production with other cluster species in the same expansions. In addition to its intrinsic importance, such an understanding of the jet-induced clustering process would have practical applications, for example the estimation of optimum conditions for the synthesis of particular ammonia-containing clusters for other studies. As a contribution to such a program, we report here the results of a study of the patterns of cluster formation in jet expansions of ammonia-chlorobenzene mixtures.

The experiments were carried out with the apparatus described in refs. [8,9], making use of a tunable vacuum ultraviolet beam provided by the National Synchrotron Light Source at Brookhaven National Laboratory. The composition of the expanding mixture was maintained at  $\text{NH}_3:\text{C}_6\text{H}_5\text{Cl} = 200:1$  by bubbling ammonia at 2400 torr through chlorobenzene temperature-controlled at  $25.0^\circ \text{C}$ . Of several compositions tried in preliminary experiments this one provided the highest yields of  $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$  ions in our apparatus. The diameter of the nozzle orifice was 0.100 cm. The effective beam temperatures, calculated from an empirical expression [8], ranged from 35 K to 16 K for nozzle pressures of 200 to 1200 torr, assuming that  $C_p/C_v = 1.305$  for  $\text{NH}_3$  at 300 K (ref. [10]).

To obtain the nozzle pressure dependences of the beam densities of the neutral clusters in the molecular beam collimated from the jet, the technique described in ref. [11], extended as suggested in ref. [12], was used. Here, using photoionization mass spectrometry one first measures either the ionization potential (IP) of the cluster of interest via detection of the parent ion, or the appearance

potential (AP) of a dissociative ionization product characteristic of that cluster. The VUV light is then tuned to measure the yield of this ion at an energy just below its onset from any larger cluster, typically 0.1-0.15 eV higher than its IP or AP. Since only the neutral cluster of interest now yields detectable ions, its beam density, apart from a constant factor, can be measured directly as a function of the expansion conditions. Table 1 gives the ion that was used for each cluster, together with its measured AP or IP and the wavelength at which the measurement of its beam number density was made. The AP's of  $\text{NH}_4^+$  from  $(\text{NH}_3)_2$  and  $(\text{NH}_3)_2\text{H}^+$  from  $(\text{NH}_3)_3$  are in satisfactory agreement with prior work [13,14]. Once the pressure dependences of the beam densities of the various components were known, their quantitative relationship with respect to each other was evaluated from the data by simple calculations, subject, as a boundary condition, to the known pressure dependence of the total mass transported by the beam. The latter was measured in ancillary experiments using a nude ion gauge. Of course one also needs to know the pressure dependences of the monomers; these were obtained from measurements of the yields of products that require such high energies for their formation that they are essentially not formed from clusters [9], viz.  $\text{C}_6\text{H}_5^+$  for chlorobenzene and  $\text{NH}_2^+$  for ammonia. It was assumed that the beam densities of  $(\text{C}_6\text{H}_5\text{Cl})_2$  and  $(\text{C}_6\text{H}_5\text{Cl})_2\text{NH}_3$  were negligible, because their parent ions could not be detected; as a check it was found that  $(\text{C}_6\text{H}_5\text{Cl})_2^+$  is formed strongly in chlorobenzene-argon expansions. For comparison with the results of the measurements described above, an attempt was made to analyze

the same beams using the approximate method described in ref. [9]. Unfortunately this method could not be applied here because the quantity  $M$  defined in that paper (intensity of monomer ion produced by dissociative ionization of dimers and larger clusters) could not be measured to nozzle pressures lower than 300 torr.

Figure 1, panels a to e, show the measured pressure dependences for the neutral clusters  $(\text{NH}_3)_2$ ,  $(\text{NH}_3)_3$ ,  $(\text{NH}_3)_4$ ,  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ , and  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$ . The data were represented by smooth curves, as shown, to facilitate the analysis. Figure 2 presents the analysis of the molecular beam as a function of nozzle pressure. The number densities of ammonia and its homoclusters are shown in fig. 2a, while fig. 2b depicts the fraction of the total ammonia disposed into specific species. The amount of ammonia clustered with chlorobenzene is much too small to show up on these plots. Similarly, fig. 2c presents the number densities of  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$ , and, by difference,  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_3$ , while fig. 2d shows the disposal of the total chlorobenzene. The scale of fig. 2a is a factor 80 larger than the scale of fig. 2c. In fig. 3 the nozzle pressure dependences of  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$  and  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$  are compared with that of  $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$ , where simple spectrum-stripping is applied to estimate the contributions of heterodimer and heterotrimer. Above 400 torr most of the heterodimer ion is produced by the dissociative ionization of tetramers and larger clusters, reaching about 90% by 900 torr.

The largest number density of  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$  occurs already at 350 torr, while the largest conversion of chlorobenzene to dimer is at 225 torr. At the dimer's peak the

$\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$  is about half as abundant as the  $\text{C}_6\text{H}_5\text{Cl} \cdot \text{NH}_3$ , but at half its peak density, near 180 torr, the trimer contamination is still about 10%. Monomeric chlorobenzene and ammonia retain a higher number density than any one of the clusters in which they participate, although half of the total ammonia is clustered by 200 torr, and half of the total chlorobenzene by 400 torr. One sees from figs. 2b and 2d that by 1000 torr numerous larger clusters than those measured are undoubtedly present.

All five of the clusters are characterized by a relatively rapid rise in density from low nozzle pressures, with the simpler clusters rising before the more complex, e.g. the dimers before the trimers, etc., a behavior predicted by both kinetic and thermodynamic mechanisms [11,15]. On the other hand, as already observed in other systems [11] the beam densities decrease only slowly with increasing nozzle pressure, a phenomenon not predicted by either mechanism. The hypothesis that this tailing comes from rescattering in the jet is inconsistent with the results of expansions in which a noble gas was the dominant component [15,16], because in these systems the beam densities of given clusters become strongly damped at pressures higher than their maxima. If this should prove to be a systematic effect it would be an important mechanistic clue. For the present, we speculate that the beam density of small clusters at higher nozzle pressures is sensitive to the molecular structure of the monomeric components, possibly via their vibrational modes. The imperfect correlation of the ease of formation of dimers with their dissociation energies [16] may also be evidence that

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molecular structure plays a significant role. Clearly, analyses such as the one reported here are needed for a much larger variety of mixtures.

The similarity in the onset and peak pressures of  $(\text{NH}_3)_2$  and  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$  suggests that their dissociation energies are similar. In fact, measurements using the technique of ref. [8] show that the dissociation energy of  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$  is roughly  $2 \text{ kcal mol}^{-1}$  [17], while single-photon dissociation shows that  $D(\text{NH}_3)_2 < 2.8 \text{ kcal mol}^{-1}$  [18]. It seems possible that the analysis of jet expansions of mixed gases could be developed into a useful technique to measure the dissociation energies of neutral clusters.

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Table 1  
 Probe ions used, their IP/AP's, and photon energies chosen  
 for the measurements

cluster	M/e used	photon energy (eV)		
		threshold	used for measurement	used for background
(NH <sub>3</sub> ) <sub>2</sub>	18	9.509	9.671	9.450
(NH <sub>3</sub> ) <sub>3</sub>	35	9.096	9.225	9.024
(NH <sub>3</sub> ) <sub>4</sub>	52	9.02 <sup>a)</sup>	9.150	8.952
C <sub>6</sub> H <sub>5</sub> Cl·NH <sub>3</sub>	93	8.845	8.978	8.787
C <sub>6</sub> H <sub>5</sub> Cl·NH <sub>3</sub>	94	8.926	9.057	8.862
C <sub>6</sub> H <sub>5</sub> Cl(NH <sub>3</sub> ) <sub>2</sub>	146	8.640	8.965 <sup>b)</sup>	8.592

<sup>a)</sup> Ref. [13]

<sup>b)</sup> Ancillary experiments showed that at this energy interference from tetramers, etc., is still negligible.

Fig 1. Nozzle-pressure dependence of number densities of neutral clusters in the molecular beams, measured as described in the text. (a)  $(\text{NH}_3)_2$ , measured via  $\text{NH}_4^+$ . (b)  $(\text{NH}_3)_3$ , via  $(\text{NH}_3)_2\text{H}^+$ . (c)  $(\text{NH}_3)_4$ , via  $(\text{NH}_3)_3\text{H}^+$ . (d)  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$ , via  $\text{C}_6\text{H}_5\text{NH}_2^+$  (O's) and  $\text{C}_6\text{H}_5\text{NH}_3^+$  (+'s). (e)  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$ , via  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2^+$ . The smooth curves drawn through the data points were used to obtain the results shown in figs. 2 and 3.

Fig 2. Number densities of neutral clusters in the molecular beams, shown in relationship with each other. (a) Ammonia and its homoclusters. (b) Fraction of total ammonia disposed into monomer and homoclusters. (c) Chlorobenzene and its heteroclusters. (d) Fraction of total chlorobenzene disposed into monomer and heteroclusters. Relative ordinate uncertainties, about one s.d., are: monomers,  $\pm 5\%$ ; dimers,  $\pm 10\%$ ; trimers and tetramers,  $\pm 30\%$ .

Fig 3. Yield of  $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$  at 700 Å as a function of nozzle pressure. The solid curves indicate the approximate resolution of these data into contributions from the photoionization of neutral  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3$  and  $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_3)_2$ , the dashed curve being their sum. The remainder of the  $(\text{C}_6\text{H}_5\text{Cl}\cdot\text{NH}_3)^+$  comes from the dissociative ionization of larger clusters.

RELATIVE NUMBER DENSITY IN BEAM

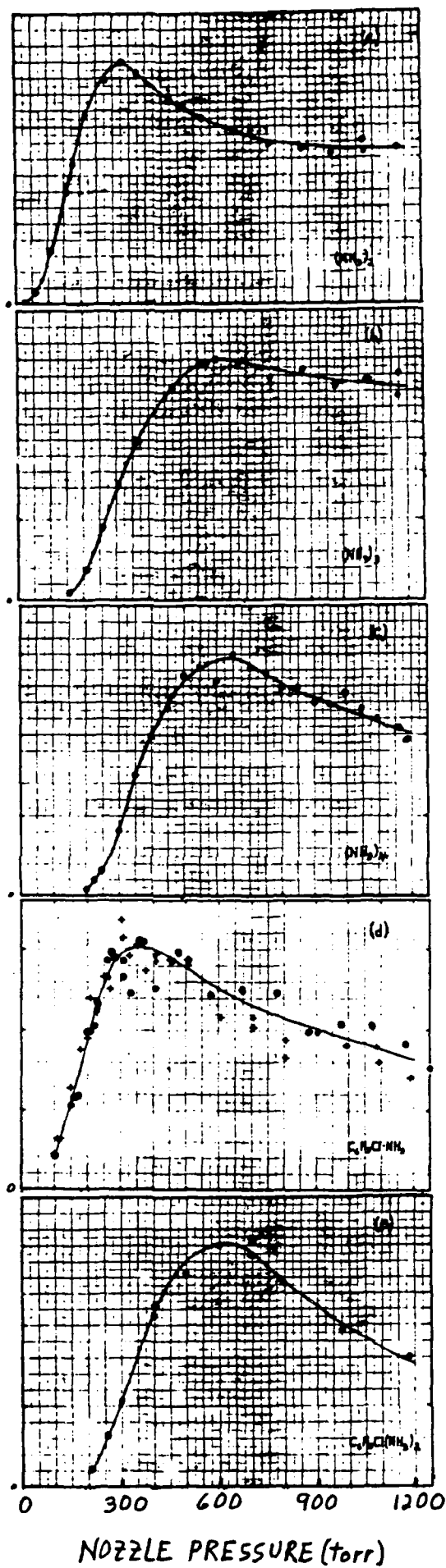


Fig. 1

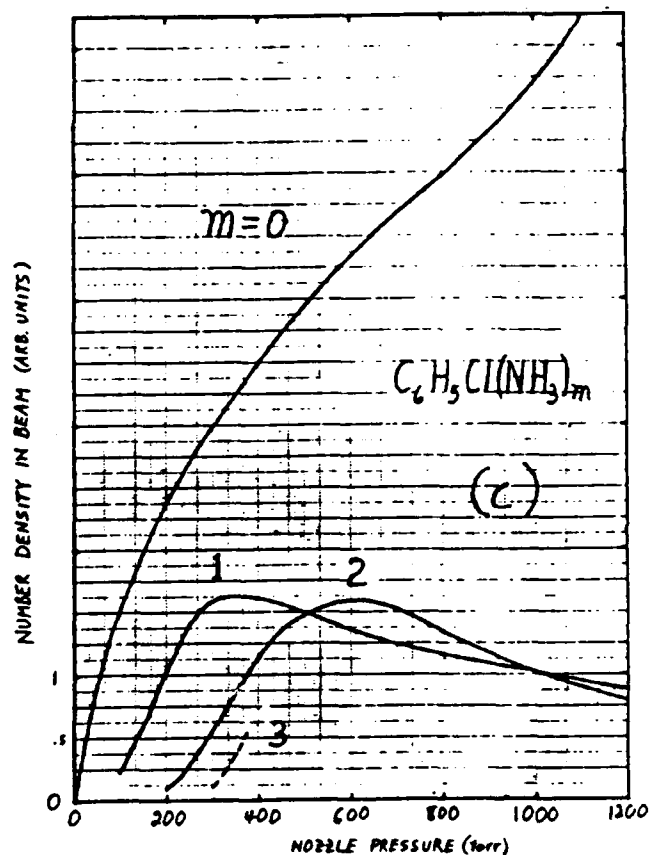
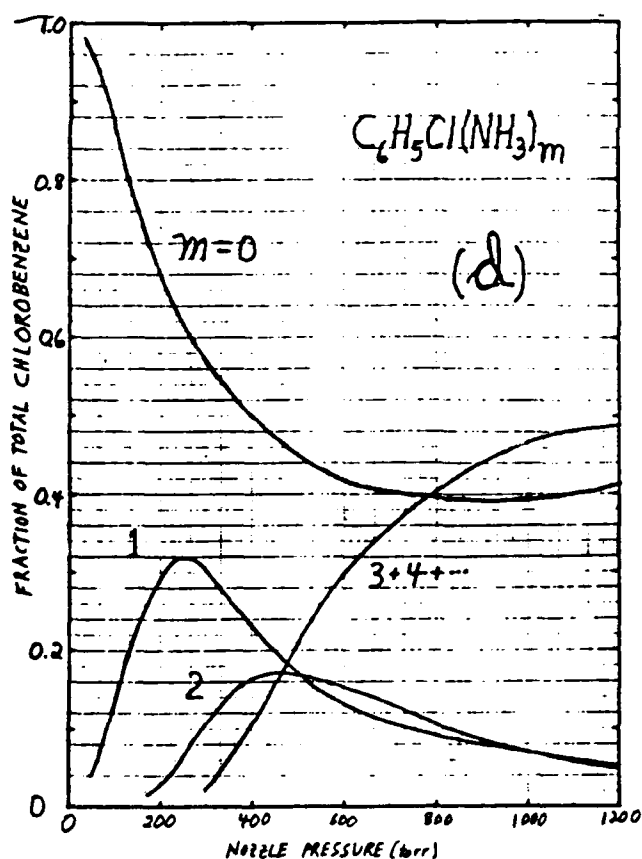
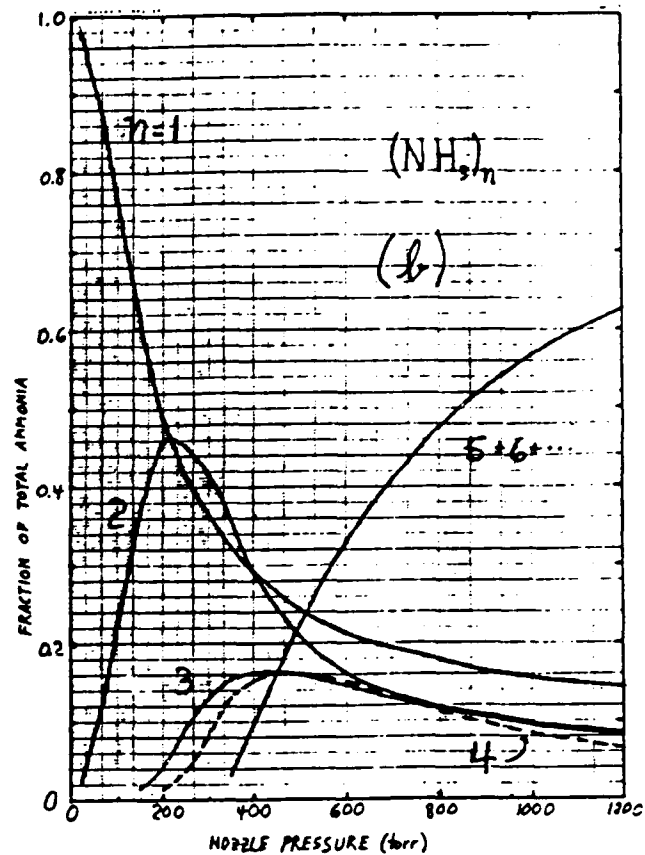
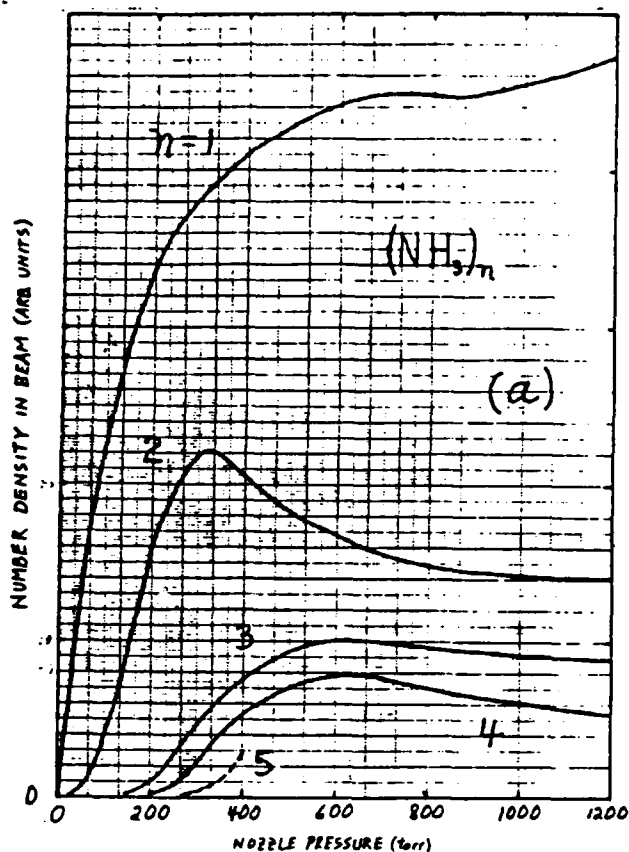


Figure 2

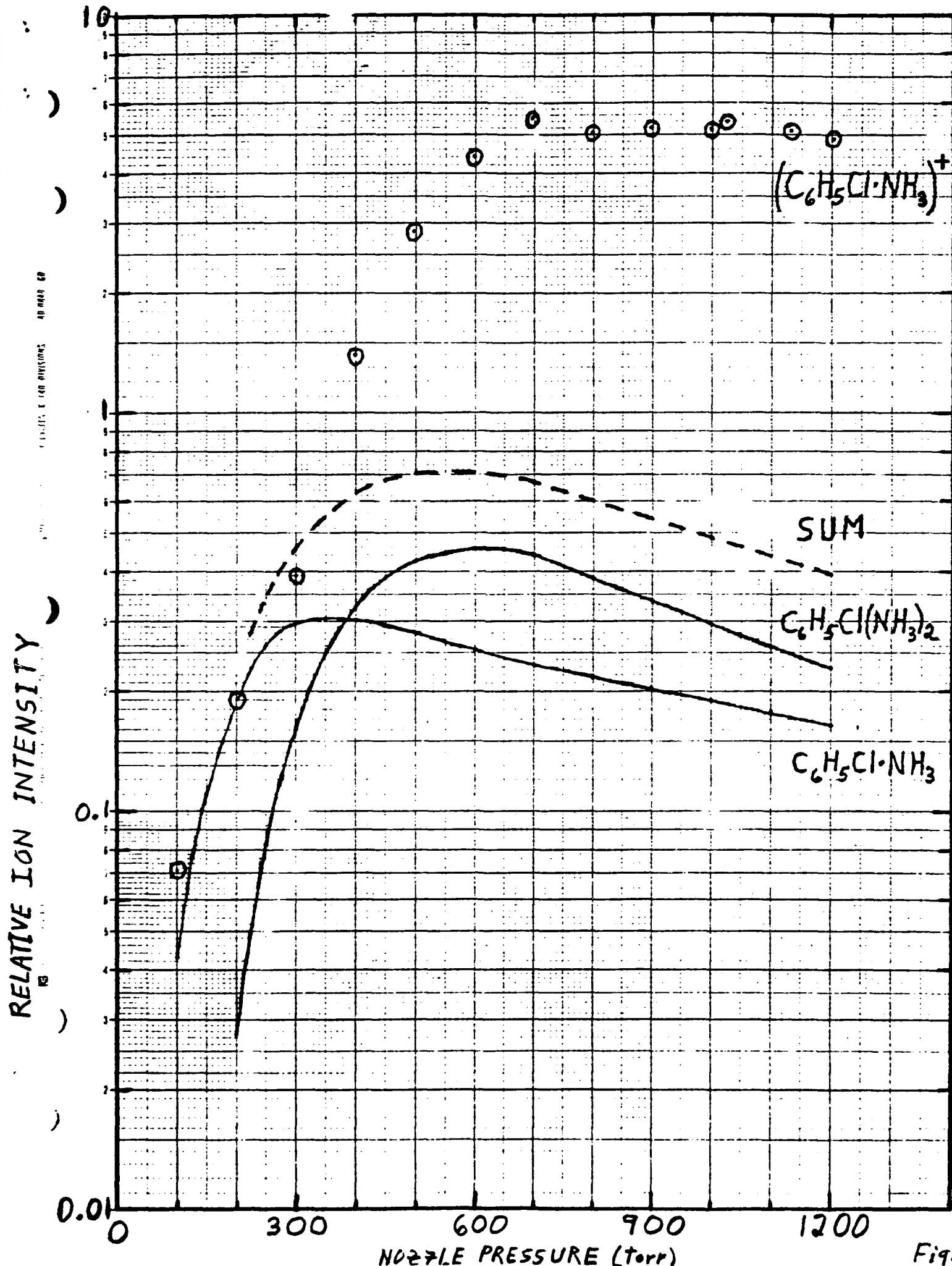


Fig. 3