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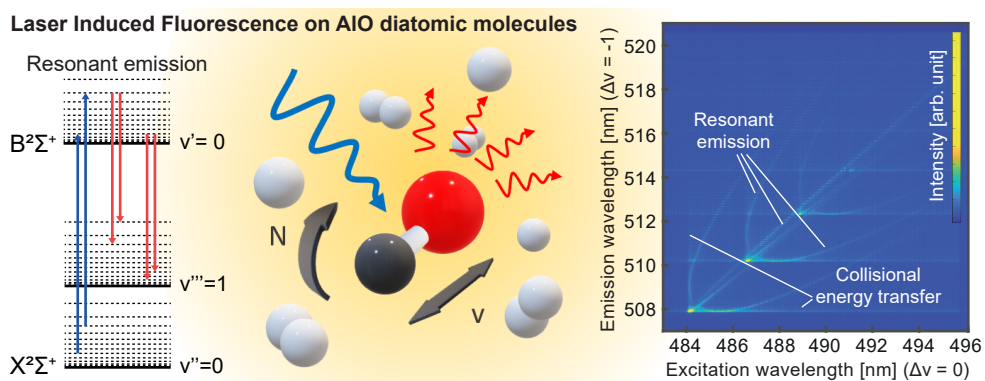
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Graphical Abstract

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Highlights

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- Determination of ground state rotational temperature from resonant laser-induced fluorescence.
- Rotational temperatures in both ground and excited states are consistent.
- LIF spectra reveal energy redistribution in the excited electronic state with rotational energy transfer up to $\Delta N = -100$.

On the use of Laser-Induced Fluorescence to probe the thermodynamic equilibrium in laser-generated plasmas.

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Abstract

In this work, we investigate thermodynamic equilibria in a laser-generated plasma from ro-vibrational population distributions in the AIO molecule. We address the congruence between the rotational temperatures of diatomic molecules in their excited state and in their ground state, the latter being assumed to correspond to the kinetic temperature of the species in the plasma. The model system consists of AIO molecules produced by ablation of an alumina target in ambient air using a nanosecond laser pulse. Using laser induced fluorescence spectroscopy, we can directly probe the population of the rotational levels in the ground electronic state $X^2\Sigma^+$ of AIO and deduce the corresponding rotational temperature. This temperature is then compared to the population of the rotational levels in the excited state $B^2\Sigma^+$ deduced from the thermal $B - X$ rovibronic emission. In such plasma, AIO molecules in the excited state are believed to be formed by chemical reaction and might be strongly out of equilibrium, but we find that emission from the $B^2\Sigma^+$ excited state provides a useful indication of kinetic temperature of the species in the plasma for delays longer than a few microseconds.

Keywords: Laser-Induced Fluorescence, collisionally induced fluorescence, rovibronic emission, rotation-vibration relaxation, AIO, laser-induced plasma, thermodynamic equilibrium, rotational temperature.

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1. Introduction

This paper explores just one of the several avenues of study of molecular emission from laser ablation plasmas discussed in the review by Di Giacomo and Hermann [1], exploring non-equilibrium energy distributions in rotational and vibrational degrees of freedom [2]. Measurement of temperatures in laser-generated plasma is a useful diagnostic for the data analysis in laser-induced breakdown spectroscopy (LIBS) [3, 4] and to model nanoparticle growth in the framework of laser-generation of particles such as pulsed laser deposition (PLD) and ablation in air [5], cluster sources [6] and laser ablation in liquids (LAL) [7, 8]. Regarding elemental analysis, diatomic molecules sometimes offer possible advantages in LIBS diagnostics when molecular signatures fall in a more convenient spectral region than the strongest atomic transitions. A particularly striking practical illustration was the diagnostic for fluorine content in minerals via CaF bands, proposed by Alvarez *et al.* [9] in 2014, and successfully applied in the analysis of Martian soil with ChemCam one year later [10].

In this article, we are addressing temperature measurement in AlO molecules, one of the molecular species mentioned in the context of diatomics offering possible advantages in LIBS. We developed a fitting procedure on partially-resolved laser induced fluorescence (LIF) spectra in order to handle separately direct fluorescence (resonant emission, DLIF) and laser-then-collisionally induced fluorescence (LCIF). Using DLIF, we have probed the population of the rotational levels in the ground electronic state $X\Sigma^+$. The rotational temperature of the ground electronic state is then deduced. Using LCIF, We have focused on energy redistribution in the excited $B^2\Sigma^+$ state of AlO.

Regarding the energy redistribution in the excited electronic state, it is well established that there are no selection rules governing collisional energy transfer in a non-symmetric molecule, and a single collision can result in large changes in ΔN and ΔJ , if ΔE commensurate with $k_B T$, even with unreactive collision partners [11, 12]. Changes up to $\Delta J = 70$ have been reported in alkali dimers [13], under controlled conditions of temperature and pressure. Here, more collisional partners are possible, including Al or O atoms, as well as atmospheric oxygen or nitrogen. Spectra reveal extensive rotational energy transfer up to $\Delta J = -100$.

A second issue deals with the measurement of the kinetic temperature of the heavy species in laser generated plasma. An established strategy consists of measuring the rotational temperatures of diatomic molecules from

38 emission spectroscopy assuming an equilibrium between the internal degrees
39 of freedom of the molecules and the kinetic temperature of the species in
40 the plasma. This is true when molecules are excited by collision with the
41 electrons in the plasma. In that case, the population of the rotational lev-
42 els in the excited state maps the population of the rotational levels in the
43 ground electronic state, which is supposed to be at equilibrium with the ki-
44 netic temperature of the species in the plasma. If molecules are formed in
45 the excited state by chemical reactions, equilibrium may not be achieved if
46 emission lifetimes of the excited state of the molecule are shorter than the
47 characteristic time of collision between the species in the plasma. In such a
48 case, the emission from newly produced diatomic molecules will contribute
49 to the emission spectrum. Hence, the kinetic temperature in transient laser-
50 generated plasma might not match the rotational temperature deduced from
51 the rovibronic emission. Indeed, the imaging of the spatial distribution of
52 AlO emission following the ablation of an Al target or an Al₂O₃ target in
53 air shows a spatial localisation of the emission restricted to the edge of the
54 plasma plume. This observation suggests that the AlO emission comes from
55 the newly-produced molecules at the interface between the plasma plume
56 and the ambient air [14, 15, 16, 17]. To determine if the rovibronic emission
57 from diatomic molecules can be used to assess the kinetic temperature of
58 the species in the plasma, one needs to check the consistency between the
59 temperatures deduced from the rovibronic emission (from plasma emission),
60 characterising the populations in the excited electronic state, and a direct
61 measurement of the rotational temperature (from DLIF) characterising the
62 population of the rotational levels in the ground electronic state.

63 The synthetic computation of emission spectra for the B-X system of
64 AlO is well described in literature [18, 19] and spectroscopic temperature
65 determination of aluminium monoxide in laser ablation was reported many
66 years ago [20]. Although packages exist to simulate electronic spectra of
67 diatomics, for example PGOPHER [21], ExoMol or programs from Parigger’s
68 group [22], we have produced our own routines and developed in house C++
69 library to compute the spectra (see supplementary materials) and a Matlab
70 program for the fitting procedure.

71 2. Experimental Set-up

72 The experimental set-up is described in figure 1. The fourth harmonic of
73 a pulsed Nd:YAG laser (266 nm, 5 ns, 20 Hz, 30 mJ per pulse) is focused

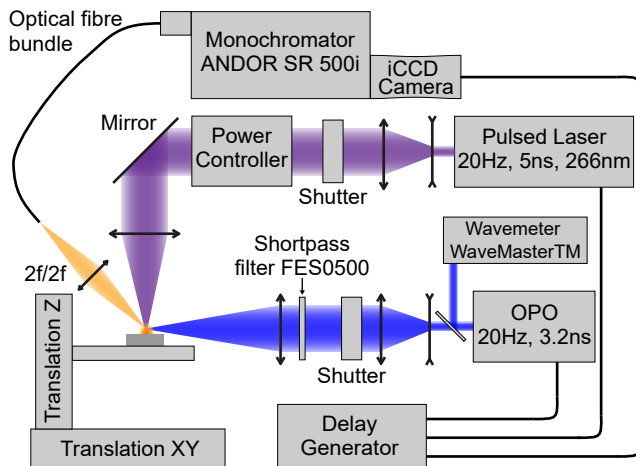


Figure 1: Scheme of the laser induced fluorescence (LIF) experimental set-up.

74 vertically by a UV lens ($f = 50$ mm) on a mono-crystal of alumina, creat-
 75 ing a plasma. The plasma is re-excited by a second laser pulse generat-
 76 ed by an NT230-50 Optical Parametric Oscillator (OPO) with SH/SF exten-
 77 sion from EKSPLA (NT230 series) using non-linear mixing of an Nd:YAG
 78 laser in order to produce broad wavelength coverage (220-1500 nm, 3.2 ns,
 79 20 Hz). A shortpass filter (FES0500, Thorlabs) is introduced on the excita-
 80 tion line to remove any contribution above 500 nm. In the excitation range
 81 of the AIO molecules used in this work (483 – 496 nm) the laser line-width
 82 is 66 pm FWHM (2.6 cm⁻¹). It was measured using a DEMON spectrom-
 83 eter (Lasertechnik Berlin) with a resolution of about 1 pm. The energy per
 84 pulse 17 ± 2 mJ was measured with a pyroelectric head on a Nova II ener-
 85 gometer (Ophir). A few percent of the laser beam is sent to a wavemeter
 86 WaveMasterTM from Coherent, measuring the excitation wavelength with an
 87 accuracy of 5 pm for each LIF spectrum. The beam is focused on the centre of
 88 the plasma, about 1 mm above the target surface. Emission from this part of
 89 the plasma is collected perpendicularly to the OPO beam path by a 1/2-inch
 90 achromatic lens ($f=25$ mm) imaging about 1 mm of the plasma on a bun-
 91 dle of 19 optical fibres (core diameter of 200 μ m) in a $2f/2f$ configuration.
 92 Light is diffracted in an Andor Shamrock 500i spectrometer (Czerny-Turner
 93 optical design) using a 2400 l/mm (blaze 240 nm) grating and an entrance
 94 slit of 10 μ m. The spectrometer is equipped with DHT340-25F-03 intensified
 95 CCD camera from ANDOR with full vertical binning. The spectrometer is

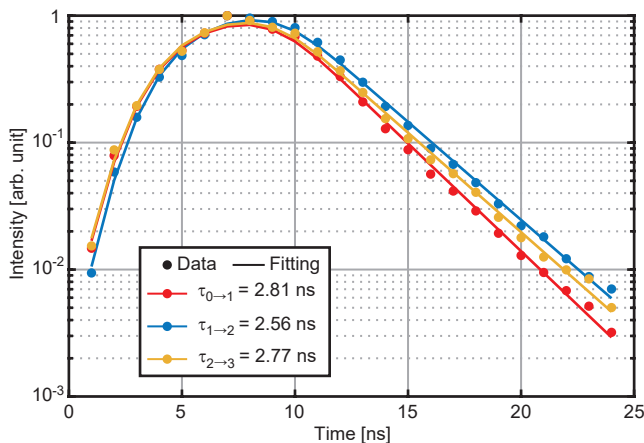


Figure 2: Time dependence of the normalised integrated intensity of the bandheads of three vibronic $B-X$ transitions (v', v'''): red dots correspond to the transition (0, 1), blue dots to (1, 2), and yellow dots to (2, 3). Bandheads are integrated over 0.5 nm. The delay 0 is arbitrary. Solid lines correspond to the fitting procedure described in the text and taking into account the Gaussian excitation pulse, with a pulse width of 3.2 ns FWHM, and a time gate of 5 ns. The deduced emission lifetime for each $v' - v'''$ transition is displayed in the inset.

96 calibrated before each measurement using scattered light from the OPO at
 97 different wavelengths. 22 spectra are recorded by shifting the OPO line by a
 98 step of 0.5 nm. For each spectrum, the peak position is fitted by a Lorentzian
 99 peak function. The resulting set of measured peak positions is then associ-
 100 ated with the set OPO wavelengths and a 3rd order polynomial fit is used for
 101 the calibration. The overall resolution of the acquisition system is 0.05 nm.
 102 The gate width is set to 5 ns to reduce the background signal with respect to
 103 the LiF signal. The delays between the ablation pulse, the excitation pulse
 104 and the measurement are controlled using a digital delay/pulse generator
 105 DG645 from Stanford Research Systems. During measurement, the target
 106 is moved in the horizontal plane by the translation stage with a precision of
 107 about 10 μm and moving at about 1 mm/s. This ensures ablation from a
 108 clean surface and provides repeatable ablation conditions and plasma char-
 109 acteristics. The spectral sensitivity response of the system is characterised
 110 by measuring a calibrated black body lamp in the exact configuration of
 111 the measurement. The measured spectrum is fitted by a 4th degree polyno-
 112 mial curve and divided by the tabulated spectrum. The resulting correction
 113 function is then applied to all the measurements.

114 3. Quantum numbers and notation

115 The observed bands belong to the electronic $B^2\Sigma^+ - X^2\Sigma^+$ system of
116 AIO. We use Hund’s case b) notation [19], designating the excited state
117 $B^2\Sigma^+$ by a *prime* symbol (n', v', N', J') and the ground state $X^2\Sigma^+$ by a
118 *double prime* symbols (n'', v'', N'', J'') in absorption. *Triple prime* symbols
119 (n''', v''', N''', J''') indicate ground state populations following the $B - X$ rovi-
120 bronc emission. n stands for the electronic levels. v is the vibrational quan-
121 tum number and J stands for the quantum number associated with the total
122 angular momentum. $J = N \pm 1/2$ for the $^2\Sigma^+$ electronic states, while N
123 corresponds to the quantum number associated with the rotational angular
124 momentum of the nuclei. The variation of each quantum number A is al-
125 ways given following $\Delta A = A^{upper} - A^{lower}$ (for example, $\Delta J = J' - J''$ or
126 $J' - J'''$), likewise we write (v', v'') for excitation and (v', v''') for emission.
127 Both $X^2\Sigma^+$ and $B^2\Sigma^+$ states have been extensively studied; assignments were
128 straightforward using parameters from Saksena *et al.* [23].

129 4. Emission lifetime measurements

130 The lifetime of the $B^2\Sigma^+$ state of AIO molecules is measured 10 μ s after
131 the creation of the plasma. This delay was chosen as a good compromise be-
132 tween maximizing the LIF signal and minimizing the plasma emission since
133 the plasma already cooled down significantly. The OPO wavelength is set
134 to 487 nm corresponding to the resonant absorption of the (1, 1) bandhead.
135 The acquisition gating is set to its minimum (5 ns). The delay between the
136 OPO and the acquisition is changed by 1 ns steps and starts about 5 ns
137 before the OPO pulse. Each measurement represents an averaged signal over
138 100 pulses. Figure 2 displays LIF intensity corresponding to bandheads at
139 507.9 nm (0,1), 510.2 nm (1, 2), and 512.3 nm (2, 3) integrated over 0.5 nm
140 and normalised with respect to the maximum intensity observed. The ex-
141 citation pulse and detection gate duration being similar to the deexcitation
142 time of the molecules, their shapes have to be taken into account to fit the
143 emission spectra display in Figure 2. Assuming a non depleted ground state,
144 the excitation rate of the molecules remains proportional to the instanta-
145 neous intensity during the whole laser pulse duration. Excitation intensity
146 evolves as a Gaussian function $\mathcal{G}(t)$ with a pulse width of 3.2 ns FWHM.
147 The emission intensity is given by the convolution product of the OPO pulse

148 intensity and an exponential decay:

$$I(t) = \mathcal{G}(t) \otimes \left[e^{-\frac{t}{\tau}} H(t) \right], \quad (1)$$

149 with $H(t)$ the Heaviside step function. During the measurement, the emission
150 is integrated over a gate $\Pi(t)$ of 5 ns time duration. The signal recorded $S(t)$
151 is the convolution product of the Rectangular function $\Pi(t)$ with the emission
152 $I(t)$:

$$S(t) = \Pi(t) \otimes I(t). \quad (2)$$

153 The solid lines correspond to fits of the data by the function described above.
154 It provides a measurement of the emission lifetime for the three (v' , v''') tran-
155 sitions considered: $\tau_{0 \rightarrow 1} = 2.8$ ns, $\tau_{1 \rightarrow 2} = 2.6$ ns, $\tau_{2 \rightarrow 3} = 2.8$ ns. These values
156 are very short compared to the radiative lifetime tabulated by the National
157 Institute of Standards and Technology (NIST), with values from 100 ns [24]
158 to 130 ns [25] for $v' = 0, 1, 2$. Indeed, the typical lifetime from NIST has
159 been measured at low pressure (20 Pa) while our measurements are made
160 at atmospheric pressure. Lifetime of a few nanoseconds has been previously
161 discussed by Nagli et al. [26]. They assume that the shorter lifetime is due to
162 collisional quenchings. Knowing the true effective value is important when
163 using this emission lifetime to determine the ratio of species in the plasma
164 from emission ratios [8, 27], so care is taken to measure the effective emission
165 lifetime in similar conditions.

166

167 5. Excitation Emission maps

168 Emission-excitation maps of atoms and molecules in the laser generated
169 plasma are obtained by changing the excitation wavelength and measuring
170 the emission of the plasma. The delay between the ablation and the OPO
171 pulses is set to 30 μ s. The acquisition starts just after the OPO pulse, and
172 the gate width is 5 ns. The wavelength of the OPO is changed from 483 nm
173 to 492 nm in steps of 0.05 nm. This value is similar to the FWHM of the
174 laser. The background spectrum of the plasma emission acquired in the same
175 conditions but without the OPO excitation pulse is subtracted from each
176 spectrum. All the spectra are corrected for the spectral sensitivity of the op-
177 tical and detection system using the black body calibration. A background
178 contribution determined from the average intensity for $\lambda < 507.5$ nm is also
179 subtracted. The resulting 2D map is presented on figure 3 (c). The largest

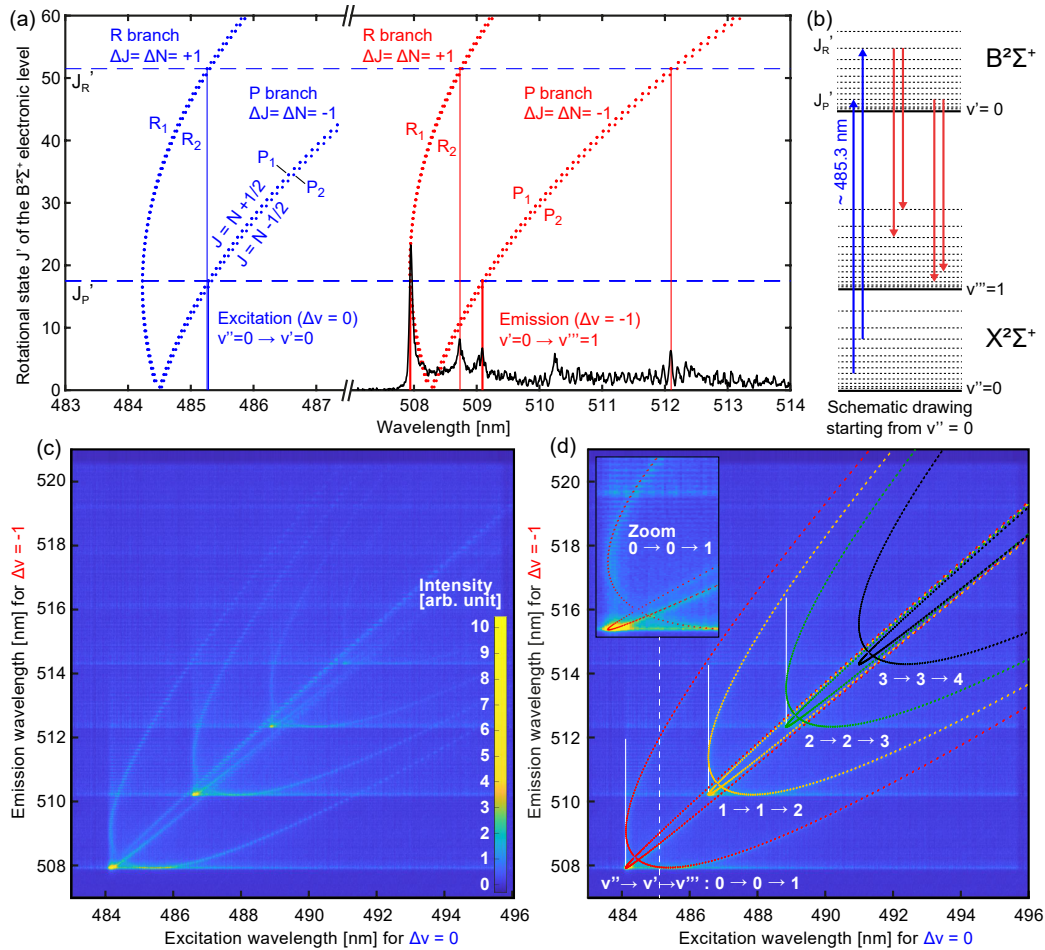


Figure 3: (a) Computed Fortrat diagram for the vibronic $B - X$ transition $(0,0)$ in blue and $(0,1)$ in red. Only the main branches characterised by $\Delta J = \Delta N = \pm 1$ are displayed, i.e. the R_1 -branch, R_2 -branch, P_1 -branch, and P_2 -branch. Indexes 1 and 2 correspond to the spin splitting. 1 stands for $J = N + 1/2$ while 2 stands for $J = N - 1/2$. Satellite branches ${}^P Q_{12}$ and ${}^R Q_{21}$ are not displayed because their intensity is weak for large J' values with respect to the intensity of the R-branch and P-branch. A given excitation wavelength can excite a few states (v', N', J') in the R-branches and P-branches. As an illustration, for an absorption around 485.3 nm (vertical blue line), we highlight two excited states $(0, N'_R, J'_R = N'_R + 1/2)$ and $(0, N'_P, J'_P = N'_P + 1/2)$. Each excited state leads to two emission lines (red vertical lines), one corresponding to a the R-branch and one corresponding to a P-branch. The highlight emission lines appear in the LIF spectrum (black). (b) Same example represented on an energy level scheme with arrows displayed for the resonant emission (DLIF). (c) 2D excitation/emission of an AIO molecule for a delay of 30 μs . (d) Superposition of the 2D excitation/emission spectrum with theoretical transitions assuming resonant excitation and emission from the (v', N', J') state. Satellite branches ${}^P Q_{12}$ and ${}^R Q_{21}$ are not displayed. The spectrum displayed in (a) corresponds to the white dashed line. Intersection with the four red branches correspond to the four emission peaks highlighted in (a) and (b). Vertical white lines show collisionally induced fluorescence following absorption in the bandheads $\Delta v = 0$.

180 intensities correspond to the the R-branch heads in absorption and emission.
 181 A bandhead is characterised by a large density of nearly-overlapping rovi-
 182 bronc transitions (See Fortrat diagram 3 (a)). In the excitation-emission
 183 map, a large density of transitions leads to intense emissions at 507.9 nm,
 184 corresponding to the bandhead of the (0,1) R-branch, following an excitation
 185 at 484.2 nm, corresponding to the bandhead of the (0,0) R-branch. In the
 186 same way, an intense emission is observed at 510.2 nm following an exci-
 187 tation at 486.7 nm (bandhead of (1,2) and (1,1) transitions), as well as at
 188 512.3 nm following an excitation at 488.9 nm (bandhead of (2,3) and (2,2)
 189 transitions). Furthermore, the transitions involving low vibrational levels,
 190 namely (0,0) excitation and (0,1) de-excitation, have a larger intensity, re-
 191 flecting enhanced populations, and large Franck-Condon factors (for (0,0)
 192 at least).

193 The curved branches on figures 3 (c) and (d) correspond to direct flu-
 194 orescence from the rotational states J' populated by the resonant OPO
 195 pulse excitation according to transition enabled by selection rules. For AlO
 196 $B^2\Sigma^+ - X^2\Sigma^+$ system, these include $\Delta N = \Delta J = \pm 1$ corresponding to the
 197 four branches R_1, R_2 and P_1, P_2 represented in blue on figure 3 (a). The spin
 198 component F_1 indicates levels $J = N + 1/2$, and F_2 $J = N - 1/2$. R-branches
 199 correspond to $\Delta J = +1$. P-branches correspond to $\Delta J = -1$. In the case
 200 of AlO, the satellite branches $^PQ_{12}$ and $^RQ_{21}$ corresponding to $\Delta N = \pm 1$
 201 and $\Delta J = 0$ are almost lost beneath the $\Delta N = \Delta J$ R and P branches. For
 202 $J > 5$, their intensities are at least 100 times lower than those of the main
 203 branches R and P. For simplicity, they are not plotted on the figures, but
 204 are taken into account when fitting the spectra.

205 In figure 3, excitation is performed in the $\Delta v = 0$ sequence while emission
 206 is observed in the spectral range $\Delta v = -1$. A given excitation wavelength can
 207 excite a few states (v', N', J') in the R-branches and P-branches according
 208 to the laser line-width. As an illustration, two states excited by 485.3 nm
 209 photons are highlighted in figure 3 (a) by the vertical blue lines, one in
 210 the R_1 branch and one in the P_1 branch for $(v', v'') = (0, 0)$. Assuming
 211 spin conservation, and looking at the transitions $\Delta v = -1$, each of these
 212 two excited states can decay by spontaneous emission through 2 channels
 213 following the selection rules $\Delta N = \Delta J = \pm 1$, *i.e.* one in the R-branch and
 214 one in the P-branch. In this example, it leads to 4 transitions indicated by
 215 the red vertical lines on figure 3 (a). The black spectrum in figure 3 (a)
 216 corresponds to a measured spectrum for an excitation at 485.3 nm. One
 217 can observe 4 groups of transitions centred around 507.95, 508.7, 509.1 and

218 512.1 nm. This relaxation scheme applied on all excitation wavelengths leads
219 to the 4 red branches for $v' = 0$ in the excitation/emission map on figure 3 (d).
220 The example given in figure 3 (a) corresponds to the white dashed line of
221 figure 3 (d). This reasoning also stands for the other vibrational levels and
222 the branches are represented in yellow for $v' = 1$, green for $v' = 2$ and black
223 for $v' = 3$. The inset in figure 3 (d) corresponds to a zoom on the wavelength
224 ranges corresponding to the bandhead transitions for (0,0) excitation and
225 (0,1) emission. It shows the good agreement between the measured spectrum
226 and the transition conserving J' .

227 The branches highlighted on figure 3 (d) correspond to direct fluorescence,
228 but no matter the excitation wavelength, some excited molecules undergo in-
229 elastic energy transfer, spreading the population in the rotation and vibration
230 quantum numbers. The black spectrum on figure 3 (a) clearly exhibits collisionally
231 induced fluorescence in addition to direct fluorescence. Collisionally
232 induced fluorescence especially leads to bright horizontal lines and vertical
233 lines on figure 3 (c). Vertical lines correspond to bandheads $\Delta v = 0$ in
234 absorption. They are shown with vertical white line in figure 3 (d). For
235 instance 484.2 nm corresponds to the (0,0) bandhead, 486.7 nm to the (1,1)
236 band-head and so on. For an excitation wavelength at a bandhead, the light
237 absorption is drastically increased because many transitions are excited si-
238 multaneously, populating multiple (v', N', J') levels, and then the collisionally
239 induced fluorescence signal increases accordingly. Horizontal lines correspond
240 to bandhead exaltation with $\Delta v = -1$. We observe that regardless of the
241 excitation wavelength, the collisionally induced fluorescence is concentrated
242 around bandhead wavelengths simply because of a larger density of lines. In
243 particular, one can notice horizontal lines corresponding to emission band-
244 heads at 507.9nm for the (0,1) transitions, 510.2 nm for the (1,2) transitions,
245 512.3 nm for the (2,3) transitions and so on.

246 Such Excitation/Emission maps show that, despite dense plasmas and
247 large collision rates, one can observe emission from partially thermalised
248 molecules exhibiting clear patterns according to selection rules of transitions.
249 These 2-D patterns resemble Fortrat diagrams and could be used to deter-
250 mine the validity of molecular constants in hot states (above 3000 K). Our
251 measurements match well the tabulated values for AIO within the precision
252 of the presented measurements.

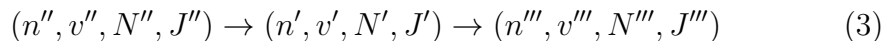
253 The lowest horizontal line corresponding to (0,1) bandhead emission at
254 507.8 nm appears following excitation anywhere out to 496 nm, where the
255 laser is resonant with $J'' > 120$ transitions in the (0,0) band, and lower J''

256 transitions in (1,1), (2,2) or (3,3) hot bands. Collisional energy transfer is
 257 responsible for transferring these excited state populations down to $v' =$
 258 0 , $J' \approx 20$, with $\Delta J'$ as much as -100 , and $\Delta v' = -1, -2, -3$. Gain in
 259 energy is evident, too, as illustrated by the vertical line formed following
 260 (0,0) laser excitation at 484.2 nm, extending to 512.3 nm. In this case,
 261 the emission signal comes from molecules in $v' = 0$ vibrational state with J
 262 values larger than 60, implying rotational energy transfer up to $\Delta J = +40$, or
 263 from molecules with v up to 2, corresponding to vibrational energy transfer
 264 up to $\Delta v = +2$. Horizontal lines for excitation wavelengths shorter than
 265 an excitation bandhead $\Delta v = 0$ reveal vibrational energy transfer. As an
 266 example, emission at 514.3 nm in the bandhead for the (3,4) transitions after
 267 excitation at 485 nm is only possible if there is a collisional energy transfer
 268 from $v' = 0$ to $v' = 3$. There are no selection rules governing collisional energy
 269 transfer in a non-symmetric molecules. These experiments with selective
 270 excitation and detection give direct evidence for collisional energy transfer
 271 propensities in AIO.

272 6. LIF spectrum simulation

273 In order to calculate the LIF spectrum, one has to consider both the exci-
 274 tation and de-excitation processes between the $X^2\Sigma^+$ (n'', n''') and $B^2\Sigma^+$ (n')
 275 electronic states. The LIF spectrum can be described as the superposition
 276 of direct fluorescence (DLIF), where the excited state (n', v', J', N') involved
 277 in the absorption and the emission is the same (resonant fluorescence), and
 278 laser-then-collisionally induced fluorescence (LCIF) after collisional popula-
 279 tion transfer in the excited state (ro-vibrationally relaxed fluorescence). The
 280 population redistribution can be approximated by independant vibrational
 281 and rotational Boltzmann distributions. By fitting spectral profiles to a linear
 282 combination of both contributions to LIF spectra, direct fluorescence and
 283 collisionally induced fluorescence, we are able to determine effective temper-
 284 atures describing the populations in the rotational and vibrational manifolds
 285 of X and B states independently. [We are following formalisms available in](#)
 286 [standard textbooks \[19, 28, 29\].](#)

287 To calculate the direct fluorescence spectrum, we consider the following
 288 excitation/de-excitation channel:



289 In the following, the set of quantum numbers (n, v, N, J) is noted l in the
 290 equations. The population of the ground state n'' ($X^2\Sigma^+$) is described by a
 291 rotational and vibrational temperatures T''_{rot} and T''_{vib} such that the density
 292 of molecules in the state (n'', v'', N'', J'') is:

$$N_{l''} = \frac{N_{n''}}{2} \cdot (2J'' + 1) \cdot \frac{\exp\left(-\frac{hc \cdot G_{n''}(v'')}{k_B \cdot T''_{vib}}\right)}{Q_{vib_{n''}}(T''_{vib})} \cdot \frac{\exp\left(-\frac{hc \cdot F_{n'',v'',i}(J'')}{k_B \cdot T''_{rot}}\right)}{Q_{rot_{n'',v''}}(T''_{rot})} \quad (4)$$

293 with $N_{n''}$ the total population of the electronic state, Q the partition func-
 294 tions, G the vibrational energy, and F the rotational energy. i corresponds
 295 to the spin splitting. $i = 1$ stands for $J = N + 1/2$ and $i = 2$ stands for
 296 $J = N - 1/2$. Considering only transitions from the $X^2\Sigma^+$ electronic state,
 297 $N_{n''}$ and Q_{vib} are assumed constant. Since we have $kT_{rot} \gg B_{n'',v''}$ (with
 298 $B_{n'',v''}$ the rotational constant for the state (n'', v'')), Q_{rot} is approximated
 299 using the rigid rotator model [27]:

$$Q_{rot_{n'',v''}} \simeq \frac{k_B T_{rot}}{B_{n'',v''}}, \quad (5)$$

300 and from equation 4,

$$N_{l''} \propto (2J'' + 1) \cdot \frac{B_{n'',v''}}{k_B T''_{rot}} \cdot \exp\left(-\frac{hc \cdot G_{n''}(v'')}{k_B \cdot T''_{vib}}\right) \cdot \exp\left(-\frac{hc \cdot F_{n'',v'',i}(J'')}{k_B \cdot T''_{rot}}\right) \quad (6)$$

301 The population of the upper state (n', v', N', J') is considered to be zero
 302 prior to excitation. This is not strictly true, but remaining plasma emission
 303 is very much weaker than LIF signal at the delay considered, and in any
 304 case the plasma emission contribution is subtracted from LIF spectra in our
 305 data processing. **Considering only the absorption of the excitation pulse**, the
 306 population variation of the upper state $N_{n',v',J'}$ is:

$$\frac{dN_{l'}}{dt} = \rho(\nu) \cdot B''_{l'} \cdot N_{l''} \quad (7)$$

307 with $B_{l''}'$ the Einstein coefficient for absorption and $\rho(\nu)$ [J.s.m⁻³] the ra-
 308 diance of the OPO pulse at the resonant wavelength. ν stands for the
 309 wavenumber of the transition. The population of the upper state is given
 310 by the integration of this transition rate over the duration of the OPO pulse.
 311 The radiance $\rho(\nu)$ is assumed undepleted on the whole plasma plume. The
 312 number of molecules in the ground state being large compared to the number
 313 of molecules excited by the pulse, one can consider that $N_{l''}$ remains constant.
 314 The Einstein coefficient for absorption can be related to the Einstein coeffi-
 315 cient for spontaneous emission $A_{n''',v''}'$ through the following relation:

$$B_{l''}' = \frac{(2J' + 1)}{(2J'' + 1)} \frac{c^3}{8\pi h \nu^3} A_{n''',v''}' \frac{S_{J''}^{J'}}{2J' + 1} \quad (8)$$

316 $S_{J''}^{J'}$ denotes the Hönl-London coefficient [19]. Combining equation 6, 7 and
 317 8 we obtain the number of molecules in the excited state after the pulse
 318 absorption:

$$N_{l''} \propto \frac{\rho(\nu)}{\nu^3} \cdot A_{n''',v''}' \cdot S_{J''}^{J'} \cdot \frac{B_{n''',v''}'}{k_B T_{rot}''} \cdot \exp\left(-\frac{hc \cdot F_{n''',v''},i(J'')}{k_B \cdot T_{rot}''}\right) \cdot \exp\left(-\frac{hc \cdot G_{n''}(v'')}{k_B \cdot T_{vib}''}\right) \quad (9)$$

319 The emission intensity from the state (n', v', N', J') to (n''', v''', N''', J''') is
 320 thus proportional to the population of the excited state multiplied by the
 321 Einstein coefficient for spontaneous emission $A_{n''',v'''}^{n',v'}$:

$$I_{l'''}' \propto A_{n''',v'''}^{n',v'} \cdot \frac{S_{J'''}^{J'}}{(2J' + 1)} \cdot N_{n',v',J'} \\
I_{l'''}' \propto \frac{\rho(\nu)}{\nu^3} \cdot A_{n''',v'''}^{n',v'} \cdot A_{n''',v''}^{n',v'} \cdot \frac{S_{J'''}^{J'} \cdot S_{J''}^{J'}}{(2J' + 1)} \frac{B_{n''',v''}'}{k_B T_{rot}''} \\
\times \exp\left(-\frac{hc \cdot F_{n''',v''},i(J'')}{k_B \cdot T_{rot}''}\right) \cdot \exp\left(-\frac{hc \cdot G_{n''}(v'')}{k_B \cdot T_{vib}''}\right) \quad (10)$$

322 Within the effective excited state life-time, the excited state (n', v', N', J')
 323 population is partially redistributed over other quantum levels. Because of
 324 the limited experimental resolution, the population redistribution of excited
 325 states cannot be determined directly from spectral analysis. Here we chose

326 to model the population after relaxation using two Boltzmann distributions
 327 with effective temperatures T'_{vib} and T'_{rot} for vibration and rotation. One
 328 should consider these temperatures as fitting parameters. The higher these
 329 parameters, the larger the population in states with high quantum levels.
 330 The intensity of each transition is proportional to:

$$I'_{J'''} \propto A'_{n''',v'''} \cdot S_{J'''} \cdot \frac{B_{n',v'}}{k_B T'_{rot}} \cdot \exp\left(-\frac{hc \cdot F_{n',v',i}(J')}{k_B \cdot T'_{rot}}\right) \cdot \exp\left(-\frac{hc \cdot G_{n'}(v')}{k_B \cdot T'_{vib}}\right) \quad (11)$$

331 The energy of each state, including the electronic energy, the vibrational
 332 energy $G_n(v)$ and the rotational energy $F_{n',v',i}(J')$, is computed using the
 333 data from Saksena *et al.* [23] (See supplementary materials). The rotational
 334 constant $B_{n,v}$ are also taken from Saksena *et al.* [23]. Figures 3 (a) and
 335 5 (a) show Fortrat diagrams calculated for electric-dipole allowed transitions
 336 between these states, verifying predicted wavenumbers with the lines lists
 337 given by Launila and Berg [30]. Each spectrum is calculated by summing
 338 the contribution of all allowed transition convoluted by a Gaussian function of
 339 width σ , and using the Einstein coefficient $A'_{n'',v''}$ (and $A'_{n''',v'''}$) from Hebert
 340 and Nicholls [31]. Both direct fluorescence (DLIF) spectrum and laser-then-
 341 collisionally induced fluorescence (LCIF) spectrum are normalised by their
 342 integral over the wavelength range. The final spectrum is the sum of both
 343 contributions, weighted by coefficient x :

$$I = x \times \frac{I_{LCIF}}{\int I_{LCIF}} + (1 - x) \frac{I_{DLIF}}{\int I_{DLIF}} \quad (12)$$

344 x is the fraction of the collisionally induced fluorescence with respect to the
 345 total emission. The closer the value of x to one, the more important is re-
 346 laxation in the excited electronic state.

347

348 7. LIF spectrum fit and results

349 Band contour fits have been performed for each excitation wavelength λ_e
 350 corresponding to the measured wavelength of the OPO pulse. The curve-
 351 fitting is performed using functions available in Matlab to solve nonlinear

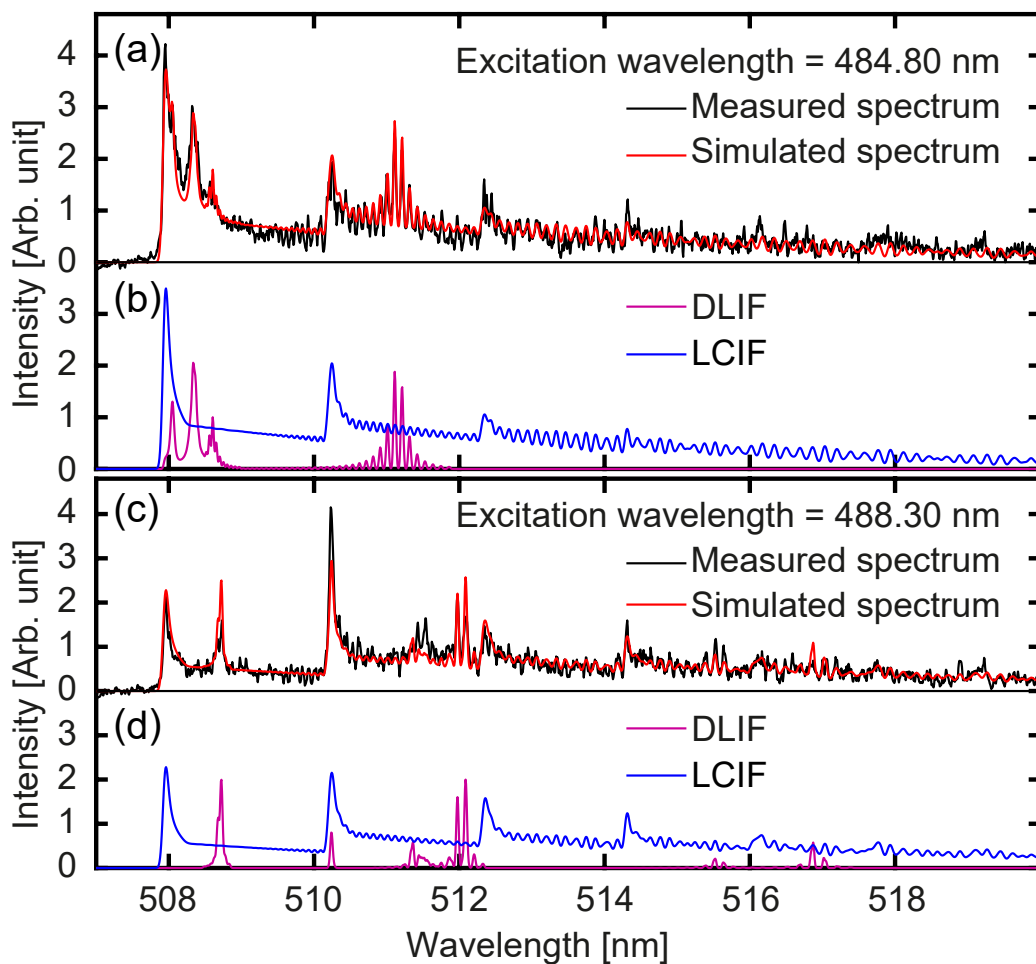


Figure 4: Example of fitted LIF spectrum (red) on measured spectrum for a delay of $30 \mu\text{s}$ (black) for the excitation wavelength 484.80 nm (a) and 488.30 nm (c) considering a single temperature $T_{X^2\Sigma^+}$ for the electronic ground state $X^2\Sigma^+$, and two temperatures, T'_{rot} and T'_{vib} , for the electronic excited state $B^2\Sigma^+$. Fitted values at 484.80 nm are $T'_{rot} = 4520 \text{ K}$, $T'_{vib} = 1330 \text{ K}$, and $T_{X^2\Sigma^+} = 2380 \text{ K}$. Fitted values at 488.30 nm are $T'_{rot} = 4450 \text{ K}$, $T'_{vib} = 2970 \text{ K}$, and $T_{X^2\Sigma^+} = 2720 \text{ K}$. Panels (b) and (d) show the collisionally induced fluorescence contribution in blue (LCIF) and the direct fluorescence contribution in magenta (DLIF) for each excitation wavelength.

352 least-squares regression. The radiance of the OPO pulse $\rho(\nu)$ is taken pro-
 353 portional to a Lorentz function centered on λ_e with a line-width of 66 pm
 354 FWHM. The fitting parameters are $T_{X^2\Sigma^+}$ describing the population in the
 355 $X^2\Sigma^+$ state, T'_{rot} and T'_{vib} describing the population in the $B^2\Sigma^+$ relaxed state,
 356 the width σ of the Gaussian function used to compute the synthetic spectra
 357 and the ratio x defined in equation 12. The average value of the fitted σ is
 358 0.084 nm (FWHM) with a standard deviation of 0.006 nm. $T''_{rot} = T''_{vib} =$
 359 $T_{X^2\Sigma^+}$ is assumed in the fitting process as we consider the equilibrium for the
 360 molecules in the ground state to be reached. Leaving both parameters free in
 361 the optimisation process is not relevant as T''_{vib} has little effect on the shape
 362 of the emission for the $\Delta v = 0$ transitions we measured here. In order to fit
 363 both temperatures of the ground state, one should consider exciting other
 364 transitions such as $\Delta v = \pm 1$. Furthermore, for excitation wavelengths lower
 365 than 486.5 nm, $v'' = 0$ is the only excited state and the fit does not depend
 366 on T''_{vib} .

367 Figures 4 (a) and (c) represent the calculated LIF spectrum (in red) fit-
 368 ted on the LIF spectrum measured (in black) for an excitation of 484.80 nm
 369 and 488.30 nm respectively. Figure 4 (b) and (d) represent the direct fluo-
 370 rescence contribution in magenta and the collisionally induced fluorescence
 371 contribution in blue in the calculated spectrum. The calculated LIF spectrum
 372 accurately reproduces the shape and intensities of the measured LIF spec-
 373 trum. On this spectral range, direct fluorescence represents only 6 to 16% of
 374 the integrated intensity signal. However, direct fluorescence remains easy to
 375 identify in tight spectral windows. Most of the intensity, about 90%, corre-
 376 sponds to collisionally induced fluorescence. Despite the short lifetime of the
 377 excited state (2.7 ns), collisions efficiently redistribute population amongst
 378 excited states v' and J' .

379

380 Results of the fitted temperatures for each excitation wavelength are dis-
 381 played on figure 5. Figure 5 (a) shows the Fortrat diagram of AlO molecules
 382 in the excitation range $\Delta v = 0$, from $v' = v'' = 0$ to $v' = v'' = 4$. Vertical
 383 dashed lines in figures 5 (a) and (b) indicate bandheads. Figure 5 (b) shows
 384 plots of fitted T'_{rot} and T'_{vib} describing the relaxed excited state.

385 Wavelengths below 484.2 nm cannot excite any bands in the $\Delta v = 0$
 386 sequence, but may be resonant with $\Delta v = +1$ transitions with large values
 387 of J'' . We find $T'_{rot} \simeq 6000 K$ and $T'_{vib} \simeq 4500 K$. Collisionally-induced
 388 fluorescence retains some memory of the excitation channel. Initial excitation
 389 of high values of J' and v' always results in high T'_{rot} and T'_{vib} temperatures

390 (obvious in the right hand side of figure 5 (b)).

391 Between 484.2 nm and 486.5 nm, the (0,0) transitions are excited, lead-
392 ing to a strong LIF signal. $T'_{vib} \simeq 1000 K$ is much lower here because only
393 the lower vibrational level $v' = 0$ is excited. After mixing, most of the
394 molecules remain in a low vibrational state, leading to a low effective vibra-
395 tional temperature. Around 484.2 nm, the rotational temperature T'_{rot} drops
396 to $\simeq 4000 K$ because the excitation corresponds to the (0,0) bandhead with
397 a large density of rovibronic transition with low values of J . Then, T'_{rot} in-
398 creases between 484.2 nm and 486.5 nm as the excited transitions have larger
399 and larger values of J .

400 Between 486.7 nm and 488.8 nm, both (0,0) and (1,1) transitions are
401 excited, leading to a higher T'_{vib} . At 486.7 nm, the density of (1,1) transition
402 is large (bandhead) and most of the excited molecules end in this vibrational
403 state explaining the peak in the vibrational temperature. On the contrary,
404 the rotational temperature first drops before increasing for the same reason
405 as presented for pure (0,0) transitions. The amplitude of the variation is
406 weaker as there are also contributions from the high-J resonances in the (0,0)
407 band, giving more "strating point" for collisional energy transfers. This pat-
408 tern for T'_{rot} and T'_{vib} repeats for each of the excited (v', v'') bands.

409
410 Figure 5 (c) shows the fitted temperatures $T_{X^2\Sigma^+}$ for the ground state. For
411 each OPO pulse centred on an excitation wavelength away from the band-
412 head, at least two sets of J'' values are excited, one belonging to R-branch
413 and the other to the P-branch. The large difference between these two sets
414 of J'' numbers allows obtaining a value of $T_{X^2\Sigma^+}$ for each excitation wave-
415 length longer than 485 nm. For wavelengths longer than 490 nm, the direct
416 fluorescence signal is too weak to achieve convergence and deduce $T_{X^2\Sigma^+}$.
417 Figure 5 (c) shows that $T_{X^2\Sigma^+}$ remains stable as it depends on the plasma
418 thermodynamic state only, and not on the excitation process. One can no-
419 tice a slight peak for the (1,1) bandhead, but also for the (2,2) bandhead.
420 In this region, large resonant intensity and self-absorption might impact the
421 fitting procedure, but the possible consequences of an optically thick sam-
422 ple are not considered here. To determine the temperature of the ground
423 state, we average $T_{X^2\Sigma^+}$ values from excitation wavelength between 485 and
424 486.5 nm (shaded area in figure 5 (c)). In that range, the emission shape
425 does not depend on T''_{vib} since only one vibrational state is involved, and we
426 then assume $T_{X^2\Sigma^+} = T''_{rot}$. The histogram for the $T_{X^2\Sigma^+}$ distribution from
427 the shaded area is plotted in figure 5 (d). The average value is 3150 K, the

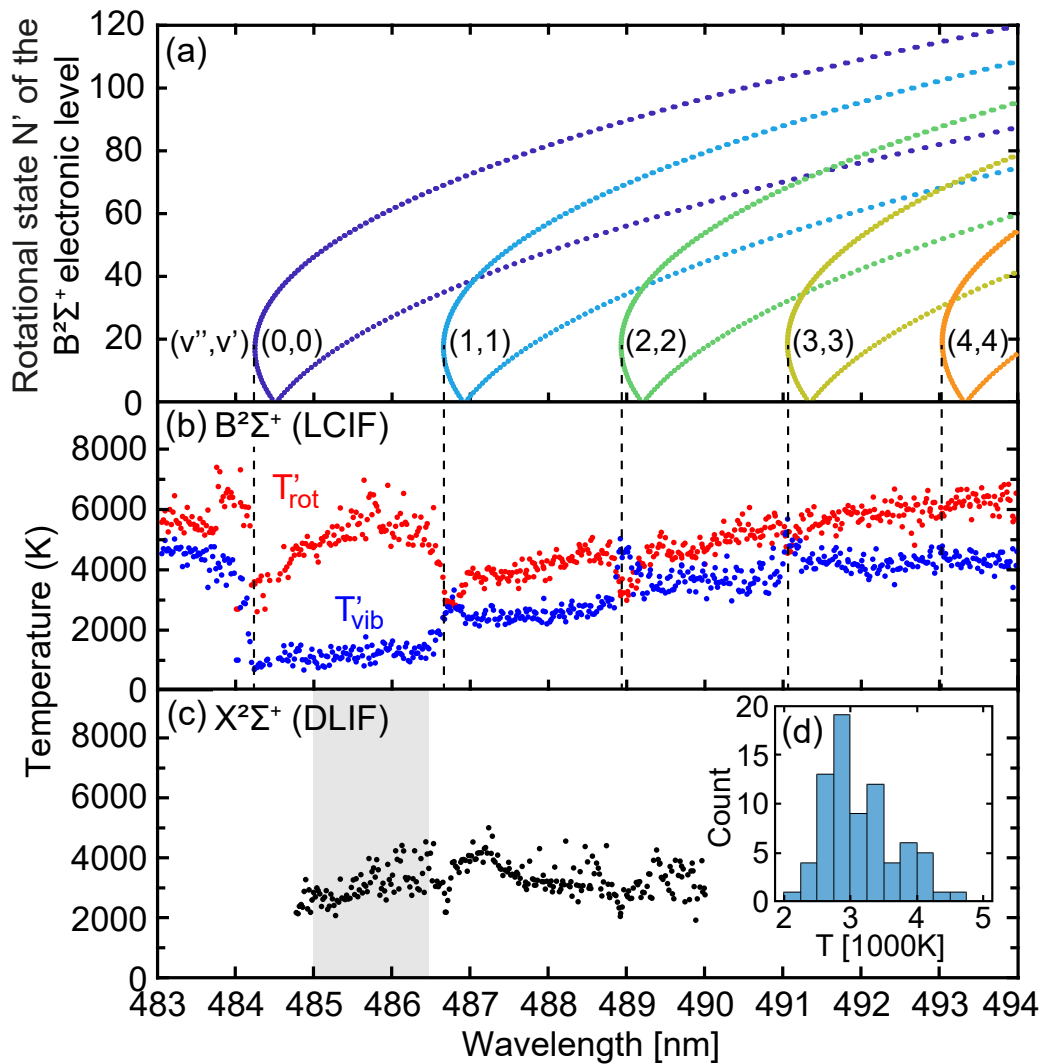


Figure 5: (a) Fortrat diagram for the $\Delta v = 0$ excited transitions. (b) Rotational (red) and vibrational (blue) temperatures describing the collisionally induced fluorescence (LCIF) depending on the excitation wavelength. (c) Temperature of the ground state ($X^2\Sigma^+$) depending on the excitation wavelength measured from the direct fluorescence (DLIF). (d) Histogram of the ground state ($X^2\Sigma^+$) temperatures corresponding to the selected excitation range shaded area. The average value is 3150 K, the standard deviation is 552 K and the temperature interval for a confidence level of 70% (two-sided) is ± 67 K.

428 standard deviation is 552 K and the temperature interval for a confidence
429 level of 70% (two-sided) is ± 67 K.

430 This temperature can be compared to the vibrational and rotational tem-
431 peratures of the $B^2\Sigma^+$ excited state measured from emission spectroscopy.
432 Emission of AIO molecules has been measured before and after the 2D scan-
433 ning without OPO excitation and fitted as presented in the supplementary
434 materials following the method presented in Lam *et al.* [27]. The value ob-
435 tained for the vibrational temperature is 5620 ± 330 K (confidence level of
436 70%) at a delay of $30 \mu s$. The value obtained for the rotational temperature
437 is 3130 ± 100 K. The rotational temperature of the excited state $T_{rot}^{B^2\Sigma^+}$ is in
438 good agreement with the rotational temperature of the ground state $T_{X^2\Sigma^+}$
439 measured by LIF. These measurements confirm that after $30 \mu s$, the mea-
440 surement of the rotational temperature of the excited state from the emission
441 of the plasma is a good probe of the rotational temperature of the ground
442 state.

443 In order to test it for shorter delay time in the plasma, the same experi-
444 ment was run with a delay of $5 \mu s$. The average value of $T_{X^2\Sigma^+}$ is 3700 K, the
445 standard deviation is 530 K and the temperature interval for a confidence
446 level of 70% (two-sided) is ± 64 K. $T_{X^2\Sigma^+}$ at $5 \mu s$ is larger than after $30 \mu s$ as
447 the plasma cools down. In comparison, the direct fluorescence provides a vi-
448 brational temperature of the excited state $T_{vib}^{B^2\Sigma^+} = 6860 \pm 350$ K (confidence
449 level of 70%) and a rotational temperature of $T_{rot}^{B^2\Sigma^+} = 3850 \pm 100$ K. Here
450 again, the values are in agreement considering the error of the measurement.
451 These temperatures are consistent with the ones reported for AIO molecular
452 temperatures for the same delay in laser-generated plumes from metals [32].

453 8. Conclusion

454 We used time resolved 2D LIF to study the out-of-equilibrium properties
455 of excited AIO molecules formed in a laser-generated plasma. Laser induced
456 plasmas are usually characterised using emission spectroscopy to determine
457 temperature and composition. This approach probes only the excited state
458 of the molecules that are likely to be directly formed in the plasma. Ground-
459 state distributions are likely to be different. By tuning a laser to chosen
460 molecular transitions, we can probe rovibrational distribution in the ground
461 state as well.

462 LIF was used to measure the effective lifetime $\tau = 2.7 \pm 0.2$ ns of the
463 $B^2\Sigma^+$ state of AIO molecules at atmospheric pressure. This lifetime is much

464 shorter than tabulated values in vacuum because of collisional quenching
465 in the plasma. Effective lifetimes are key parameters for the calculation of
466 molecular concentrations in LIBS.

467 By fitting both direct and collisionally induced fluorescence contributions
468 to spectra of AlO molecules 5 μ s and 30 μ s after ablation, we were able to
469 determine the temperature of the ground electronic state of AlO($X^2\Sigma^+$) and
470 the effective temperatures describing the relaxed state of the molecules par-
471 tially thermalised. Their population appears to be well described by Boltz-
472 mann populations using effective rotational and vibrational temperatures.
473 These temperatures are different, and depend on excitation channel. Clearly
474 molecules do not reach full internal equilibrium, or equilibrium with the
475 plasma kinetic temperature. In such a plasma, collisions are not sufficient to
476 ensure equilibrium of the excited molecule population from an initial state
477 strongly out of equilibrium.

478 On the contrary, the rotational temperature deduced from standard plasma
479 emission, without re-excitation of the plasma, is consistent with the rota-
480 tional temperature of the ground state deduced from LIF, both after 5 μ s
481 and 30 μ s. The AlO molecules formed in the excited state $B^2\Sigma^+$ in the
482 plasma reach the equilibrium before emission. This might be because they
483 are not formed far from equilibrium, unlike the molecules excited by LIF. The
484 measurement of the temperature in the plasma considering the rotational
485 temperature of the excited state of the diatomic molecules is confirmed to be
486 valid.

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490 **Disclosures**

491 The authors declare no conflicts of interest.

492 **CRedit authorship contribution statement**

493 **Arsene Chemin**: Methodology, Investigation, Formal analysis, Visu-
494 alization, [Software](#), Writing - Original Draft. **Amanda Ross**: Validation,
495 Writing - Review & Editing. **Sylvain Hermelin**: Methodology, Writing -

496 Review & Editing. **Patrick Crozet**: Validation, Writing - Review & Edit-
497 ing. **Vincent Motto-Ros**: Conceptualization, Methodology, Validation,
498 Writing - Review & Editing. **Gilles Ledoux**: Conceptualization, Method-
499 ology, Writing - Review & Editing. **Christophe Dujardin**: Funding ac-
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501 Visualization, Data Curation, Software, Writing - Original Draft, Supervi-
502 sion.

503 **Declaration of Competing Interest**

504 The authors declare that they have no known competing financial inter-
505 ests or personal relationships that could have appeared to influence the work
506 reported in this paper.

507 **Data availability**

508 Data will be made available on request.

509 **Appendix A. Supplementary material**

510 The supplementary materials describes the energy level calculations, in-
511 cluding the parameters used, and the transition probability calculation. It
512 also shows the plasma emission spectra at 5 μs and 30 μs with their fits.

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