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Production of carbon disulphide dimers by an adiabatic gas expansion method

Andrzej Pelc, Leszek Michalak*

Institute of Physics, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

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Abstract

The production of carbon disulphide dimers by adiabatic gas expansion of a mixture comprised of CS_2 vapour and Ar is studied by using an electron impact ion source and a double focusing sector field mass spectrometer. Results of measurements of the generation of $(CS_2)_2^+$ cluster ions versus the stagnation pressure (0–160 kPa) at several stagnation temperatures (267–300 K) are described. An empirical formula describing the carbon disulphide dimer production is proposed. (Int J Mass Spectrom 194 (2000) 85–91) © 2000 Elsevier Science B.V.

Keywords: Gaseous cluster; Carbon disulphide

1. Introduction

If a gas expands from a high pressure chamber through a small orifice (nozzle) into a vacuum, then production of neutral gaseous clusters can be observed. In this process collisions of molecules during the hydrodynamic expansion give rise to the unique properties of a supersonic beam, i.e. cooling of the rotational, vibrational, and translational degrees of freedom and condensation via supersaturation [1–3]. The amount of condensation is determined by the structure and energetic properties of molecules, the gas stagnation pressure p_o and its temperature T_o, the diameter D and the shape of the expansion nozzle, and the temperature T of the expanded beam [4–7]. The shape of the nozzle influences the time of the gas expansion and the size of generated clusters (number of atoms or particles per cluster). Variation of the temperature T with the distance x from the nozzle is

$$T(x) = T_o C(\gamma)(x/D)^{2-2\gamma} \tag{1}$$

where $C(\gamma)$ is a constant depending on γ and $\gamma = C_p/C_v$ [8].

The temperature T_b of the expanded beam (when collisions between molecules become negligible) can be calculated from [9,10]

$$T_b \cong T_o[1 + 0.585(\gamma - 1)(\lambda/D)^{-0.8}]^{-1} \tag{2}$$

where λ is the mean free path of the gas in the stagnation chamber. All these variables define the conditions of the gas flow and thus the condition of cluster formation. For a given gas and shape of the nozzle, only two parameters, i.e. T_o and p_o influence the amount of condensation, from a practical point of

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* Corresponding author. E-mail: michalak@tytan.umcs.lublin.pl

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view. The maximum pressure of the gas in the stagnation chamber is limited by the pumping speed of the particular vacuum system. For liquid probes the maximum driving pressure is limited by their vapour pressure. For these probes an inert rare gas may be added to increase the pressure and finally, to enhance the effect of adiabatic expansion [11–14].

Usually the expanded beam is introduced through a skimmer to an ion source of a mass spectrometer for analysis [15–17]. If the energy of electrons or photons colliding with clusters in the ion source is greater than the critical value, some of the neutral clusters will be ionised.

Studies have shown that the yield and size of generated clusters are not a simple function of the parameters T_o and p_o. Moreover, these dependencies are different for different sizes and clusters of the same gas. Therefore, in many articles these dependencies are reported for small gaseous clusters, in particular for dimers. Investigations of dimers are important because these clusters are considered to exhibit the properties, structure, stability, and chemical behaviour of their higher homologues. Studies of the dimers Ar_2, $(H_2)_2$, Ne_2, $(N_2)_2$, and $(NO)_2$ have shown that the intensity I^+ of the respective cluster ion signals are given by

$$I^+ \sim \frac{p_o^\alpha}{T_o^{\alpha\beta}} \tag{3}$$

where α and β are constants that depend on the gas investigated [18–24]. Values of these parameters range from 1–2.8 for α and 1–2.85 for β for gases mentioned above. Generally, for these gases and the established temperature T_o, the intensity of generated dimers does not decrease versus the gas stagnation pressure p_o.

A quite different situation prevails for liquid probes for which the maximal driving pressure is limited by their vapour pressure. In these cases the increase of pressure in the gas stagnation chamber by using an inert rare gas enhances the effect of adiabatic expansion, but at the same time the percentage abundance of the investigated sample decreases in the expanded beam [25]. For these cases an optimal pressure p_o for the established temperature T_o is observed, in terms of the dimer [26].

In this work results of measurements of the generation of carbon disulphide dimers and their homologues versus the stagnation pressure p_o (0–160) at several temperatures T_o (280–300) are presented.

2. Experimental

The apparatus used for measurements presented here was described in detail previously [27–29]. Briefly, the gas mixture (CS_2/Ar) expands through a 40 μm nozzle (a round orifice in the wall of 0.15 mm thickness) into an evacuated chamber ($p \leq 10^{-1}$ Pa) pumped by a diffusion pump (800 L s^{-1}). The expansion region is separated from the ion source by a conical skimmer (0.4 mm inner diameter) at 0.7 cm distance from the nozzle. The cluster beam is introduced to the ion source [($p \leq 10^{-4}$ Pa) pumped by diffusion pump 700 L s^{-1}] where it is crossed with an electron beam. The cluster ions produced are analysed by a double focusing sector field mass spectrometer. An oscilloscope and computer counting system is used for data acquisition.

The ion source pressure is controlled by a Balzers Compact Full Range Gauge PKR 250 (Pfeiffer Vacuum GmbH, Asslar) placed on the axis of the cluster beam at a distance 12 cm from the ion source. The pressure of the ionisation chamber is estimated to be higher by a factor of 10.

The stagnation pressure of the investigated sample is controlled by the Balzers Compact Piezo Gauge APR 262 and the temperature by the chromel-alumel thermocouple placed near the nozzle. In all experiments presented here the pressure in the gas stagnation chamber was varied in the range 0–160 kPa. For pressures higher than 160 kPa, the vacuum in the evacuated region deteriorates significantly.

3. Results and discussion

The carbon disulphide (99+%, spectrometric grade) and argon (>99.998%) were purchased from

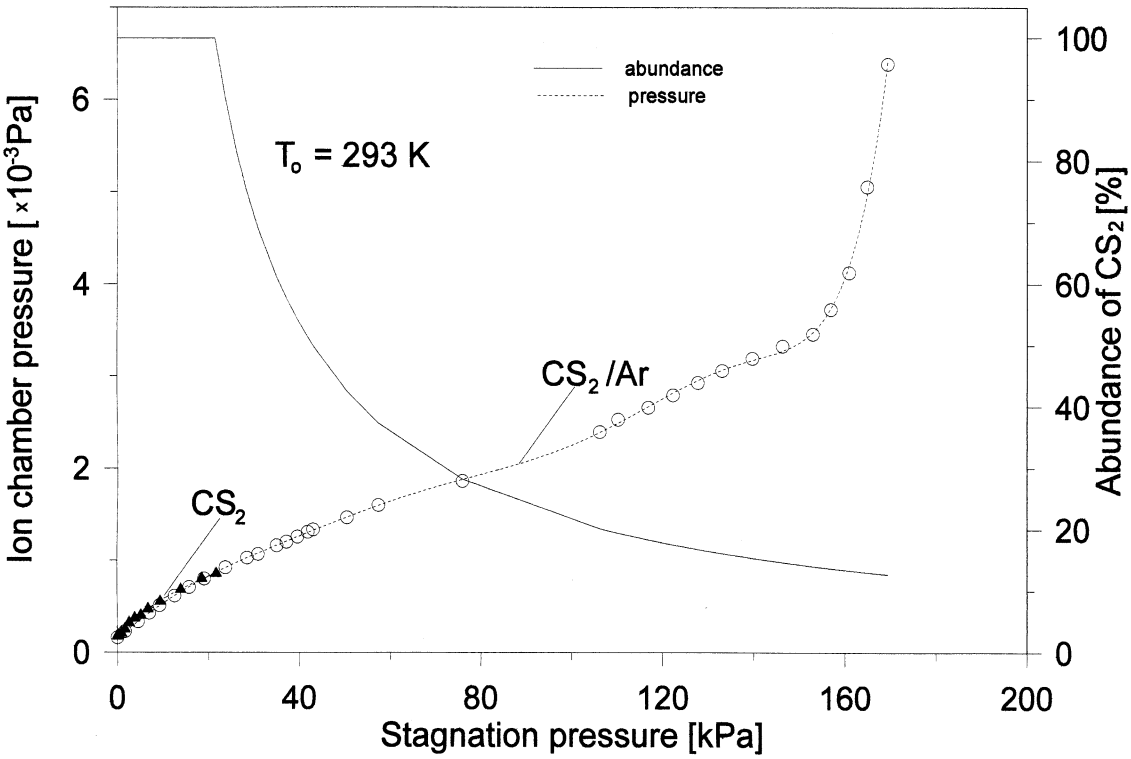

Fig. 1. The estimated ionisation chamber pressure (filled triangle for pure CS_2 and circle for CS_2/Ar mixture) and the percentage abundance of CS_2 in the expanded beam vs. the gas stagnation chamber pressure p_o at the temperature $T_o = 293$ K.

Aldrich Chemical (Milwaukee, WI) and Marc Schuchardt (München), respectively, and were used for investigations that are presented here without further purification.

Fig. 1 shows the estimated ionisation chamber pressure versus the gas stagnation pressure p_o at the temperature $T_o = 293$ K, for two cases of the expanded beam: CS_2 (carbon disulphide vapour in the gas stagnation chamber, only) and CS_2/Ar (mixture of CS_2 and Ar). Clusters $(CS_2)_n$ were observed for the CS_2/Ar beam, only. In the same figure the percentage abundance of CS_2 in the expanded beam is also marked.

The typical mass spectrum of $(CS_2)_n^+$ ($n \leq 11$) clusters and their homologues acquired with a total gas pressure in the gas stagnation chamber of 133 kPa at 280 K temperature, is shown in Fig. 2. Moreover, this mass spectrum shows a broadening of peaks with increasing mass. This is due to fragmentation processes of the cluster. These peaks cause the metastable ion decay, which occurs in different places along the trajectory of ions between the ion source and the ion detector [1,2].

The dimer $(CS_2)_2^+$ ion current as a function of the pressure of the mixture CS_2/Ar in the stagnation chamber at several stagnation temperatures is presented in Fig. 3(a). Fig. 3(b) shows normalized ion current intensities for observed homologues at temperatures 273 K and 300 K. All of the dependencies presented in Fig. 3 have the same character. For each of the temperatures T_o (except $T_o = 267$ K of dimers and $T_o = 273$ K for homologues) we observe an optimal pressure p_{opt} for which the dimer–ion current intensity is highest. This optimal pressure as well as the maximal intensity of the ion current is lower for higher temperatures of the gas in the

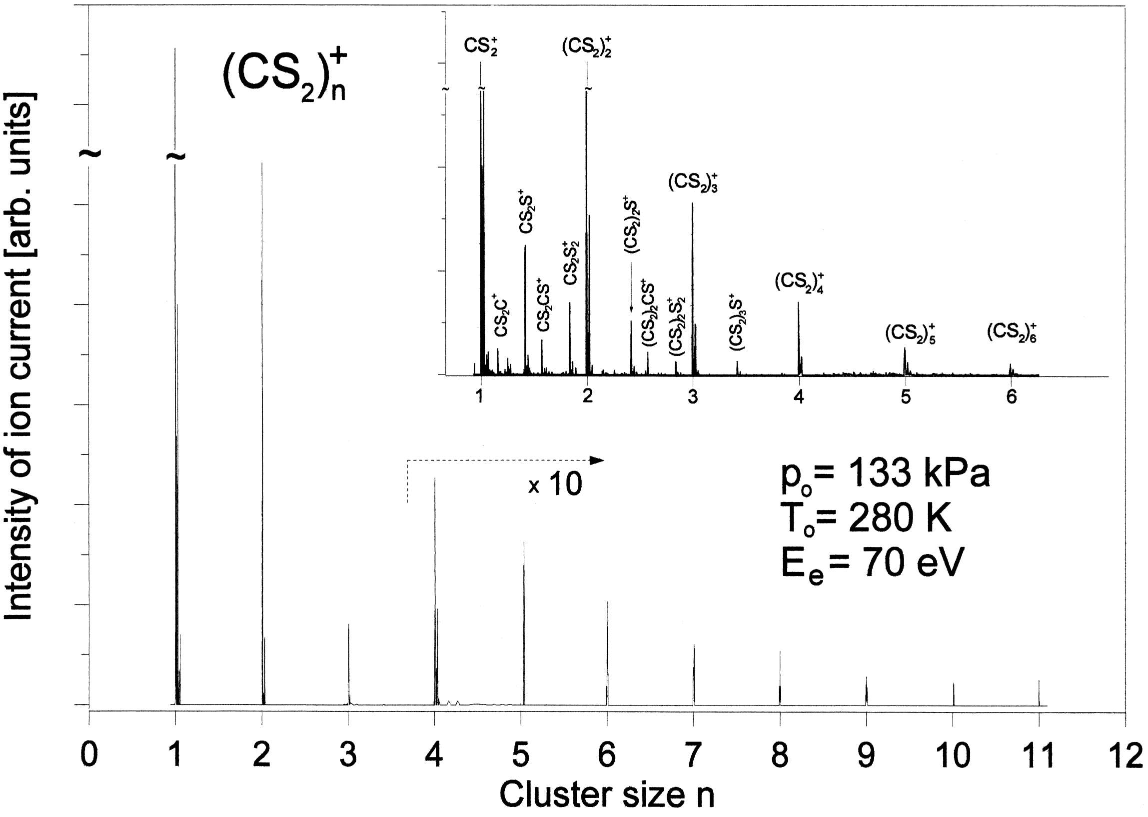

Fig. 2. The electron impact mass spectrum of carbon disulphide clusters. The total pressure (CS_2 + Ar) in the gas stagnation chamber is 133 kPa at $T_o = 280$ K. Electron energy and the intensity of the electron beam is 70 eV and 40 μA, respectively.

gas stagnation chamber (see Fig. 4). Similar dependencies for the $(H_2O)_n$ clusters were observed by Haberland et al. [26].

The simple interpretation of results presented here is more complicated than in the gas case. Clusters $(CS_2)_n$ are produced by collisions of particles during the hydrodynamic expansion of the CS_2/Ar mixture. In this process the following reactions take place:

$$CS_2+(CS_2)_n \rightarrow (CS_2)_{n+1} \tag{4a}$$

$$\rightarrow (CS_2)_{n-1} + CS_2+CS_2 \tag{4b}$$

$$Ar+(CS_2)_n \rightarrow Ar(CS_2)_n \tag{5a}$$

$$\rightarrow Ar+(CS_2)_{n-k} + (CS_2)_k \tag{5b}$$

$$Ar+Ar_n \rightarrow (Ar)_n \tag{6}$$

$$n = 1,2,3, \ldots; k = 0,1, \ldots, n-1.$$

In our investigations for applied temperature T_o and pressure p_o we do not observe clusters from reactions (5a) and (6). The low intensity of clusters with $n > 3$ (see spectrum) suggests that in the production of dimers $(CS_2)_2$, reactions (4a), (4b), and (5b) for $n \leq 3$ can play a significant role. The observed intensity I^+ of dimer ion currents results from: (1) the total number of collisions of molecules in the expanded beam from the nozzle to the distance x_b, where the temperature of this beam is T_b [see Eqs. (1) and (2)], and (2) various electron ionisation processes of $(CS_2)_n$ clusters in the ion source of the mass spectrometer:

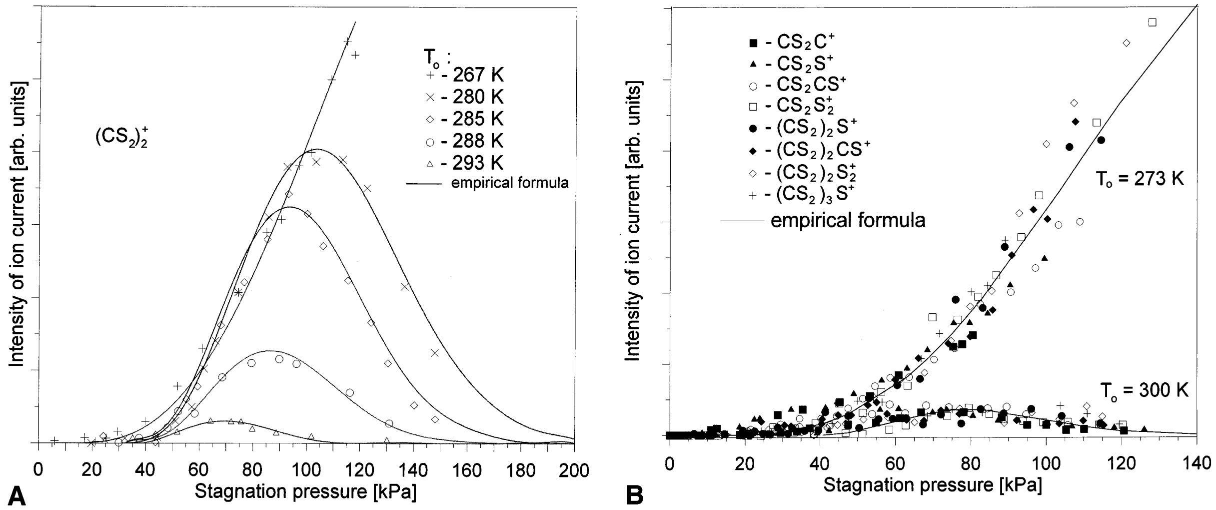

Fig. 3. The intensities of (a) $(CS_2)_2^+$ and (b) observed homologous ion currents as a function of the stagnation pressure p_o of the mixture CS_2/Ar at several temperatures T_o at $E_e = 80$ eV, $I_e = 40$ μA.

$$(CS_2)_n + e \rightarrow (CS_2)_n^* + e \qquad \rightarrow (CS_2)_n + h\text{v} + e \qquad \text{-fluorescence} \tag{7}$$

$$\rightarrow (CS_2)_n + (CS_2)_k + e \qquad \text{-predissociation} \tag{8}$$

$$\rightarrow (CS_2)_n^+ + 2e \qquad \text{-autoionisation} \tag{9}$$

$$\left.\begin{array}{l} \rightarrow (CS_2)_{n-k}^+ + (CS_2)_k + 2e \\ \rightarrow (CS_2)_{n-k-1}CS + S + (CS_2)_k + 2e \\ \rightarrow (CS_2)_{n-k-1}S^+ + CS + (CS_2)_k + 2e \\ \rightarrow (CS_2)_{n-k-1}C^+ + S + S + (CS_2)_k + 2e \end{array}\right\} \quad \begin{array}{l}\text{-autoionisation/} \\ \text{fragmentation}\end{array} \tag{10}$$

$$\rightarrow [(CS_2)_n^+]^* + 2e$$

$$\rightarrow (CS_2)_n^+ + h\text{v} + 2e \qquad \text{-ion fluorescence} \tag{11}$$

$$\left.\begin{array}{l} \rightarrow (CS_2)_{n-k}^+ + (CS_2)_k + 2e \\ \rightarrow (CS_2)_{n-k-1}CS^+ + S + (CS_2)_k + 2e \\ \rightarrow (CS_2)_{n-k-1}S^+ + CS + (CS_2)_k + 2e \\ \rightarrow (CS_2)_{n-k-1}C^+ + S + S + (CS_2)_k + 2e \end{array}\right\} \quad \text{-ion fragmentation} \tag{12}$$

for $n = 1,2, \ldots$; $k = 0,1, \ldots (n - 1)$, and $s = 0,1, \ldots (n - k - 1)$.

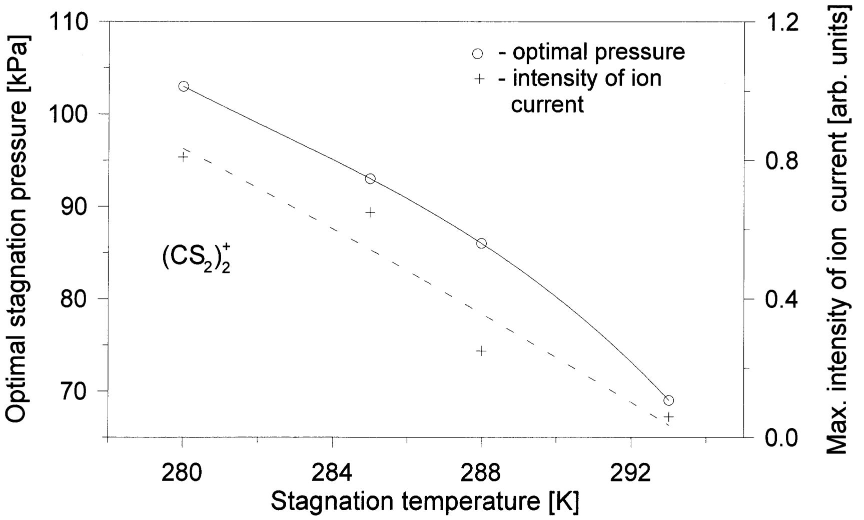

Fig. 4. The optimal pressure (solid line) for production of $(CS_2)_2^+$ ion clusters and the maximal intensity of ion current (dashed line) as a function of the stagnation temperature.

In these experiments the density n_{Ar} of argon increases with the increase of the pressure (CS_2 + Ar) in the gas stagnation chamber. The ratio of specific heats changes from $\gamma_{CS_2} = 1.23$ to $\gamma_{Ar} = 1.67$, proportional to the abundance of CS_2 in the expanded gas. In our case the abundance of CS_2 changes from 100% to 13% in the investigated pressure range. Moreover, for the different concentrations of expanded beams, the temperatures T_b for which collisions between molecules become negligible, as well as the number of reactions (4a), (4b), and (5b), also differ. Therefore the simple theoretical construction of the formula describing the intensity of the dimer ion current as a function of the pressure p_o and temperature T_o is difficult.

On the basis of our results we constructed the empirical formula (13) that describes well the intensity I^+ of the carbon disulphide dimer ion current as a function of p_o and T_o,

$$I^+ \sim \frac{(p_o - p_{ap})^3}{\exp\left(\frac{(p_o - p_{ap})^2}{\alpha T_o}\right)} \tag{13}$$

where p_{ap} is an appearance pressure of an observed cluster, dependent on the cluster/size and temperature T_o, and α is a fitted parameter dependent on temperature T_o for established cluster size.

Table 1
Values of parameters p_{ap} and α for the curves presented in Fig. 3(a)

T[K]	P_{ap} [kPa]	α[10^6 Pa/K]
267	20	66
280	31	12.5
285	35	9.1
288	37	7.1
293	40	3.3

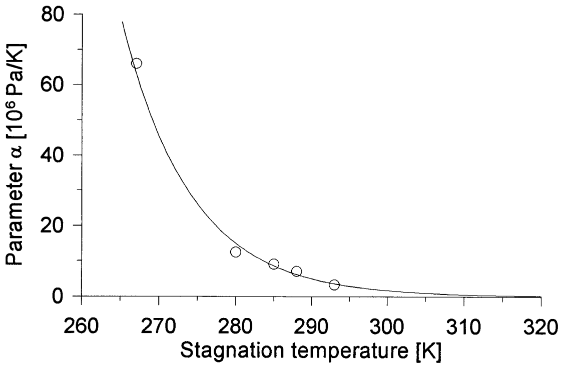

Fig. 5. The values of parameter α as a function of temperature T_o of a CS_2/Ar mixture in the gas stagnation chamber.

This formula is the first proposed formula for liquid probes, to our knowledge. We reported the results of measurements of the appearance pressure for $(CS_2)_n^+$ $(n \leq 8)$ clusters previously [27]. Table 1 shows the values used for the parameters p_{ap} and α for the curves presented in Fig. 3(a). Fig. 5 shows the values of the parameter α as a function of temperature T_o.

4. Conclusion

The double focusing sector field mass spectrometer was applied for investigations of $(CS_2)_2$ clusters, produced by the adiabatic gas expansion. For liquid probes the presence of an inert gas in the expanded beam plays an important role in the cluster production. At higher pressures, collisions between molecules of the gas sampled and inert gas occur very frequently and may lead to the cluster destruction. The results presented here show that the intensity of a carbon disulphide dimer is not a simple function of pressure and temperature of the gas in the stagnation chamber. For this case the optimal pressure for different temperatures T_o is observed. On the basis of these results we derived an empirical formula that described well the intensity of carbon disulphide dimer ion current as a function of p_o and T_o. This formula is the first proposed for liquid probes, to our knowledge.

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