MOLECULAR DESORPTION BY SYNCHROTRON RADIATION AND STICKING COEFFICIENT AT CRYOGENIC TEMPERATURES FOR H₂, CH₄, CO AND CO₂

V. Baglin, I.R. Collins, O. Gröbner, C. Grünhagel and B. Jenninger

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1. Introduction

In the cryogenic elements of the Large Hadron Collider (LHC), the proton beams will be contained inside a perforated 'beam screen' (BS), operating at a temperature between 5 K and 20 K. The BS is designed to intercept the heat loads induced by synchrotron radiation (SR), photonelectrons and resistive wall losses to avoid dissipation in the 1.9 K cold bore (CB) of the superconducting magnets. To provide the required beam lifetime of ~ 100 hours, the density of the rest gas must remain below a value determined by the residual gas nuclear scattering of the proton beam (e.g. for $H_2$ ~ $10^{15}$ molecules.m$^{-3}$). The density is controlled by perforations in the form of 'pumping slots' along the BS such that molecules can reach the CB surface and be cryosorbed [1].

In a cryogenic vacuum system which is exposed to intense SR, the molecular densities are determined by the following effects [2]: 1) 'primary' photodesorption as described by the molecular desorption yield, $\eta$, which constitutes a steady source of ‘new’ gas, 2) wall pumping characterised by the effective sticking coefficient, $\sigma$, 3) pumping via the BS slots $C$, 4) redesorption of condensed gas molecules, $\eta'$ i.e. the 'recycling' of previously physisorbed molecules by photons and/or by photonelectrons and finally 5) vapour pressure, $n_v$ of the condensed species on the cold surfaces.

Due to these effects, the gas densities may increase beyond the specified limit if the correct parameters have not been used for the vacuum system design. Therefore the knowledge of all these parameters over the relevant operating temperature range is of vital importance. A Cold Bore Experiment (COLDEX) has been designed and constructed in collaboration with the NIKHEF Laboratory, with the specific objectives to simulate closely and to validate the operational aspects of the LHC cryogenic vacuum system [3]. This apparatus has been installed at the CERN Electron Positron Accumulator (EPA) using an available SR beam line as the photon source.
2. Experimental

The COLDEX apparatus has been described in detail elsewhere [3]. The essential parts are two concentric tubes, \( \sim 2 \) m long, with independent temperature control. The outer tube, which represents the CB tube of the cryo-magnets is screened by the BS from the direct SR, the inner one, representing as closely as possible the BS of the LHC can be irradiated by SR. The CB, which constitutes the UHV vacuum envelope, is made of 316 LN stainless steel. The BS is made from extruded OFE copper to be representative of the inner Cu surface of the LHC BS and to ensure temperature uniformity. All materials were cleaned according to CERN standards. The CB has been constructed as a double walled liquid helium container. The BS tube has an inner diameter of 47 mm. It is cooled by circulating gaseous He through two parallel cooling channels located on the outside perimeter. To simulate the conditions of the LHC vacuum system, the BS is perforated with 264 round holes of 4 mm diameter equally distributed over the full length and representing 1\% of its surface area. Two ports for vacuum gauges are placed in the center of the BS, the upper one for a room temperature (RT) ‘chimney’ and the lower one for the extractor gauge (EXG). A 1 mm annular gap was provided to avoid direct thermal contact between the BS ports and the chimney or the cover of the EXG. In this way it is possible to minimise parasitic adsorption on the chimney surfaces and thus to obtain a reliable measurement at RT of the pressure in the test chamber using RGA 3 and BA 4. During a typical run the CB temperature would be set to 3.1 K and the BS temperature would be controlled from 4.5 to 90 K. Alternatively, when the BS is operated above 90 K, the CB temperature is set to 5 K. All 300 K data were obtained with the entire apparatus at RT i.e. both CB and BS.

The beam line for the COLDEX apparatus is shown in Fig. 1. To shorten the irradiation time for a given photon dose, a critical energy of 194 eV was chosen yielding the maximum photon flux from EPA of \( 3.4 \times 10^{16} \) photons m\(^{-1}\) s\(^{-1}\) - about one third of the LHC flux. The SR is collimated by a rectangular aperture (7.5 mm horizontally, 11 mm vertically). The vertical collimation attenuates photons with energies < 4 eV and thus reduces the photon flux (transmission factor of 0.8). In previous RT studies, this reduction of the low energy tail of the spectrum was not considered important since the desorption of the strongly bound species requires a few eV photons, capable of producing photoelectrons and thus of breaking chemical bonds. This situation is different in a cryogenic system with physisorbed molecules, since molecular desorption by low energy photons with energies of less than 1 eV and even by thermal radiation has been demonstrated to occur [4]. During the setting-up phase COLDEX is aligned according to the theoretical 'straight through' position and the photon beam is centred by adjusting the electron beam orbit. During data taking, COLDEX is moved in the horizontal plane with respect to the 'straight-through' position and the SR irradiates the BS at a grazing incidence with a mean angle of \( 11 \pm 2.7 \) mrad. In this position, the SR illuminates the BS over 95 \% of the total cold length. The COLDEX vacuum system is pumped at each extremity through a conductance of 73.8 \( l.s^{-1} \) for \( N_2 \). Each of the end pumping systems is a combination of a 200 \( l.s^{-1} \) for \( N_2 \) ion pump and two titanium sublimation pumps of 1000 \( l.s^{-1} \) for \( H_2 \). Six calibrated Bayard-Alpert gauges (BA1 to 6) and one EXG are installed. The gas composition is measured with two quadrupole gas analysers fitted with secondary electron multipliers, RGA2 and RGA3.
3. Principles

In a cold vacuum system, the sum of the primary photodesorption yield (PPY), $\eta(T)$ and of the recycling photodesorption yield (RPY), $\eta'(T)$ can be expressed by equation (1). This equation involves three unknown quantities, which implicitly depend on the temperature, $T$: $\eta(T)$, $\eta'(T)$ and the sticking coefficient, $\sigma(T)$.

$$\Gamma = \eta(T) + \eta'(T) = \frac{G(T) [\sigma(T) S(T) + C(T)] P \sqrt{\frac{T}{300}}}{\Gamma}$$

$G(T)$ is a constant converting from pressure to molecular density, $S(T)$ is the ideal surface pumping speed of the BS, $C(T)$ represents the pumping speed by the holes, $P$ is the partial pressure and $\Gamma$ is the total photon flux. The pumping speed $C(T)$ takes into account the Clausing factor (~0.7) and the parasitic pumping due to the space between the BS and its surrounding thermal screen (~0.7 % of the total surface as determined experimentally with an unperforated BS). The square root factor accounts for thermal transpiration. A further condition, which must be fulfilled to use equation (1) is that the vapour pressure can be neglected. This implies either sufficiently low temperatures and/or sufficiently low surface coverages.

If it can be ensured at the beginning and throughout a measurement that the surface coverage remains sufficiently low, the dynamic pressure rise is dominated entirely by the PPY. In this case, the RPY of equation (1) can be neglected, one obtains a simplified expression (2) which involves in addition to known and measured quantities the PPY and the sticking coefficient. In this work, a specific procedure has been adopted to achieve experimental conditions for which this simplified equation can be applied.

$$\eta(T) \approx \frac{G(T) [\sigma(T) S(T) + C(T)] P \sqrt{\frac{T}{300}}}{\Gamma}$$

Fig.1. Layout of the beam line with COLDEX.
For H₂, a low surface coverage has been achieved readily by cooling down first the CB and subsequently the BS. This aspect was verified in a control experiment without SR during which the CB was cooled to 3.4 K while the BS was maintained initially at 30 K and only subsequently cooled down to 6.6 K for 70 hours. From the release of H₂ during the following warming up of the BS an average condensation rate of $6 \times 10^{11}$ cm⁻² h⁻¹ could be deduced, equivalent to about $10^{-3}$ monolayer h⁻¹. Since RPY of H₂ is 0.1 molecules/photon at one monolayer [2, 5, 6, 7], assuming a linear dependence with coverage, the recycling effect would account for a desorption yield of $10^{-4}$ H₂ molecules/photon. This yield being about equal to the PPY one would conclude that the build-up of the condensed layer of H₂ on the BS could lead to a modest overestimate of the PPY by up to a factor of two.

The same method of controlled sequential cool down and warm-up has also been used for the other gas species CH₄, CO and CO₂. The upper limits of the condensation rate during a typical COLDEX run which could be measured for these molecular species is $4 \times 10^{11}$ molecules cm⁻² h⁻¹. However, since the RPY for these molecules are much smaller than for H₂ [6, 7], the resulting errors in the measurements of the PPY are proportionally smaller and the uncertainties are in the range of $3 \times 10^{-7}$ to $3 \times 10^{-6}$ molecules photon⁻¹.

From equation (2) follows that the pressure in the system depends on both PPY and the sticking coefficient. A practical procedure to evaluate the PPY independently is based on the fact that the dynamic pressure during SR irradiation initially increases but reaches an equilibrium value after a sufficiently long irradiation time [8]. This condition is characterised by the fact that the rate of condensation of molecules on the inner BS surface equals the rate of redesorption due to the recycling effect by the SR. A consequence of this balance is that the surface coverage has reached a constant value. Expressed in different terms, the effective sticking coefficient vanishes since the flow of desorbed gas entering the system is balanced by the flow of gas leaving the system through the holes in the BS. Once this equilibrium pressure $P_{eq}$ has been established, the PPY is obtained.

$$
\eta(T) = \frac{G(T) C(T) P_{eq} \sqrt{\frac{T}{300}}}{\Gamma}.
$$

In the case of H₂ its large RPY makes it possible to reach the equilibrium within a reasonably short time, i.e. an irradiation time which is readily obtained in an EPA run lasting a few hours only.

For the other gas species, as a consequence of lower RPY than hydrogen, the pressure increase is small, hence difficult to observe, and it may simply take too long to reach the equilibrium. To overcome this difficulty an alternative method to measure the PPY has been used based on the following. Low surface coverage could be achieved by operating the BS above a temperature, $T_{H}$ at which the sticking coefficient of a specific molecular species was sufficiently small. With reference to equation (2) this implies that $\sigma$ vanishes. Since physisorbed molecules exhibit well defined activation energies, the recording of the pressure with temperature during a controlled warm-up shows distinct desorption peaks attributed to the respective residual gas species. Due to the exponential dependence of the thermal desorption rate on temperature, the condensed gas is released rapidly within a narrow temperature interval. These desorption peaks depend weakly on the heating rate range (< 5 K for 300 meV activation energy and heating rates of 200 mK/min). Above $T_{H}$ molecules no longer condense on the surface since the sojourn time becomes so short that no significant gas surface phase exists. Therefore, above $T_{H}$ the PPY is evaluated using equation (3). For temperatures below $T_{H}$, the pessimistic assumption has been made that the PPY remains
constant and equal to its value at $T_H$. Below $T_H$ equation (2) has been used to calculate the sticking coefficient using as input value $\eta(T_H)$. The limiting temperatures for the different gas species are 30, 80, 65 and 125 K for H$_2$, CH$_4$, CO and CO$_2$ respectively.

$$\eta(T) = \begin{cases} \eta_{for \ T > T_H} & \text{for } T > T_H \\ \eta(T_H) & \text{for } T \leq T_H \end{cases}$$

(4)

4. Results

To avoid any significant cleaning of the surface during the measurements the BS was pre-exposed to a dose of $3 \times 10^{22}$ photons m$^{-1}$. Based on the results of a previous experiment at 77 K a dependence of the PPY with dose$^{-1/3}$ had been found [5]. Since in all the subsequent measurements the accumulated dose was intentionally limited to $4 \times 10^{21}$ photons.m$^{-1}$, the PPY should have remained constant to within 4 %. Fig. 2 shows the PPY as a function of the BS temperature between 5 K and 300 K. It should be noted that measurements below the limit temperature $T_H$ are not included in this figure with the exception of H$_2$, for which these data points could be obtained by the independent measurement based on the equilibrium pressure measurement. It can be seen that the PPY decreases with decreasing temperature. The 300 K data were obtained after an accumulated dose of $3.5 \times 10^{22}$ photons.m$^{-1}$. The error bars for each of the measurements derive from the propagation of the individual errors of the partial pressure measurements which have been estimated as 30 % and result from the calculation of the pressure difference with and without photon irradiation. The sequence of measurements was first from 135 K to 5 K and subsequently from 100 K to 300 K.

Fig. 2. Primary photodesorption yield for an OFE copper BS irradiated with 194 eV critical energy SR as a function of temperature. The BS had been pre-exposed to an accumulated dose of $3 \times 10^{22}$ photons/m. With the exception of H$_2$, measurements below the limiting temperature $T_H$ have not been included.
Fig. 3 shows the calculated sticking coefficient from the measured pressure increase using equation (2) and the PPY data in figure 4. The hatched area represents the propagated error derived from the numerical treatment of the data and the partial pressure measurements of each gas species. Below 20 K, the sticking coefficients of all the gases are found to be in the range of a few percent. These values correspond to a ‘bare surface’ with less than $10^{14}$ physisorbed molecules/cm$^2$. Comparison with published data of CO$_2$ at 77 K shows one order of magnitude lower values than given here [9]. Therefore, if the CO$_2$ sticking coefficient was overestimated by one order of magnitude in our experiment, the corresponding PPY of CO$_2$ would proportionally decrease to $10^5$ molecules.photon$^{-1}$.

Fig. 3. Sticking coefficients for a ‘bare’ OFE copper surface below the limiting temperature $T_H$.

5. Implications for the LHC

To estimate the residual densities and the resulting nuclear scattering beam life time in the LHC, the rather pessimistic assumption has been made that the PPY of all species in the temperature range from 5 K to 20 K is equal to its value at the limiting temperature $T_H$. Table 1 summarises the PPY measured at the indicated temperature $T$ (Fig. 2), the sticking coefficient at 15 K (Fig. 3), the RPY from Ref [7], the nuclear scattering equivalent gas density with respect to H$_2$, the beam life time corresponding to the individual densities and in the last column, the resulting total beam life time. The nuclear scattering lifetime at 7 TeV of H$_2$ has been calculated using the cross section value $\sigma(H_2) =$
95 \ 10^{-31} \text{ m}^2. The values of the beam life time have been computed for a nominal beam current (0.56 A) and for a BS at the average temperature of 15 K with 4.4% pumping holes having a Clausing factor of \sim 0.5. The beam life time is dominated by CO$_2$ followed by CO and with third importance only by H$_2$.

Table 1

Primary photodesorption yield, temperature, recycling yield, relative nuclear scattering cross section at 7 TeV as well as individual and total beam life times.

<table>
<thead>
<tr>
<th>Gas</th>
<th>(\eta) (molecules/photon)</th>
<th>(T) (K)</th>
<th>(\sigma)</th>
<th>(\eta') [7] (molecules/photon)</th>
<th>(n_{\text{H}<em>2}/n</em>{\text{gas}})</th>
<th>(\tau_{\text{gas}}) (h)</th>
<th>(\tau) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>(2.0 \times 10^{-4})</td>
<td>5-20</td>
<td>0.02</td>
<td>0.1</td>
<td>1</td>
<td>1620</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>(6.0 \times 10^{-6})</td>
<td>78</td>
<td>0.05</td>
<td>(1 \times 10^{-4})</td>
<td>6.0</td>
<td>3200</td>
<td>99</td>
</tr>
<tr>
<td>CO</td>
<td>(2.0 \times 10^{-5})</td>
<td>69</td>
<td>0.02</td>
<td>(2 \times 10^{-5})</td>
<td>9.0</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>(3.5 \times 10^{-5})</td>
<td>114</td>
<td>0.15</td>
<td>(1 \times 10^{-4})</td>
<td>13.9</td>
<td>142</td>
<td></td>
</tr>
</tbody>
</table>

Using the data from Table 1, Fig. 4 shows the evolution of the gas density with running time. Due to its large recycling coefficient, H$_2$ reaches its equilibrium state within a very short time as compared to the other gas species which may take many months of running.

![Fig. 4. Evolution of the gas density with LHC running time using the input data from Table 1. The gas densities have been normalised with respect to the values for a 100 hour beam lifetime (\(n_{\text{H}_2}\) for hydrogen = \(10^{15} \text{ H}_2 \cdot \text{m}^{-3}\)).](image)

A reduction of the PPY with photon dose is known from RT measurements and has also been observed at 77 K \[5, 6\] but has not yet been confirmed below 20 K. Concerning the dominant effect of CO$_2$, there exist controversial results between experiments performed at CERN and at
BINP in Novosibirsk which obtain a much lower desorption yield of CO\textsubscript{2} at 5 K - 10 K. Due to the importance of its contribution to the global beam lifetime a smaller yield for CO\textsubscript{2} would lead to a significant increase of the beam lifetime. Finally, it has been assumed that the PPY of CO\textsubscript{2} and CO are constant between 114 K-20 K and 78 K-20 K respectively. But, it is known that the PPY decreases significantly in this temperature range [2, 5, 6, 8]. The results for the gas species other than H\textsubscript{2} should thus be taken as upper limits. Nevertheless, one may conclude that even with these pessimistic assumptions, the required vacuum performance of the LHC can be reached safely.

Fig. 5 shows the dynamic pressure evolution in the case of a pre-condensed gas layer on the inner wall of the BS. During a magnet quench, the gas load which has been accumulated on the CB, e.g. during 1000 hours of operation, is desorbed during the warming up. Subsequently, in case the system would be cooled down in the wrong sequence so that the BS would be at a lower temperature than the CB, an excessive amount will condense on the BS. The gas is assumed to be condensed in equal proportions on the inner and outer surface of the BS. The respective surface coverage of each gas species would be 25.1 \(10^{15}\) H\textsubscript{2}.cm\textsuperscript{-2}, 0.75 \(10^{15}\) CH\textsubscript{4}.cm\textsuperscript{-2}, 2.5 \(10^{15}\) CO.cm\textsuperscript{-2} and 4.4 \(10^{15}\) CO\textsubscript{2}.cm\textsuperscript{-2}. During operation, the recycling of this excess amount of surface gas will lead to a transient pressure rise. Again, the redistribution of H\textsubscript{2} occurs fast while the other species may take several weeks to reach their equilibrium. Minimisation of BS surface coverage will avoid undesirable pressure transient. The photocracking of CH\textsubscript{4} and of CO\textsubscript{2} molecules into CO and H\textsubscript{2} respectively [6, 7] implies that the condensed CO\textsubscript{2} would be transformed predominantly into CO. The overall effect will be that the equivalent density remains below the curve shown in Fig. 5.

![Fig. 5. Dynamic pressure evolution due to an excess amount of pre-condensed gas on the inner wall of the BS. The gas load is assumed to correspond to 1000 hours of operation.](image)

6. Conclusions

PPY and the sticking coefficients as a function of temperature have been measured for an OFE copper BS subjected to SR. The photodesorbed gas species are H\textsubscript{2}, CH\textsubscript{4}, CO and CO\textsubscript{2}. For
the purpose of the measurement method: a) care was taken to minimise the surface coverage on the BS and thus the recycling yield for each gas species and b) the PPY was assumed to be constant below the limiting temperature of thermal desorption $T_H$.

It is shown that the PPY decreases with decreasing temperature. For irradiation with SR of 194 eV critical energy, the PPY of $H_2$ below 20 K and after an accumulated dose of $3.5 \times 10^{22}$ photons.m$^{-1}$ is in the range $10^{-4}$ molecules.photon$^{-1}$. The PPY of the other gases is in the range of $10^{-5}$ molecules.photon$^{-1}$. The sticking coefficient on a ‘bare surface’ decreases with increasing temperature. Below 20 K, it is of the order of a few percent for all gases. At 15 K nominal LHC operation, the beam lifetime due to proton-nuclear scattering can be estimated as 100 hours even without beam conditioning. Regarding photon induced molecular desorption, a very modest cleaning of the BS by less than a factor of two will be sufficient to meet and even exceed the design goal for the LHC vacuum. To avoid undesirable pressure transients, the cool down of the BS should be controlled such that its temperature is higher than the CB. Temporarily raising the BS temperature up to about 100 K should be considered as it would permit a fast transfer of gas from the BS to the CB prior beam operation.

Acknowledgements

The work performed by NIKHEF during COLDEX design and construction is gratefully acknowledged. We would like to thank Drs J-P. Potier and L. Rinolfi as well as the operating team for running the EPA machine with excellent beam quality. Discussions with Drs. V. Anashin, J. Gómez-Goñi, J-M. Laurent and O. Malyshev have greatly improved our understanding of the LHC cryogenic vacuum system.

References