

Aspects on Rotational Cooling of Glyoxal Using Carrier Gases He and Ar

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Molecular beam characterization performed for the carrier gases He and Ar reveals particularities in glyoxal fluorescence signal and beam rotational temperature related to the carrier gas. The dependence of the $K' = 0 \leftarrow K'' = 1$ $0_0^0 S_1 \leftarrow S_0$ fluorescence signal on stagnation pressure at constant glyoxal partial pressure shows that the signal has a maximum that is higher for He than for Ar. The estimation of the effective nozzle diameter, d_{eff} , for different stagnation pressure values, p_0 , suggests that the decrease of the fluorescence intensity at higher p_0 can be attributed, at least in part, to d_{eff} . On the other hand, Ar has the higher rotational cooling efficiency. Also the results show that the velocity slip (i.e. the difference between the mean velocities of the species in the binary mixture expansion) between glyoxal and carrier gas is not responsible for the difference in rotational cooling efficiencies of He and Ar.

Keywords: glyoxal, fluorescence, supersonic jet expansion, rotational cooling efficiency, velocity slip.

Supersonic jet expansion constitutes a very powerful technique with manifold applications in modern physical chemistry [1,2]. This technique can be used as a versatile analytical means, not only for basic research on pure substances, but also for practical trace analysis of chemical species in multi-component samples (e. g. in biological monitoring) [3]. Nowadays, the techniques for supersonic beams try to reach rotational and translational temperatures as low as possible. Pulsed supersonic expansion of CO and CO₂ at stagnation conditions above their critical point reveals very low translational temperatures (below 0.1K). This efficient cooling is quite promising for the spectroscopic studies of biological systems [4]. Another aspect in the researchers' attention is the characterization of the supersonic beams in detail [5-7].

In the last two decades, the stagnation conditions (temperature, pressure) of the beam expansion were pushed further and regions where quantum effects become important were reached. An example is the appearance of small and large helium clusters in the expansion [8]. Tunable diode laser spectrometers developed for the study of pulsed supersonic beams can be used to study helium clusters [9]. Supersonic jet method is also used in material research. Recent studies are focused on the use of supersonic beams for the manipulation of nanoparticles in order to obtain nanostructured materials [10].

In the present study, we show aspects on rotational cooling of glyoxal using carrier gases He and Ar. For this, the fluorescence spectroscopy and pulsed supersonic jet expansion are used. The $K' = 0 \leftarrow K'' = 1$ $0_0^0 S_1 \leftarrow S_0$ fluorescence band is monitored at different conditions of the expansion (stagnation pressure, glyoxal partial pressure). The influence of the nozzle opening on the fluorescence signal is also studied. The conclusions are that Ar has a higher cooling efficiency than He has and the velocity slip (i. e. the difference between the mean velocities of the species in the binary mixture expansion) is not responsible for this.

Experimental part

Glyoxal monomer (C₂H₂O₂), in the *trans* form referred herein as glyoxal, has been synthesized by controlled

heating of the glyoxal trimer in the presence of a drying agent P₂O₅ [11]. This was studied by fluorescence spectroscopy in a supersonic jet expansion. The molecular beam apparatus consists of a vacuum system with a molecular beam source, an excimer-pumped dye laser, a 1.7 m Czerny-Turner monochromator, and a gated fluorescence system connected to a computer. The carrier gases used for investigation were He and Ar. The carrier gas was bubbled through the sample of glyoxal held at different temperatures (regulated with a dry ice-acetone bath). The gaseous mixture was then admitted to the vacuum chamber by a pulsed solenoid nozzle of 0.5 mm in diameter, and then the beam was skimmed. The skimmer opening was of 2 mm. The excitation of the glyoxal molecule was achieved in the collision free region of the expansion by absorption of UV light. The UV light was produced by doubling the frequency of a Lambda Physik ScanMate 2E dye laser pumped by a Lambda Physik EMG 201 excimer laser operating at 10 Hz. The dye used for the study was Coumarin 440. The beam power at the exit of the dye laser was of 10 mJ/pulse. At this power, the transitions of interest are saturated and there should be little anisotropy in the angular distribution of electronically excited molecules [12,13]. The total fluorescence was imaged onto a photomultiplier tube (PMT) type RCA 7326 and processed by a computer. The fluorescence excitation (FE) spectrum was obtained by scanning the dye laser in steps of 0.005 nm in the region of interest.

In order to investigate at which extent the changes in fluorescence signal and rotational temperature occur when using He and Ar as carrier gases and if the velocity slip effect plays an important role in the rotational cooling of glyoxal, two methods were used. The first method is based on the variation of glyoxal partial pressure (p_{gly}) in the mixture glyoxal/He at constant stagnation pressure (p_0) while monitoring the glyoxal 0_0^0 band and the $K' = 0 \leftarrow K'' = 1$ 0_0^0 sub-band in the $S_1 \leftarrow S_0$ FE spectrum. The band was acquired at 10 laser pulses/step and the sub-band at 30 laser pulses/step. The delay time between the nozzle trigger pulse and the laser pulse was 650 μ s, a value that maximized the signal. The nozzle pulse width was maintained constant at 250 μ s. The second method involves the use of Ar and He as carrier gases while

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maintaining constant the glyoxal partial pressure in the mixture and varying the stagnation pressure. The $0_0^0 S_1 \leftarrow S_0$ fluorescence excitation spectrum of glyoxal was monitored. The stagnation pressure, p_0 , ranged from 20 torr to 600 torr at a constant p_{gly} ($T_{\text{bath}} = 253$ K).

The glyoxal vapor pressure was measured in the vacuum, in the temperature range: 233-263 K with a MKS capacitance manometer. The glyoxal temperature was maintained constant in the interval 0.5 K with an acetone slush bath whose temperature was regulated with dry ice.

Results and discussions

Figure 1 shows the band in the $S_1 \leftarrow S_0$ FE spectrum of glyoxal seeded in He for free-jet expansion. The wavelength bandwidth at full width at half maximum (FWHM) was of about 0.30 cm^{-1} . Since at this bandwidth it is not possible to resolve individual rotational lines, the spectrum consists of sub-bandheads corresponding to $\Delta K = +1$ or $\Delta K = -1$ transitions. The peak marked with an asterisk consists mainly of Q branch lines [12] and represents the monitored sub-band. Figure 2 represents the variation with T_{bath} of the fluorescence intensity corresponding to the maximum of the $K' = 0 \leftarrow K'' = 1$ sub-band and the glyoxal rotational

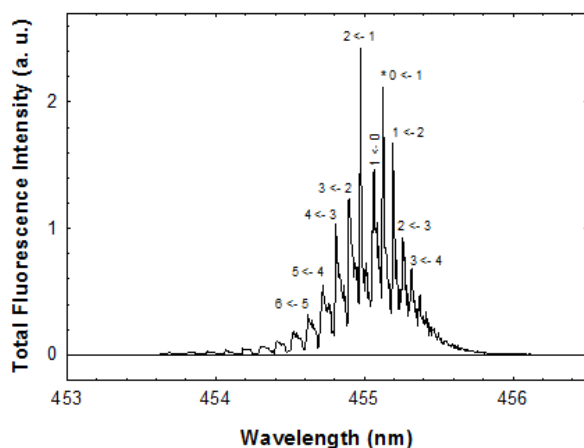


Fig. 1. The 0_0^0 band of $S_1 \leftarrow S_0$ FE spectrum for glyoxal in a supersonic jet expansion. The carrier gas is He. Each peak is assigned with the corresponding $K' \leftarrow K''$ transition. The asterisk marks the sub-band monitored in the study.

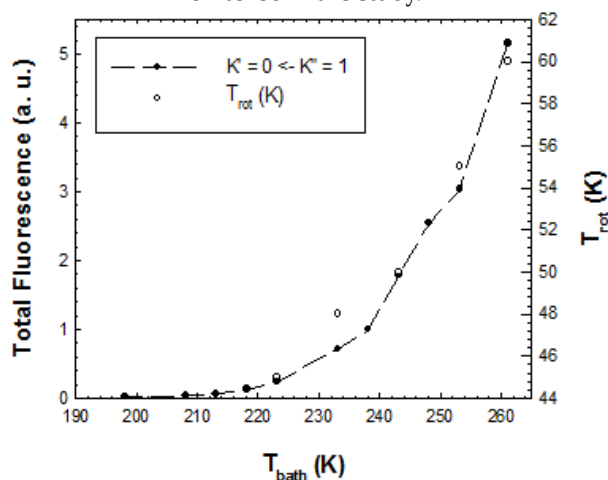


Fig. 2. The magnitude of $K' = 0 \leftarrow K'' = 1$ peak in the $0_0^0 S_1 \leftarrow S_0$ FE spectra and T_{rot} as a function of T_{bath} . The glyoxal was seeded in He and the stagnation pressure $p_0 = 160$ torr.

temperature (T_{rot}) estimated from computer-simulated $0_0^0 S_1 \leftarrow S_0$ rotational contour. As it can be seen, both T_{rot}

and peak magnitude increase with T_{bath} , i.e. with p_{gly} . T_{rot} increases from 48 K at $T_{\text{bath}} = 233$ K to 60 K at $T_{\text{bath}} = 261$ K, while the peak magnitude increases about 6 times over this T_{bath} range.

Figure 3 shows the dependence of the sub-band fluorescence intensity on p_0 for the expansions of glyoxal seeded in He (gly/He) and in Ar (gly/Ar). The curves reveal that the signal increases with p_0 until it reaches a maximum and then decreases slowly. The maximum for the carrier gas He is higher and broader than that for carrier gas Ar. Furthermore, the maximum for He occurs at a higher p_0 (~ 200 torr) than that for Ar ($p_0 \sim 60$ torr). These trends can be due to the nozzle mechanical behavior and skimmer interference.

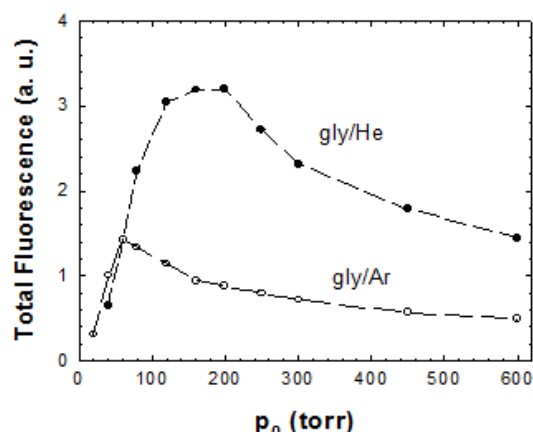


Fig. 3. The variation of $0 \leftarrow 1$ $0_0^0 S_1 \leftarrow S_0$ glyoxal fluorescence intensity maximum with p_0 for carrier gases He and Ar at constant p_{gly} ($T_{\text{bath}} = 253$ K).

Time-of-Flight (TOF) studies [14], conducted on skimmed pulsed supersonic jet expansions of rare gases (He, Ne, Ar) of diatomic molecules (H_2 , O_2) and of binary mixtures (5% O_2 /95% He), show that the time needed for the nozzle to open is nearly independent of the gas species but increases with increasing p_0 . The details are determined by the mechanical characteristics of the specific nozzle. It was found, for example, that with $p_0 = 100$ torr, the nozzle opened completely giving an effective nozzle diameter, d_{eff} , close to the nominal nozzle diameter, d . For $p_0 = 1000$ torr, the nozzle opened only partially so that the effective nozzle diameter was reduced ($d_{\text{eff}} = 0.58 d$). The decrease of nozzle d_{eff} with the increase of p_0 was considered to be due to the pressure difference across the tip during gas flow. An estimation of glyoxal nozzle d_{eff} can be made by following the next procedure. The total fluorescence intensity at the stagnation pressure p_0 , $I(p_0)$, is proportional [15] with the flow rate, Φ (molecules/s), at the nozzle exit

$$I(p_0) \propto \Phi(p_0) \propto n_{\text{ogly}}(T_{\text{bath}}) \sqrt{\frac{2kT_0}{m}} \cdot \frac{\pi d_{\text{eff}}^2(p_0)}{4} \quad (1)$$

where m is the concentration-weighted mass of the species behind the nozzle and n_{ogly} is the glyoxal number density which is constant when T_{bath} is constant. By considering $d_{\text{eff}} = d$ for $p_0 = 80$ torr, $d_{\text{eff}}(p_0)$ can be evaluated from Eq. (1) by

$$d_{\text{eff}}(p_0) = d \left(\frac{I(p_0)}{I(80)} \right)^{1/2} \left(\frac{\bar{m}(p_0)}{\bar{m}(80)} \right)^{1/4} \quad (2)$$

The results are presented in Table 1. As can be seen, the d_{eff} values decrease about 35% - 40% for $p_0 = 600$ torr. Given these results, the decrease of the fluorescence intensity at higher p_0 can be attributed at least in part to d_{eff} .

Table 1
THE RATIO EFFECTIVE NOZZLE DIAMETER TO NOMINAL
NOZZLE DIAMETER AND $0 \leftarrow 1 \ 0_0^0 S_i \leftarrow S_0$ FLUORESCENCE
INTENSITY FOR THE EXPANSION OF GLYOXAL SEEDED IN HE
OR AR AT DIFFERENT STAGNATION PRESSURES.

p_0 (torr)	gly/He		gly/Ar	
	$I(a.u.)$	$\frac{d_{eff}}{d}$	$I(a.u.)$	$\frac{d_{eff}}{d}$
40	0.6450	0.61	1.0016	0.88
60	-	-	1.4236	1.04
80	2.2368	1.00	1.3318	1.00
160	3.1846	1.08	0.9402	0.83
600	1.4433	0.65	0.4888	0.60

The FE spectra gave information on how p_0 and the carrier gas affected not only the magnitude of the fluorescence signal but also T_{rot} as evaluated from the simulation of the 0_0^0 band rotational contour. It was observed that (i) the spectra for He were broader than the corresponding spectra for Ar suggesting that $T_{rot}(\text{He}) > T_{rot}(\text{Ar})$ and (ii) the p_0 increase from 80 torr to 600 torr led to a higher rotational cooling for Ar than for He. These facts are demonstrated in the plots of figure 4 that show the variation of T_{rot} with p_0 . With the He carrier, T_{rot} is rather insensitive to stagnation pressure falling in the range 50–70 K. Rotational cooling is more effective with the Ar carrier and clearly improves at higher stagnation pressures, reaching values near 15 K.

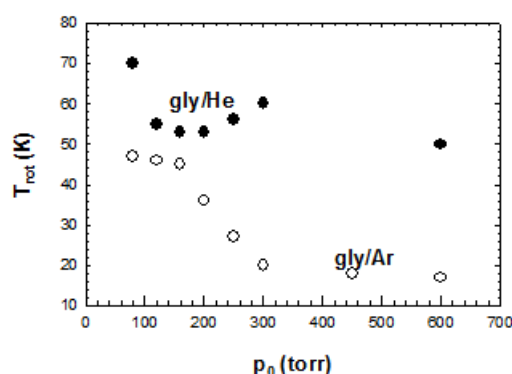


Fig. 4. The dependence of glyoxal T_{rot} on p_0 for supersonic-jet expansions of glyoxal seeded in He and Ar. ($T_{bath} = 253\text{K}$).

There are studies in the literature [16, 17] that consider the role of velocity slip on rovibrational cooling of heavy molecules (iodine (I_2), anthracene ($C_{14}H_{10}$), tetracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$), aniline ($C_6H_5NH_2$) and others) expanded in different rare gases. It was thought that a smaller velocity slip between the two partners in the expansion would lead to a lower T_{rot} of the seeding molecule, the effect being strong for all molecules mentioned above with the exception of aniline. In the case of aniline expanded in He, even though the velocity slip was smaller than for I_2/He , T_{rot} had values much higher than for I_2/He . Because of this, it was concluded that the velocity slip did not play a major role for the rotational cooling of this molecule. The fact that Ar has a higher rotational cooling efficiency than He was also found in the studies [16, 17] for the heavy molecules mentioned previously where it was claimed that the lower cooling efficiency of He was due to its higher velocity slip.

In our case, the velocity slip, v_{slip} , can be estimated by using the semiempirical relation [15]

$$v_{slip} = 0.5v(VSP)^{-1.07} \quad (3)$$

where v is the beam mean velocity and VSP is the velocity slip parameter that, by considering an attractive potential $-C_6/r^6$ between the molecules in the expansion, is given by

$$VSP = 0.96 \frac{(\mu \bar{m})^{1/2}}{|m_i - m_j|} n_0 d \left(\frac{\sqrt{C_{6i} C_{6j}}}{kT_0} \right)^{1/3} \quad (4)$$

where μ is the reduced mass, m_i and m_j are the masses of species i and j in the binary mixture, d - the diameter of the nozzle, n_0 and T_0 - the stagnation number density and temperature, C_{6i} and C_{6j} are the potential coefficients for species i and j . In order to investigate the velocity slip effect on rotational cooling for glyoxeq. (3) and eq. (4) for the experimental conditions given above. The C_6 (glyoxal) coefficient needed for the calculations was estimated from the potential [18] of the He- and Ar- formaldehyde interactions. The v_{slip} data for corresponding experimental conditions are displayed in figure 5 and figure 6. From figure 5, it can be seen that v_{slip} shows higher values for gly/He and very small values (≈ 0) for gly/Ar, the effect of p_0 increase on v_{slip} being obvious just for He. From the graphs in figure 6, it can be noticed that (i) v_{slip} has high values over the whole p_{gly} (glyoxal mole fraction) range, (ii) with the increase of glyoxal mole fraction, v_{slip} decreases while T_{rot} increases. From these two observations, it is clear that the change in T_{rot} is rather related to the glyoxal content in the mixture than to v_{slip} . The smaller the glyoxal content is, the higher v_{slip} and the smaller T_{rot} becomes. From here it can be concluded that v_{slip} driven by the change in p_{gly} and maintaining constant the stagnation pressure has an opposite effect on rotational cooling of glyoxal seeded in

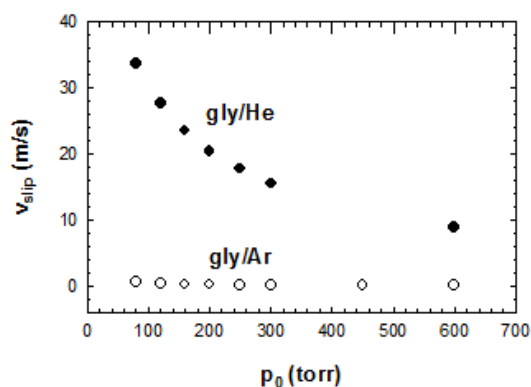


Fig. 5. The variation of the velocity slip between glyoxal and carrier gases He and Ar, respectively, in molecular beam with p_0 .

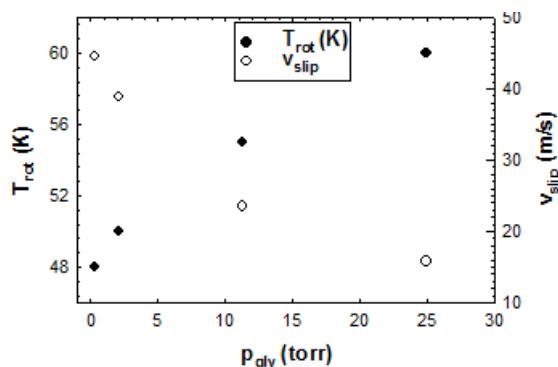


Fig. 6. The variation of T_{rot} and v_{slip} with p_{gly} for glyoxal expanded in He at a stagnation pressure of 160 torr.

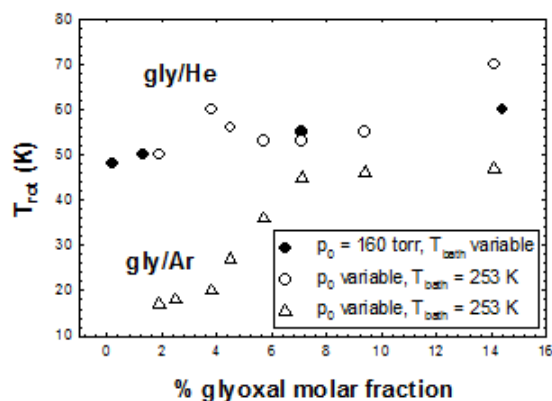


Fig. 7. T_{rot} as a function of glyoxal molar fraction (%) for carrier gases He and Ar at

He in supersonic jet expansions than it had on the rotational cooling of much heavier molecules [16, 17] mentioned above where v_{slip} was driven by the change in the stagnation pressure.

By comparing the changes in T_{rot} and v_{slip} driven by the variation of p_0 and keeping constant p_{gly} (T_{bath}) from Figs. 4 and 5 with those driven by the change in p_{gly} at constant p_0 from Fig. 6 in He case, two opposite behaviors are evident. The increase in p_{gly} leads to an increase in T_{rot} and a decrease in v_{slip} while the increase in p_0 leads to an overall tendency of decrease in T_{rot} and a clear decrease in v_{slip} . These two contrary effects of v_{slip} with respect to T_{rot} come to argue that v_{slip} is not the major factor responsible of rotational cooling. Instead this type of cooling is related to the content of glyoxal in the mixture (Fig. 7). Fig. 7 displays plots of T_{rot} against the glyoxal mole fraction. For both He and Ar carriers, T_{rot} tends to increase at higher mole fractions. The effect is small for He but pronounced for Ar. This trend suggests that glyoxal-glyoxal collisions (or complexation) in the early stages of the expansion are less effective in rotational cooling than glyoxal-rare gas collisions.

Conclusions

The use of He and Ar as carrier gases in the study of jet-cooled glyoxal with steady-state fluorescence spectroscopy shows several particularities. The variation of the $0 \leftarrow 1$ $0_0^0 S_1 \leftarrow S_0$ fluorescence signal with the stagnation pressure, p_0 , at constant glyoxal partial pressure, p_{gly} , shows that the signal increases to a maximum and then slowly decreases. This maximum is 2-3 times higher

for carrier gas He than for Ar and is localized at higher p_0 . The estimation of the effective nozzle diameter, d_{eff} , for different p_0 values, suggests that the decrease of the fluorescence intensity at higher p_0 can be attributed, at least in part, to d_{eff} . On the other hand, the molecular beam results show that Ar has a higher glyoxal rotational cooling efficiency than He has. Earlier reports [16, 17] for other molecules ascribed the higher Ar efficiency to velocity slip effects. Our fluorescence signal measurements performed with constant p_{gly} and variable p_0 on one hand, and with variable p_{gly} and constant p_0 on the other hand reveal opposite effects of velocity slip on T_{rot} . This result suggests that, at least in glyoxal case, the velocity slip is not the determining factor responsible for different Ar and He rotational cooling efficiencies.

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