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INVESTIGATION OF COLLISION-INDUCED FLUORESCENCE IN
D2:AR AND D2:HD:AR MIXTURES AT 200 K(U) MATERIALS
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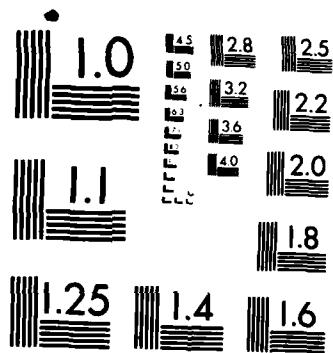
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REPORT
MRL-R-967

**INVESTIGATION OF COLLISION-INDUCED FLUORESCENCE IN
D₂:Ar AND D₂:HD:Ar MIXTURES AT 200 K**

R.C. McLeary and D.P. Juchnevicius

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ABSTRACT

The collision-induced fundamental-band fluorescence from vibrationally-excited D₂^v in high-pressure mixtures of D₂^v and Ar and D₂^v, HD and Ar has been investigated. Fluorescence intensity and vibrational lifetime have been measured at 200 K as a function of pressure and mixture ratio. The results indicate that a D₂^v:HD:Ar mixture at reduced temperature is an attractive candidate medium for an optically-pumped collision-induced-dipole laser.

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Investigation of collision-induced fluorescence in
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INVESTIGATION OF COLLISION-INDUCED FLUORESCENCE IN

D₂:Ar AND D₂:HD:Ar MIXTURES AT 200 K

1. INTRODUCTION

A previous paper [1] reported experimental fundamental-band fluorescence results obtained when high-pressure mixtures of D₂ and Ar at room temperature were optically excited by the output of a pulsed hydrogen-fluoride (HF) laser. The work reported formed part of a program investigating the possibility of achieving laser action in optically-excited high-pressure gas mixtures via the collision-induced-dipole effect. A subsequent paper [2] reported a measured value of 0.015 cm⁻¹ for the collision-induced gain coefficient at 4 μm in a room-temperature mixture of D₂ and Ar (1:2) at a total density of 730 amagat. (One amagat is the density at STP.) Due to various practical difficulties associated with the design of a potential laser based on the collision-induced-dipole effect, it is necessary to achieve gain coefficients larger than the 0.015 cm⁻¹ value obtained so far. As indicated in [2], there are two ways in which increased gain may be achieved. One is to decrease the temperature of the gas mixture. This alters the population distribution over the rotational levels of the molecule in a favourable way. It also increases the vibrational lifetime, allowing longer and more energetic pumping pulses to be employed. Both of these should lead to enhanced gain. The other method of increasing the gain is to increase the absorption of the pump radiation by the addition of hydrogen deuteride (HD) to the gas mixture. Hydrogen deuteride has an absorption coefficient [3] of approximately five times that of D₂ [4] at the pump wavelengths. The energy absorbed by the HD molecules is rapidly transferred to D₂ during collisions [5].

This report presents results of a fluorescence experiment in which high-pressure mixtures of D₂ and Ar and D₂, HD and Ar at a temperature of 200 K are excited by the output of a pulsed HF laser. The fluorescence intensity and decay time (a direct measure of the vibrational lifetime) have been measured as a function of pressure and mixture ratio. A knowledge of the vibrational lifetime is essential when choosing a pump-pulse duration for any laser design. The pulse duration is required to be short compared with the vibrational lifetime, but not short enough to give problems with optical

breakdown on window materials [2]. The results obtained for the fluorescence intensities give an indication of the relative potential for laser action of the gas media investigated.

2. EXPERIMENTAL ARRANGEMENT

The experimental arrangement is shown in Fig. 1. The output of the hydrogen-fluoride laser is brought to a line focus in the cell by a cylindrical lens L_1 . The cross section of the beam in the cell is approximately 9 mm x 0.6 mm where the 0.6 mm dimension is the full width at half intensity. Laser energy delivered to the cell is 2 J in a 1 μ s (FWHM) pulse. The reflector in the cell is polished copper and is located in a cavity 2.5 mm behind a thin sapphire disc which is mounted flush with the internal cell wall. This arrangement prevents any measurable infra-red radiation, which can be produced by incipient optical breakdown on the copper surface, reaching the detector. Fluorescence from the excited gas is collected and focused onto an InSb liquid-nitrogen-cooled detector. The filter F serves to reject scattered HF-laser radiation and to transmit fluorescence with wavelengths longer than 3.7 μ m. A disc of InAs which is effectively opaque at HF-laser wavelengths was used for the filter. A dry-ice and alcohol bath was used to cool the cell. Subsidiary insulated and heated windows (not shown in Fig. 1) were used to prevent condensation of atmospheric moisture on the sapphire windows. The volumes between the two sets of windows were evacuated.

The D_2 used in the experiments was 99.5% pure with the remaining 0.5% being H_2 , while the HD was 98% pure with a combined H_2 and D_2 impurity of 2%.

Results for the measured vibrational lifetimes and fluorescence intensities are presented as a function of the gas pressure rather than the gas density as was used in [1]. While the density is a more fundamental parameter in the collision-induced-dipole effect, the pressure is in general more important from the practical standpoint of device design.

3. EXPERIMENTAL RESULTS

3.1 D_2 :Ar Mixtures

The measured values of the reciprocal of the exponential-decay time constant τ are shown in Fig. 2 as a function of pressure for D_2 , and for a 1:3 D_2 :Ar mixture at a temperature of 200 K. After allowing for the effect of the small amount of H_2 impurity [6], the D_2 results give a value of approximately 42 amagat⁻¹ s⁻¹ for the self de-excitation rate at low pressure. This compares with a value of 48 amagat⁻¹ s⁻¹ reported in [6].

From the D_2 :Ar results of Fig. 2, a value of approximately $30 \text{ amagat}^{-1} \text{ s}^{-1}$ is obtained for the rate constant at low pressure for the de-excitation of D_2 by Ar. This value is similar to that derived from the room-temperature results presented in [1], indicating that this rate constant is relatively insensitive to temperature over the range 200-300 K. The only other measurement of this rate constant [7] is a room-temperature value approximately 0.4 times the value obtained here. The measurements of the vibrational lifetimes in these D_2 :Ar mixtures show that reducing the temperature from the room value to 200 K increases the lifetime about 3-6 times, depending on pressure and mixture ratio. Longer lifetimes allow longer and more energetic pumping pulses to be employed and this results in larger populations of vibrationally-excited D_2 molecules at the lower temperature.

Fluorescence intensities for D_2 :Ar mixtures, measured at the end of the pumping pulse, are presented as a function of D_2 concentration in Fig. 3. The results presented in this figure were obtained at a pressure of 140 MPa. However, since the fluorescence intensities in these mixtures at pressures above 70 MPa are nearly linear functions of the pressure (see the D_2 :Ar data in Fig. 4), these results are approximately correct for pressures in the range 70-200 MPa. It is seen from Fig. 3 that for low D_2 concentrations, the intensity is proportional to the D_2 concentration, but for concentrations of D_2 greater than about 35% the intensity is only a slowly varying function of the mixture ratio. Room-temperature results had been obtained previously [1] for D_2 concentrations of up to 33%. Up to this value the fluorescence intensity was found to be approximately a linear function of the concentration, as is the case here at 200 K. It was suggested in the paper reporting measurement of optical gain [2], that increasing the D_2 concentration above the value of 33% used in that work may lead to increased optical gain. The results presented here indicate that only a marginal improvement is likely at higher D_2 concentrations.

3.2 Addition of HD

The addition of HD to a D_2 :Ar mixture increases the absorption of the pump radiation and thereby increases the fluorescence intensity. The energy absorbed by the HD molecules is rapidly transferred to the D_2 molecules during collisions [5], and at the end of the pumping pulse most of the absorbed energy resides in the D_2 molecules. The major part of any fluorescence from the small population of excited HD molecules is at wavelengths which are too short to be transmitted by the InAs filter. Thus the fluorescence measured in the experiment is predominantly from the vibrationally-excited D_2 molecules in the mixture. Fig. 4 shows the fluorescence intensity of a 0.41:1:4.7 mixture of HD: D_2 :Ar as a function of pressure at a temperature of 200 K. The results for a 1:3 mixture of D_2 :Ar are also presented for comparison. These two mixtures have approximately equal ratios of diatomic molecules to buffer-gas molecules. It is seen that there is a large increase in the fluorescence intensity in the mixture containing HD. There is also some saturation of the intensity at high pressures; this is probably due to a relatively large absorption coefficient in this mixture at the pump wavelengths. The absorption coefficient has not been measured (the present apparatus is unsuitable for this task), but a value of approximately 0.9 cm^{-1} at 200 MPa is required to account for the saturation of the fluorescence intensity. There are no reported measurements of

collision-induced absorption in three-component mixtures, or in D_2 :Ar, HD:Ar or HD: D_2 mixtures at 200 K. Thus it is not possible to compare the results obtained here with estimates based on other work. The strong fluorescence and pump-beam absorption which have been observed, suggests that a mixture of D_2 :HD:Ar at reduced temperature is an attractive candidate as a medium for a collision-induced-dipole laser. The large absorption of the pump radiation in mixtures containing HD means that the pump direction can be made transverse to the laser optical axis.

The results for the reciprocal of the fluorescence decay time as a function of the pressure for the same mixtures and temperature are shown in Fig. 5. The inclusion of HD significantly increases the rate of de-excitation of the excited D_2 molecules. A value of approximately $1500 \text{ amagat}^{-1} \text{ s}^{-1}$ is obtained from these results for the rate constant at low pressure for the de-excitation of D_2 by HD. Some published results are presented in [5] for this rate constant at several temperatures in the range 100-300 K. The value derived here at 200 K lies above a smooth curve drawn through the points in [5], but the agreement is within a factor of two. While the inclusion of HD in the mixture at 200 K substantially increases the de-excitation rate of the excited D_2 molecules, a vibrational lifetime of $5 \mu\text{s}$ is still obtained at pressures around 200 MPa. This value of the lifetime is similar to that in the D_2 :Ar mixture (1:2) used for the gain measurements at room temperature [2].

3.3 Substitution of Kr for Ar

Since krypton has been found to provide larger collision-induced absorption than argon when used as the buffer gas in mixtures with H_2 [9] or HD [10],[3], it can be expected to do the same when mixed with D_2 . It was therefore decided to measure the fluorescence in a D_2 :Kr mixture and compare it with D_2 :Ar results. Because Kr has a higher critical temperature (209 K) than Ar (151 K) measurements were made at room temperature. At low pressure (30 MPa) a 1:2.5 mixture of D_2 :Kr gave a fluorescence intensity approximately twice that of a 1:3 mixture of D_2 :Ar. At high pressure (200 MPa) the ratio of the fluorescence intensities was reduced to less than 1.5, a consequence of the lower compressibility of Kr as compared with Ar. The fluorescence decay time (vibrational lifetime) for the D_2 :Kr mixture is shorter than that of an equivalent D_2 :Ar mixture. The decay time is approximately $2 \mu\text{s}$ at a pressure of 200 MPa in the 1:2.5 mixture of D_2 :Kr; this compares with a value of approximately $4 \mu\text{s}$ for a similar D_2 :Ar mixture [1]. Since replacing Ar by Kr results in a shorter vibrational lifetime, a higher critical temperature and only a modest increase in fluorescence intensity at high pressure, it appears on balance that Ar is the better choice for the buffer gas.

4. SUMMARY AND CONCLUSION

In summary, it has been found that when the temperature is reduced from 300 K to 200 K, the vibrational lifetimes of high-pressure D_2 :Ar mixtures are increased by a factor between about 3 and 6 depending on pressure and

mixture ratio. The lifetime is a weaker function of the mixture ratio at the lower temperature. At high pressures, the fluorescence intensity for a given mixture and pressure is only marginally affected by the reduction in temperature. At 200 K and low D_2 concentrations, the intensity is proportional to the D_2 concentration, but is largely independent of the concentration for mixtures containing more than about 35% D_2 . Addition of a relatively small quantity of HD to a D_2 :Ar mixture dramatically increases the fluorescence intensity but lowers the vibrational lifetime. Substitution of Kr for Ar at room temperature and high pressure marginally increases the fluorescence intensity but decreases the vibrational lifetime.

Fluorescence results have now been obtained in high-pressure gas mixtures containing Ar at room temperature and at 200 K. The gas temperature could be further reduced to near the critical value for Ar of 151 K. Another interesting extension of this work would be an investigation of collision-induced fluorescence in solutions of D_2 , or D_2 and HD, in liquid Ar.

In conclusion, a medium consisting of a suitably optimised mixture of D_2 , HD and Ar at high pressure and reduced temperature, which is transversely excited by an HF laser, appears an attractive candidate for an investigation of possible laser action based on the collision-induced-dipole effect.

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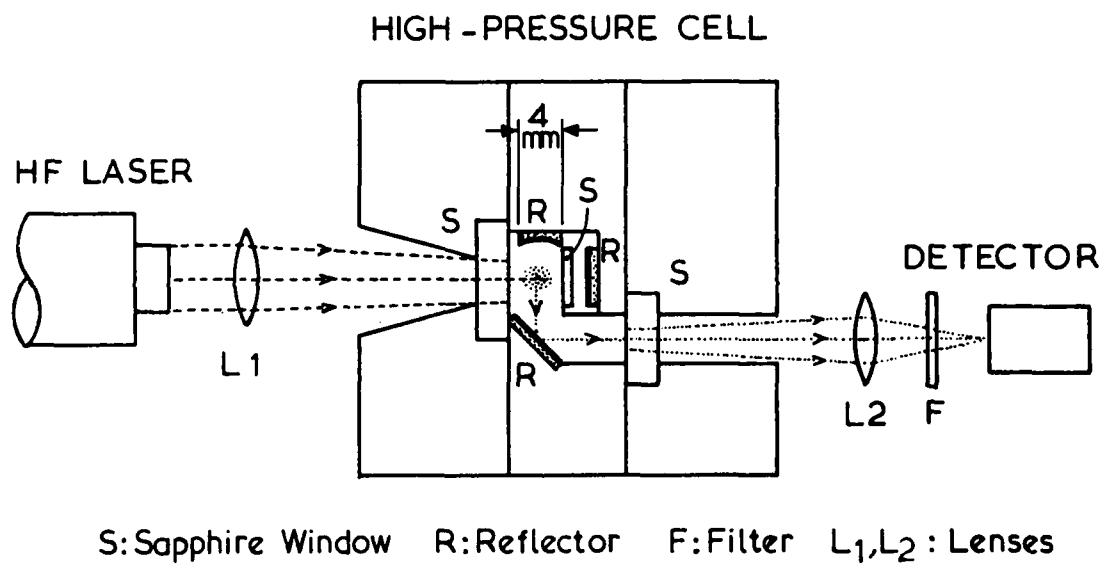


FIGURE 1. Schematic diagram of fluorescence experiment

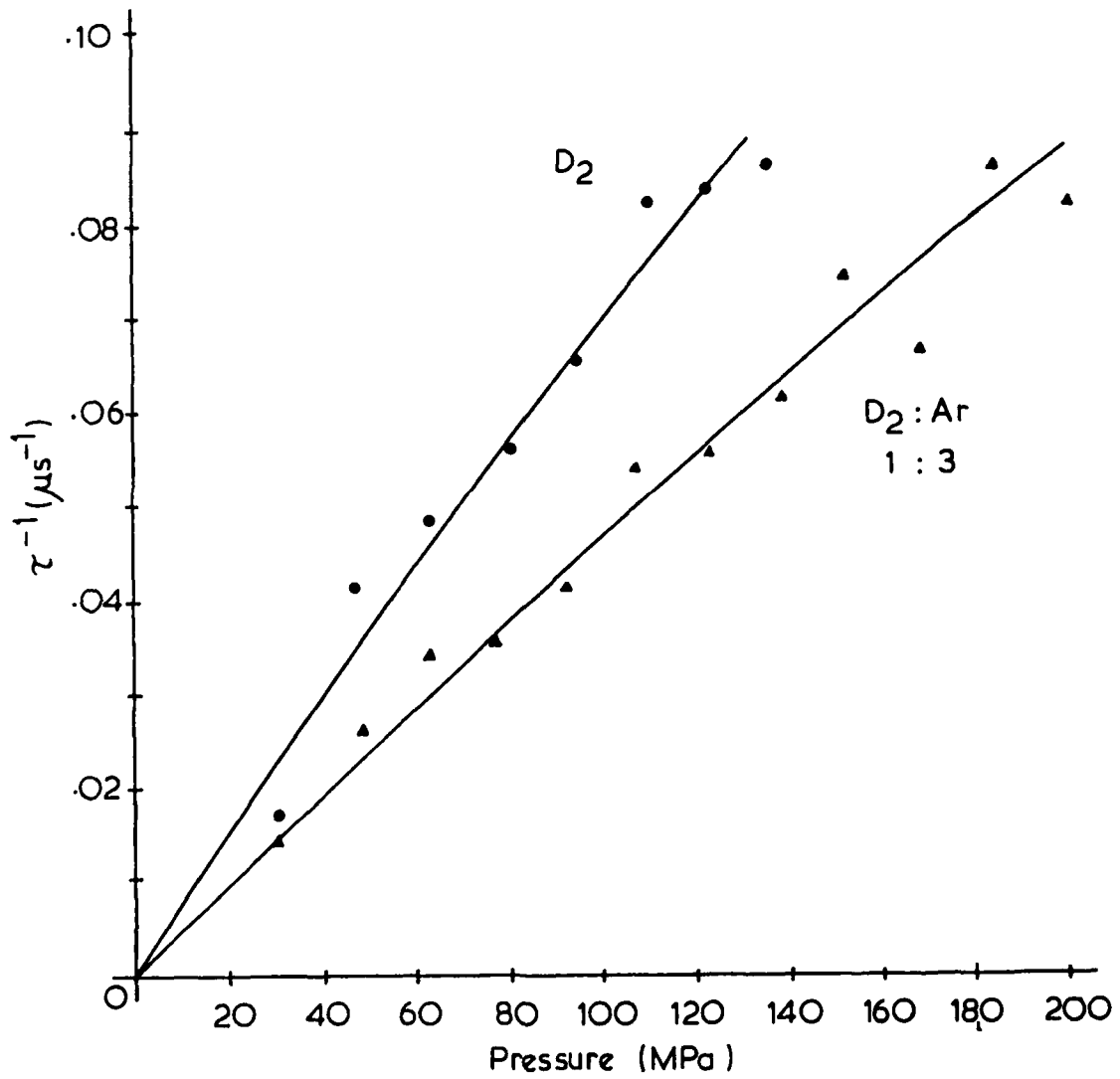


FIGURE 2. Reciprocal of the decay constant of the fluorescence signal as a function of pressure for D₂ and a 1:3 D₂:Ar mixture at 200 K.

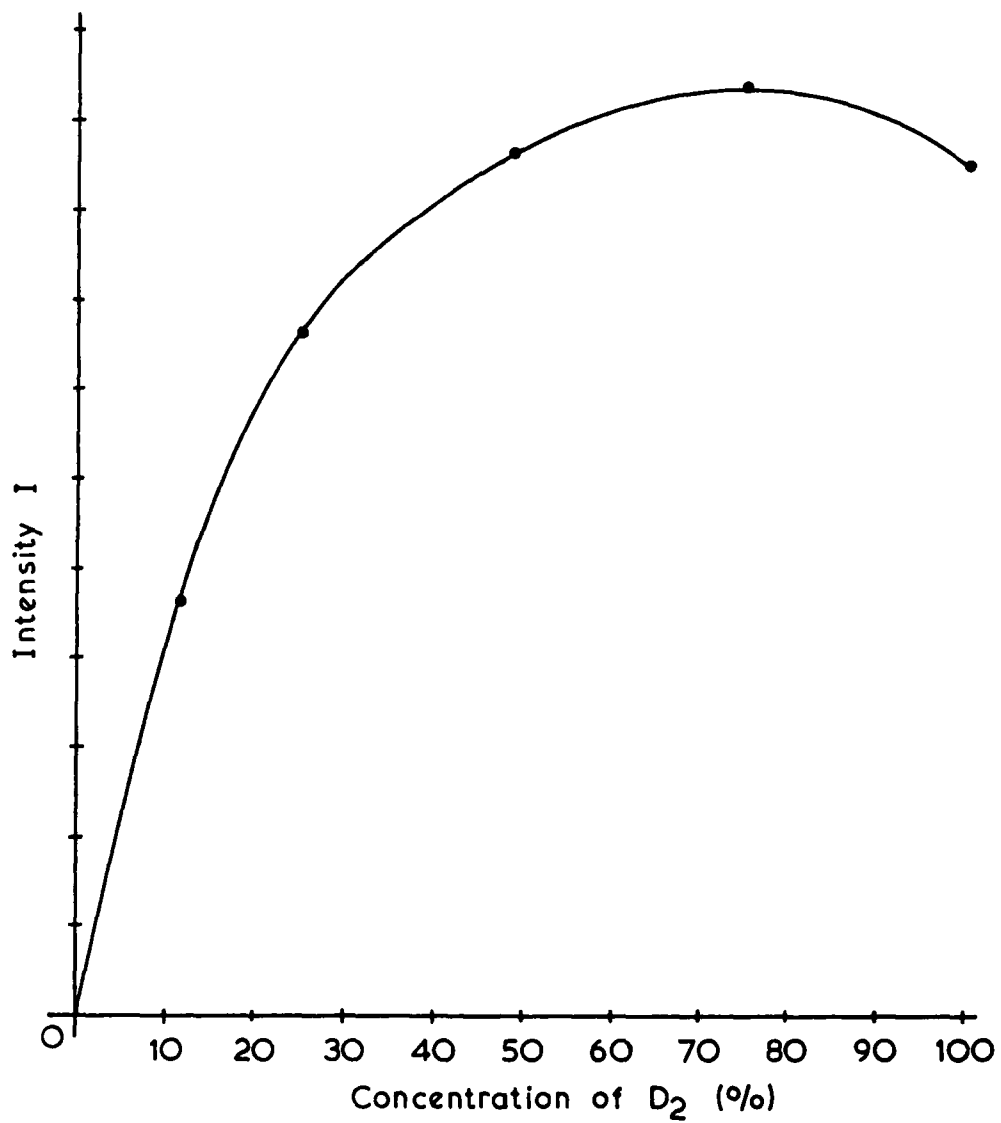


FIGURE 3. Fluorescence intensity as a function of the concentration of D₂ in D₂:Ar mixtures at a constant pressure of 140 MPa at 200 K.

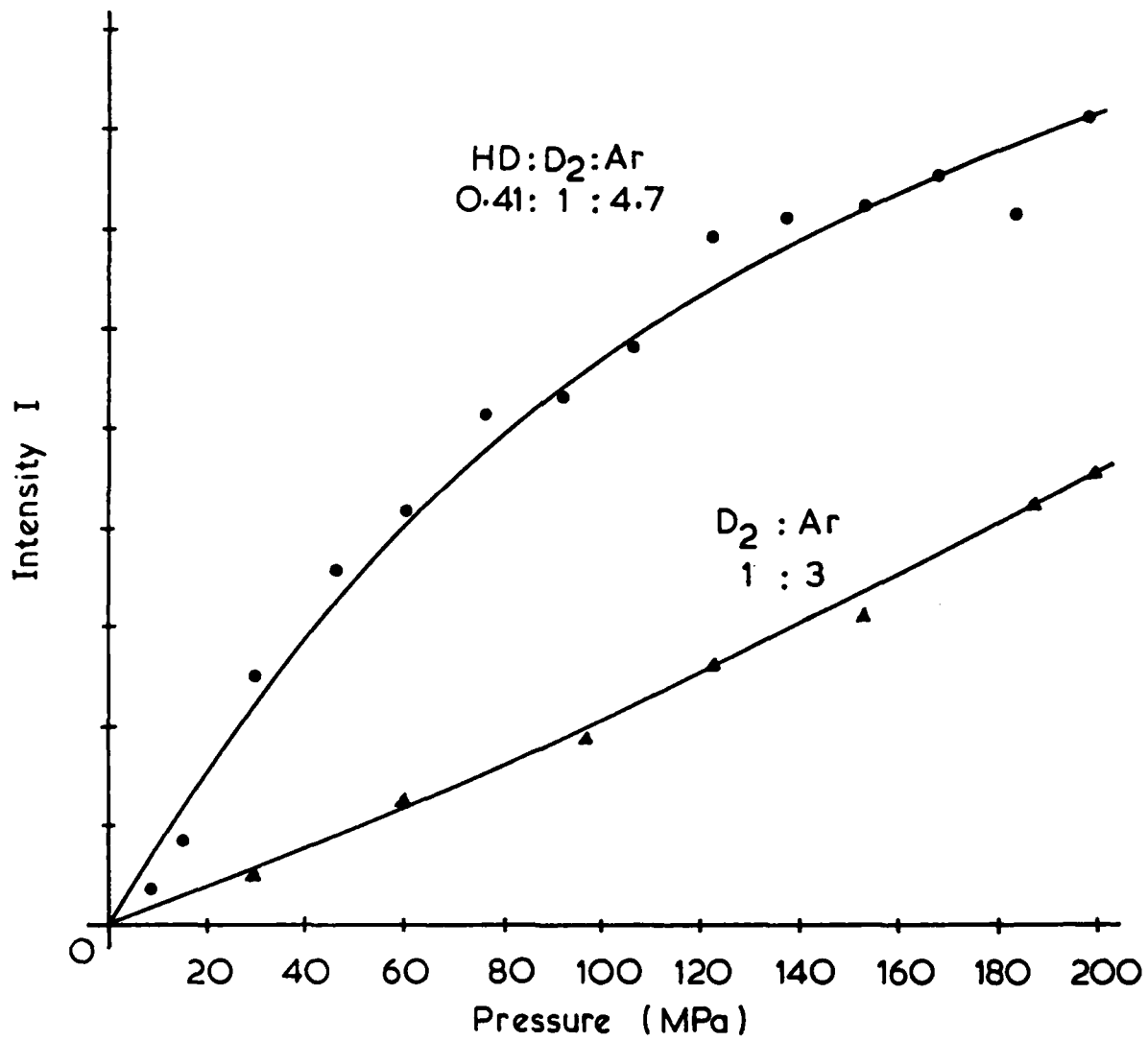


FIGURE 4. Fluorescence intensity as a function of pressure for a 0.41:1:4.7 mixture of HD:D₂:Ar and a 1:3 mixture of D₂ and Ar at 200 K.

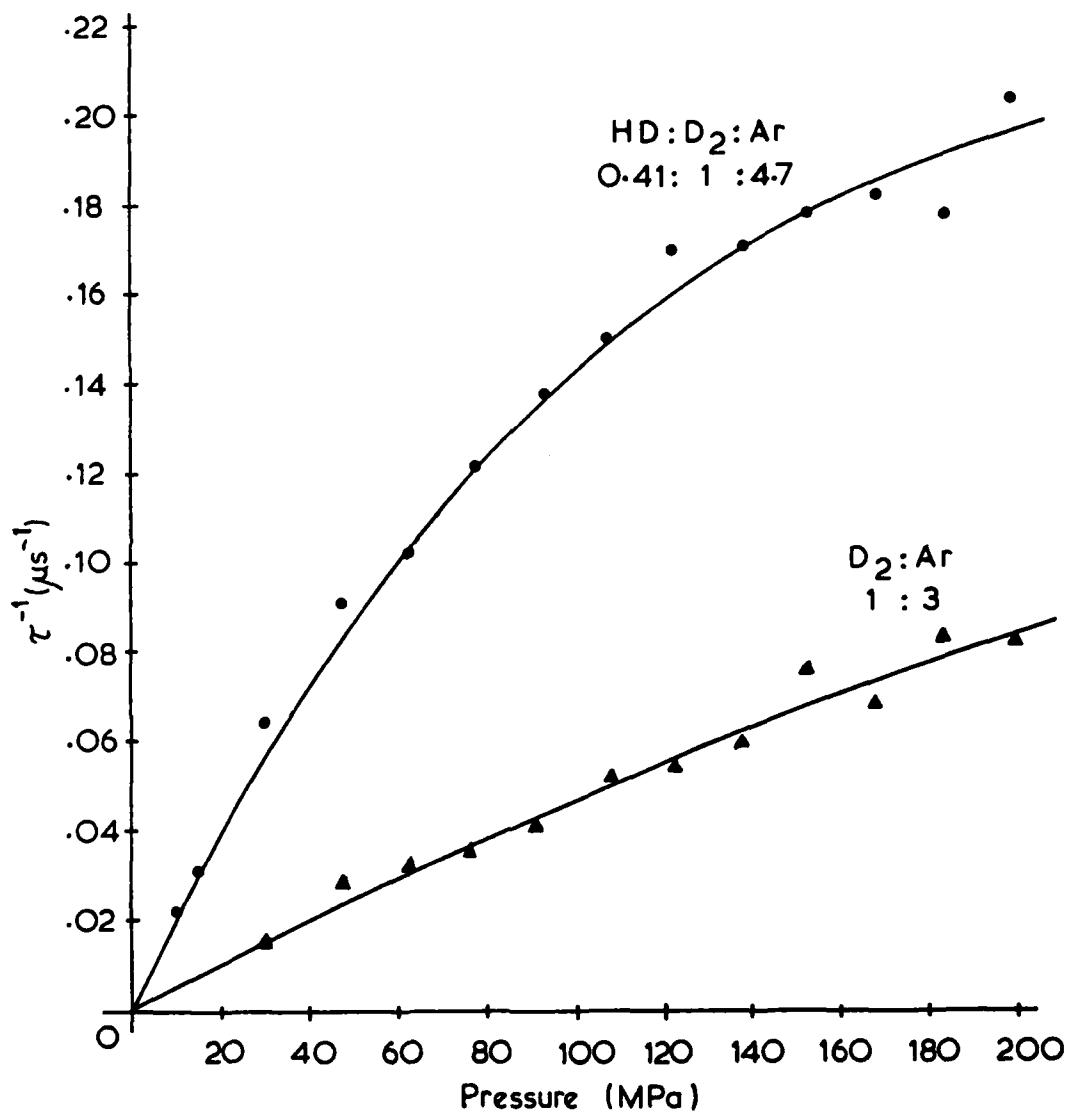


FIGURE 5. Reciprocal of the decay constant of the fluorescence signal as a function of pressure for a 0.41:1:4.7 mixture of HD:D₂:Ar and a 1:3 mixture of D₂ and Ar at 200 K.

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