LETTER TO THE EDITOR

Trans-cis molecular photoswitching in interstellar Space*

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ABSTRACT

As many organic molecules, formic acid (HCOOH) has two conformers (trans and cis). The energy barrier to internal conversion from trans to cis is much higher than the thermal energy available in molecular clouds. Thus, only the most stable conformer (trans) is expected to exist in detectable amounts. We report the first interstellar detection of cis-HCOOH. Its presence in ultraviolet (UV) irradiated gas exclusively (the Orion Bar photodissociation region), with a low trans-to-cis abundance ratio of 2.8 ± 1.0, supports a photoswitching mechanism: a given conformer absorbs a stellar photon that radiatively excites the molecule to electronic states above the interconversion barrier. Subsequent fluorescent decay leaves the molecule in a different conformer form. This mechanism, which we specifically study with ab initio quantum calculations, was not considered in Space before but likely induces structural changes of a variety of interstellar molecules submitted to UV radiation.

Key words. Astrochemistry – Line: identification – ISM: clouds – ISM: molecules – Photon-dominated region (PDR)

1. Introduction

Conformational isomerism refers to isomers (molecules with the same formula but different chemical structure) having the same chemical bonds but different geometrical orientations around a single bond. Such isomers are called conformers. An energy barrier often limits the isomerization. This barrier can be overcome by light. Photoisomerization (or photoswitching) has been studied in ice IR-irradiation experiments (e.g. Mac ñás et al. 2004), in biological processes, and, for large polyatomic molecules, also in gas-phase experiments (Ryan & Levy 2001). HCOOH is the simplest organic acid and has two conformers (trans and cis) depending on the orientation of the hydrogen single bond. The most stable trans conformer was the first acid detected in the interstellar medium, ISM (Zuckerman et al. 1971). Gas-phase trans-HCOOH shows moderate abundances towards hot cores (Liu et al. 2001) and hot corinos (Cazaux et al. 2003), in cold dark clouds (Cernicharo et al. 2012), and in cometary coma (Bockelee-Morvan et al. 2006). Solid HCOOH is present in interstellar ices (Keane et al. 2001) and in chondritic meteorites (Briscoe & Moore 1993).

The ground-vibrational state of cis-HCOOH is 1365 ± 30 cm⁻¹ higher in energy than the trans conformer (Hocking 1976). The energy barrier to internal rotation (the conversion from trans to cis) is about 4827 cm⁻¹ (Hocking 1976), approximately 7000 K in temperature units. This is much higher than the thermal energy available in molecular clouds (having typical temperatures from about 10 to 300 K). Generalizing this reasoning, only the most stable conformer of a given species would be expected in such clouds. Photoswitching, however, may be a viable mechanism producing the less stable conformers in detectable amounts: a given conformer absorbs a high-energy photon that radiatively excites the molecule to electronic states above the interconversion energy barrier. Subsequent radiative decay to the ground state would leave the molecule in a different conformer.

In this work we have searched for pure rotational lines of the trans- and cis-HCOOH conformers in the 3 millimetre spectral band. We observed three prototypical interstellar sources known to display a very rich chemistry and bright molecular line emission: (i) the Orion Bar photodissociation region (PDR): the edge of the Orion cloud irradiated by ultraviolet (UV) photons from nearby massive stars (e.g. Goicoechea et al. 2016), (ii) the Orion hot core: warm gas around massive protostars (e.g. Tercero et al. 2010), and (iii) Barnard 1-b (B1-b): a cold dark cloud (e.g. Cernicharo et al. 2012). The two latter sources are shielded from strong UV radiation fields. We only detect cis-HCOOH towards the Orion Bar. This represents the first interstellar detection of the conformer.

2. Source selection and observations

Because of its nearly edge-on orientation, the Orion Bar PDR is a template source to study the molecular content as the far-UV radiation field (FUV; stellar photons with energies below 13.6 eV, or wavelengths (λ) longer than 911 Å, the hydrogen atom ionization threshold) is attenuated from the cloud edge to the interior (Hollenbach & Tielens 1999). The impinging FUV radiation field at the edge of the Bar is about 4 × 10⁻⁴ times the mean interstellar radiation field (e.g. Goicoechea et al. 2016) and references therein). We observed three positions of the Bar characterized by a decreasing FUV photon flux.
We have used the IRAM-30 m telescope (Pico Veleta, Spain) and the 90 GHz EMIR receiver. We employed the Fast Fourier Transform Spectrometer (FFTS) backend at 200 kHz spectral resolution (0.7 km s$^{-1}$ at 90 GHz). Observations towards the Orion Bar are part of a complete millimetre (mm) line survey (80 – 360 GHz). We used the IRAM-30 m telescope (Pico Veleta, Spain) for the 13CO and HCOOH (Cernicharo et al. 2012). They include specific deep searches for CO lines in the 3 mm band towards different positions located at a distance of 14", 40", and 65" from the ionisation front (Fig. 1A). Their offsets coordinates with respect to the $\alpha_{2000} = 05h35m20.1s$, $\delta_{2000} = -05\degree25\arcmin07.0\arcsec$ position at the ionisation front are (+10", -10"), (+30", -30"), and (+35", -55"). The observing procedure was position switching with a reference position at (-600", 0") to avoid the extended emission from the Orion molecular cloud. The half power beam width (HPBW) at 3 mm ranges from ~30.8" to 21.0". We reduced and analysed the data using the GILDAS software as described in Cuadrado et al. (2015). The antenna temperature, $T_A$, was converted to the main beam temperature, $T_{MB}$, using $T_{MB} = T_A/\eta_{MB}$, where $\eta_{MB}$ is the antenna efficiency ($\eta_{MB} = 0.87 - 0.82$ at 3 mm). The rms noise obtained after 5 h integration is ~1 – 5 mK per resolution channel.

We also searched for HCOOH in regions shielded from strong FUV radiation fields (see Appendix E). We selected two chemically rich sources for which we have also carried out deep mm-line surveys with the IRAM-30m telescope: towards the hot core in Orion BN/KL (Tercero et al. 2010) and towards the quiescent dark cloud Barnard 1-b (B1-b; Cernicharo et al. 2012).

3. Results

3.1. Line identification

We specifically computed the cis-HCOOH rotational lines frequencies by fitting the available laboratory data (Winnewisser et al. 2002) with our own spectroscopic code, MADEX (Cernicharo 2012). The standard deviation of the fit is 60 kHz. For the trans conformer, higher frequency laboratory data (Cazzoli et al. 2010) were also used in a separate fit. The standard deviation of the fit for trans-HCOOH is 42 kHz. These deviations are smaller than the frequency resolution of the spectrometer we used to carry out the astronomical observations. Formic acid is a near prolate symmetric molecule with rotational levels distributed in different $K_a$ rotational ladders ($K_a = 0, 1, 2...$). Both $a$- and $b$-components of its electric dipole moment $\mu$ exist (Winnewisser et al. 2002). The dipole moments of the cis conformer ($\mu_a = 2.650$ D and $\mu_b = 2.710$ D, Hocking 1976) are stronger than those of the trans conformer ($\mu_a = 1.421$ D and $\mu_b = 0.210$ D, Kuze et al. 1982).

In total, we identify 12 rotational lines of cis-HCOOH and 10 of trans-HCOOH above 3$\sigma$ towards the FUV-illuminated edge of the Orion Bar, (+10", -10") position. The detected lines from the cis- and trans-HCOOH are shown in Figs. 2 and D.1 respectively. Lines attributed to HCOOH show a Gaussian line profile centred at the systemic velocity of the Orion Bar (10.4 ± 0.3 km s$^{-1}$). Lines are narrow, with linewidths of 1.9 ± 0.3 km s$^{-1}$. The large number of detected lines, and the fact that none of the lines correspond to transitions of abundant molecules known to be present in the Bar or in spectroscopic line catalogues, represents a robust detection of the cis conformer. The observational parameters and Gaussian fit results are tabulated in Tables E.1 and F.2 for the cis and trans conformer, respectively.

3.2. Line stacking analysis

Complex organic molecules have relatively low abundances in FUV-irradiated interstellar gas (Guzmán et al. 2014). Indeed, detected trans-HCOOH lines are faint. To improve the statistical significance of our search towards the positions inside the Bar, we performed a “line stacking” analysis. For each observed position, we added spectra at the expected frequency of several HCOOH lines that could be present within the noise level (sharing similar rotational level energies and Einstein coefficients). The spectra in frequency scale were first converted to local standard of rest (LSR) velocity scale and resampled to the same velocity channel resolution before stacking. We repeated this procedure for trans-HCOOH lines. This method allows us to search for any weak line signal from the two conformers that could not be detected individually.

Figure 1B shows a comparison of the stacking results for cis and trans-HCOOH lines towards the three target positions in the Bar. Although we detect trans-HCOOH in all positions, emis-
detection of cis HCOOH experimentally (Sugarman 1943; Ioannoni et al. 1990; Brouard & Wang 1992). Su et al. 2000) and theoretically (Beatty-Gravis et al. 2002). He & Fang 2003, Maeda et al. 2015). Dissociation of HCOOH takes place after absorption of FUV photons with energies greater than ~5 eV (λ < 2500 Å). Recently, Maeda et al. (2015) determined that this dissociation threshold coincides with the crossing of the S0 and T1 electronic states of the molecule. The specific products of the photofragmentation process (of the different photodissociation channels) depend on the specific energy of the FUV photons and on the initial HCOOH conformer. Interestingly, absorption of lower energy photons does not dissociate the molecule but induces fluorescent emission. In particular, HCOOH fluorescence from the S1 excited electronic state has been observed in laser-induced experiments performed in the λ = 2500 - 2700 Å range (Ioannoni et al. 1990; Brouard & Wang 1992). These studies indicate that the geometrical configuration of the two hydrogen atoms is different in the S0 and S1 states. The fluorescence mechanism from the S1 state is a likely route for the trans → cis isomerization. In addition, the isomerization barrier from the S1 state (~1400 cm⁻¹) is much lower than from the ground.

In order to quantify the role of the photomericizing mechanism, we carried out ab initio quantum calculations and determined the HCOOH potential energy surfaces of the S0 and S1 electronic states as a function of the two most relevant degrees of freedom, φ1, the torsional angle of OH and φ2, the torsional angle of CH (see Appendix A and Fig. A.1). With this calculation we can compute the position of the photon absorptions leading to fluorescence (those in the approximate λ = 2300 - 2800 Å range), and the probabilities to fluoresce from one conformer to the other (the trans-to-cis and cis-to-trans photomericizing cross-sections and probabilities, see Fig. 3).

With a knowledge of N_ph(λ), the FUV photon flux in units of photon cm⁻² s⁻¹ Å⁻¹, we can calculate the number of trans-to-cis and cis-to-trans photomericizations per second (ξtc and ξct, respectively. See Appendix B). In the absence of any other mechanism destroying HCOOH, the ξtc/ξct ratio provides the trans-to-cis abundance ratio in equilibrium. The time needed to reach the equilibrium ratio is then ξtc/ξct = N_ph(λ), and thus ξtc and ξct, depend on the FUV radiation sources (type of star) and on the cloud position. Describing the cloud depth position in terms of the visual extinction into the cloud (Av), one magnitude of extinction is equivalent to a column density of about 10²¹ H₂ molecules per cm⁻² in the line-of-sight. In general (for a flat, wavelength-independent FUV radiation field), HCOOH photodissociation will always dominate fluorescence (photodissociation cross-sections are larger and the relevant photons can be absorbed over a broader energy range, E > 5 eV). The strength and shape of the interstellar FUV radiation field, however, is a strong function of Av and is very sensitive to the dust and gas absorption properties. Because of the wavelength-dependence of the FUV-absorption process, N_ph(λ) drastically changes as one moves from the cloud edge to the shielded interior. In particular, the number of low-energy FUV photons (e.g. below 5 eV) relative to the high-energy photons (e.g. those above 11 eV dissociating molecules such as CO and ionising atoms such as carbon) increases with Av. In this work we used a FUV radiative transfer and thermo-chemical model (Le Petit et al. 2006) to estimate N_ph(λ) at different positions of the Orion Bar. The well-known “2175 Å bump” of the dust extinction curve, producing HCOOH fluorescence (Fig. 3, bottom panel). The resulting FUV radiation spectrum, N_ph(λ), at different Av is used.

3.3. Trans-to-cis abundance ratios

Given the number of HCOOH lines detected towards the Bar, we can determine the column density and rotational temperatures of both conformers accurately (see Appendix D). In particular, we infer a low trans-to-cis abundance ratio of 2.8 ± 1.0. The non-detection of cis-HCOOH towards the Orion hot core and B1-b (see Appendix E) provides much higher trans-to-cis limits (>100 and >60, respectively). This suggests that the presence of cis-HCOOH in the Orion Bar PDR is related to the strong FUV field permeating the region.

4. Photoisomerization rates and discussion

Photolysis of HCOOH has been widely studied, both experimentally (Sugarman 1943; Ioannoni et al. 1990; Brouard & Wang 1992; Su et al. 2000) and theoretically (Beatty-Gravis et al. 2002; He & Fang 2003; Maeda et al. 2015). Dissociation of cis-HCOOH takes place after absorption of FUV photons with energies greater than ~5 eV (λ < 2500 Å). Recently, Maeda et al. (2015) determined that this dissociation threshold coincides with the crossing of the S0 and T1 electronic states of the molecule. The specific products of the photofragmentation process (of the different photodissociation channels) depend on the specific energy of the FUV photons and on the initial HCOOH conformer. Interestingly, absorption of lower energy photons does not dissociate the molecule but induces fluorescent emission. In particular, HCOOH fluorescence from the S1 excited electronic state has been observed in laser-induced experiments performed in the λ = 2500 - 2700 Å range (Ioannoni et al. 1990; Brouard & Wang 1992). These studies indicate that the geometrical configuration of the two hydrogen atoms is different in the S0 and S1 states. The fluorescence mechanism from the S1 state is a likely route for the trans → cis isomerization. In addition, the isomerization barrier from the S1 state (~1400 cm⁻¹) is much lower than from the ground.

In order to quantify the role of the photomericizing mechanism, we carried out ab initio quantum calculations and determined the HCOOH potential energy surfaces of the S0 and S1 electronic states as a function of the two most relevant degrees of freedom, φ1, the torsional angle of OH and φ2, the torsional angle of CH (see Appendix A and Fig. A.1). With this calculation we can compute the position of the photon absorptions leading to fluorescence (those in the approximate λ = 2300 - 2800 Å range), and the probabilities to fluoresce from one conformer to the other (the trans-to-cis and cis-to-trans photomericizing cross-sections and probabilities, see Fig. 3).

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to calculate $\xi_{cis}$ and $\xi_{trans}$ (Table B.1). We determine that at a cloud depth of about $A_V = 2 - 3$ mag, and if the number of HCOOH dissociating photons is small compared to the number of photons producing photoisomerization (i.e. most photons with $E > 5$ eV have been absorbed), the cis conformer should be detectable with a trans-to-cis abundance ratio of about $3.5 - 4.1$. These values are remarkably close to the trans-to-cis ratio inferred from our observations of the Bar.

Closer to the irradiated cloud edge ($A_V = 0 - 2$ mag), photodissociation destroys the molecule much faster than the time needed for the trans-to-cis isomerization. On the other hand, too deep inside the cloud, the flux of $E > 5$ eV photons decreases to values for which the isomerization equilibrium would take an unrealistic amount of time (>10^8 years for $A_V = 5$ mag). Therefore, our detection of cis-HCOOH in irradiated cloud layers where CO becomes the dominant carbon carrier (a signature of decreasing flux of high-energy FUV photons) agrees with the photoisomerization scenario.

For standard grain properties and neglecting HCOOH photodissociation, we calculate that the time needed to achieve a low trans-to-cis abundance ratio and make cis-HCOOH detectable at $A_V = 2 - 3$ mag is $10^4 - 10^5$ years (see Table B.1). This is reasonably fast, and shorter than the cloud lifetime. In practice, it is not straightforward to quantify the exact contribution of HCOOH photodissociation and photoisomerization at different cloud positions. The above time-scales require that the flux of $E > 5$ eV dissociating photons is small compared to those producing fluorescence. This depends on the specific dust absorption properties, that sharply change with $A_V$ as dust populations evolve (Draine 2003), on the strength and width of the 2175 Å extinction bump, and on the role of molecular electronic transitions blanketing the FUV spectrum. The similar trans-HCOOH line intensities observed towards the three positions of the Bar (Fig. 1) suggest that even if the HCOOH photodestruction rate increases at the irradiated cloud edge, the HCOOH formation rate (from gas-phase reactions or desorbing directly from grain surfaces, Garrod et al. 2008) must increase as well. The inferred HCOOH abundances are not particularly high, $(0.6 - 3.0) \times 10^{-10}$ with respect to H. Hence, modest HCOOH photodestruction and formation rates are compatible with the photoswitching mechanism occurring in realistic times.

Although the observed abundances of trans- and cis-HCOOH in the Orion Bar are compatible with gas-phase photoisomerization, we note that photoswitching may also occur on the surface of grains covered by HCOOH ices. In a similar way, solid HCOOH (mostly trans) can absorb FUV photons that switch the molecule to the cis form before being desorbed. Once in the gas, both conformers will continue their photoisomerization following absorption of $\lambda \geq 2500$ Å photons. Laboratory experiments are needed to quantify the mechanisms leading to HCOOH ice photoswitching by FUV photon absorption.

Searching for further support to the FUV photoswitching scenario, we qualitatively explored two other possibilities for the trans-to-cis conversion. First, the isomerization of solid HCOOH after IR irradiation of icy grain surfaces (as observed in the laboratory, Maçôas et al. 2004; Olbert-Majkut et al. 2008) and subsequent desorption to the gas-phase. Second, the gas-phase isomerization by collisions of HCOOH with energetic electrons (~0.5 eV). We concluded that if these were the dominant isomerization mechanisms, emission lines from cis-HCOOH would have been detected in other interstellar sources (see Appendix C).

Isomerization by absorption of UV photons was not considered as a possible mechanism to induce structural changes of molecules in interstellar gas. The detection of cis-HCOOH towards the Orion Bar opens new avenues to detect a variety of less stable conformers in Space. This can have broad implications in astrochemistry and astrobiology.

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References
Beatty-Travis, L. M., Moule, D. C., Lim, E. C., & Judge, R. H. 2002, J. Chem. Phys., 117, 4831
Blake, G. A., Sutton, E. C., Masson, C. R., & Phillips, T. G. 1987, ApJ, 315, 621
Bockelée-Morvan, D., Lis, D. C., Wink, J. E., et al. 2000, A&A, 353, 1101
Bischof, J. F. & Moore, C. B. 1993, Meteoritics, 28, 330
Brouard, M. & Wang, J.-X. 1992, J. Chem. Soc., Faraday Trans., 88, 3511
Cardelli, J. A., Clayton, G. C., & Mathis, J. S. 1989, ApJ, 345, 245
Canca, S., Tielen, A. G. M., Ceccarelli, C., et al. 2003, ApJ, 593, L51
Cazzoli, G., Puzzarini, C., Stopkowicz, S., & Gauss, J. 2010, A&A, 520, A64
Cernicharo, J. 2012, in EAS Publications Series, Vol. 58, 251–261
Cernicharo, J., Kissel, Z., Tercero, B., et al. 2016, A&A, 587, L4
Cernicharo, J., Marcelino, N., Roueff, E., et al. 2012, ApJ, 759, L43
Cuadra, S., Gisocchio, J. R., Pillier, P., et al. 2015, A&A, 575, A82
Draeme, B. T. 1978, ApJS, 36, 595
Draine, B. T. 2003, ARA&A, 41, 241
Garrod, R. T., Wicdics Weaver, S. L., & Herbst, E. 2008, ApJ, 682, 283
Gerin, M., Pety, J., Fuente, A., et al. 2015, A&A, 577, L2
Appendix A: *Ab initio* estimation of fluorescence cross-sections and photoisomerization probabilities

In this appendix, we demonstrate that the detected *cis*-HCOOH towards the Orion Bar can be produced by a gas-phase photo-switching mechanism. To estimate the FUV photon absorption cross-sections and probabilities of the *trans-cis* photoisomerization process, we start calculating the potential energy surfaces of the HCOOH $S_0$ and $S_1$ electronic states as a function of the two most relevant degrees of freedom, the torsional angle of OH ($\phi_1$), and the torsional angle of CH ($\phi_2$) (see Fig. A.1).

We performed ic-MRCI-F12 *ab initio* calculations using the MOLPRO suite of programs with the VDZ-F12 basis set. The obtained results agree with the stationary points previously reported by Maeda et al. [2012, 2015]. The molecular orbitals and reference configurations were determined with a CASSCF calculation using 16 active orbitals. The optimized equilibrium geometries in the $S_0$ and $S_1$ electronic states are in agreement with previous results, corresponding to planar and bent trans-HCOOH conformers, respectively. They are listed in Table A.1.

For *trans*-HCOOH, the normal modes in the $S_0$ state have the following frequencies: 628.59, 662.86, 1040.64, 1117.90, 1316.0, 1416.22, 1792.32, 3083.01, and 3749.88 cm$^{-1}$. The two lowest frequencies correspond to the torsional angles of the OH and CH bonds, respectively.

For the two lower singlet states, $S_0$ and $S_1$, we calculate a two-dimensional grid composed of 37 equally spaced points for $\phi_1$ and $\phi_2$, fixing the rest of coordinates to the corresponding values listed in Table A.1. These points are interpolated using a two-dimension spline method to get the potential energy surfaces, $S_0$ and $S_1$, at any desired geometry, including the two conformers.

The potential energy surface of the $S_0$ electronic state presents two minima for $\phi_2 = 0^\circ$, one at $\phi_1 = 0^\circ$ or 360° (*trans*), and a second at $\phi_1 = 180^\circ$ (*cis*). As illustrated in Fig. A.1, both minima correspond to a planar geometry. The potential for the $S_1$ excited state presents two equivalent wells for the *trans*-conformer ($\phi_1 = 300^\circ$, $\phi_2 = 120^\circ$ or $\phi_1 = 60^\circ$, $\phi_2 = 240^\circ$). Therefore, the minimum geometrical configuration in the $S_1$ excited state is no longer planar. The *cis* conformer minimum transforms into a shoulder of the potential. This is shown in the one-dimensional cut shown in Fig. A.1 for the case of $\phi_2 = 120^\circ$. In this case, the potential energy surface as a function of $\phi_1$ is rather flat, while it shows a double-well structure as a function of $\phi_2$, corresponding to geometries above and below the molecular plane.

### Table A.1. Optimized geometries for *trans*-HCOOH in the ground ($S_0$) and excited electronic state ($S_1$). Distances are in Angstroms and angles in degree units.

| Geometry of | $S_0$ ground-state | $S_1$ excited-state |
|-------------|------------------|------------------|
| **trans-HCOOH** | **geom-$S_0$** | **geom-$S_1$** |
| R(CO$_1$) | 1.1987 | 3.683 |
| R(CO$_2$) | 1.3600 | 1.3840 |
| $\theta$(O$_1$CO$_2$) | 122.38 | 111.17 |
| R(CH$_1$) | 1.1008 | 1.0751 |
| $\theta$(O$_1$CH$_1$) | 124.01 | 113.06 |
| R(OH$_1$) | 0.9663 | 0.9661 |
| $\theta$(CO$_2$H$_2$) | 108.72 | 107.51 |
| $\phi_1$(H$_1$O$_1$CO$_1$) | 0.00 | 55.32 |
| $\phi_2$(H$_1$CO$_2$O$_2$) | 180.00 | 232.28 |

We solved the two-dimensional Schrödinger equation for $\phi_1$ and $\phi_2$ and obtained the vibrational eigenfunctions. The first six vibrational levels of the $S_0$ electronic state correspond to the *trans* conformer, the seventh energy level corresponds to the ground-vibrational state of *cis*-HCOOH. In the $S_1$ excited electronic state, the presence of a double well as a function of $\phi_2$ implies that two degenerate vibrational states appear. The two well depths are different in geom-$S_0$ and geom-$S_1$ which means that their nodal structure significantly changes.

In a second step, we calculate the transition dipole moments for the two-dimensional grids of geom-$S_0$ and geom-$S_1$, and determine the transitions between the $S_0$ state and the $S_1$ state. We derive the absorption spectra starting from both *trans*-HCOOH ($\nu = 0$) and *cis*-HCOOH ($\nu = 7$) in the $S_0$ electronic ground-state, to the first 200 vibrational levels of the $S_1$.
where we separate the contributions of the \( \nu' \) levels corresponding to the \textit{trans} or \textit{cis} conformers and normalize the sum to 1. We then normalize the above values and compute \( P_{\text{cis}}(\nu)(P_{\text{cis}}(\nu)+P_{\text{trans}}(\nu)) \) and \( P_{\text{trans}}(\nu)(P_{\text{cis}}(\nu)+P_{\text{trans}}(\nu)) \) for \( \nu \) levels corresponding to absorption energies below about 40000 cm\(^{-1}\) \((E < 5 \text{ eV})\), approximately the energy for which the dominant photodissociation channel opens and fluorescence starts to become negligible.

In summary, with these \textit{ab initio} calculations we estimate the \textit{cis-} and \textit{trans-HCOOH} cross-sections \( \sigma_{\text{cis}} \) for absorption of photons with energies lower than about 40000 cm\(^{-1}\) (those producing fluorescence). These absorptions radiatively excite the molecule to the \( S_1 \) electronic excited-state. We explicitly compute the \( \sigma_{\text{cis}} \) values for each photon energy as well as the probabilities to fluoresce back to a specific \textit{cis} or \textit{trans} state (i.e. we determine the normalized probabilities of the different \textit{trans} \( \rightarrow \textit{cis}, \textit{trans} \rightarrow \textit{trans}, \textit{cis} \rightarrow \textit{cis}, \textit{cis} \rightarrow \textit{trans} \) bound-bound transitions). The \( \sigma_{\text{cis}}(\textit{trans}) \) and \( \sigma_{\text{cis}}(\textit{cis}) \) cross-sections and the \( P_{\text{cis} \rightarrow \text{trans}} \) and \( P_{\text{cis} \rightarrow \text{cis}} \) probabilities are plotted in Fig. 3.

Appendix B: Estimation of the photoisomerization rate in the Orion Bar

The number of photoisomerizations per second depends on the flux of FUV photons with energies below 5 eV. The \textit{trans}-to-\textit{cis} and \textit{cis}-to-\textit{trans} photoisomerization rates \((\xi_{dc} \text{ and } \xi_{cd})\) are derived from the discrete sums:

\[
\xi_{dc} = \sum \lambda_i N_{ph, \lambda_i} \cdot \sigma_{\lambda_i}(\text{trans}) \cdot P_{\text{trans} \rightarrow \text{cis}}
\]

(B.1)

and

\[
\xi_{cd} = \sum \lambda_i N_{ph, \lambda_i} \cdot \sigma_{\lambda_i}(\text{cis}) \cdot P_{\text{cis} \rightarrow \text{trans}}
\]

(B.2)

where \( \sigma_{\lambda_i} \) is the absorption cross-section of a given conformer (in cm\(^{-2}\) photon\(^{-1}\)) and \( P \) is the probability to fluoresce from one isomer to the other. Both quantities are determined from our \textit{ab initio} calculations (previous section). \( N_{ph, \lambda_i} \) (photon cm\(^{-2}\) s\(^{-1}\)) is the flux of photons at each wavelength producing absorption.

In order to estimate the most realistic \( \xi_{dc} \) and \( \xi_{cd} \) rates for the FUV-irradiation conditions in the Orion Bar, we used the Meudon PDR code \( \text{(Le Petit et al. 2006)} \) and calculate \( N_{ph, \lambda_i}(\lambda) \) at different cloud depth \( \chi \) values. Following our previous studies of the Bar \( \text{ (Cuadrado et al. 2015; Goicoechea et al. 2016)} \) we run a model of an isobaric PDR \( (P_{\text{th}} = 10^6 \text{ cm}^{-3}) \) illuminated by \( \chi \approx 4 \times 10^4 \times \text{the mean interstellar radiation field (Draine 1978).} \) For photons in the \( \lambda = 2000 - 3000 \text{ Å} \) range, we adopt \( N_{ph, \lambda_i}(\lambda) = 4 \times 10^4 \times 732 \times \lambda^{0.7} \) photon cm\(^{-2}\) s\(^{-1}\) Å\(^{-1}\) at the PDR edge \( (A_V = 0) \) \( \text{(van Dishoeck & Black 1982).} \) We use a constant dust composition and size distribution that reproduces standard interstellar extinction curve \( \text{(Cardelli et al. 1989).}} \)

Table 3B shows the resulting photoisomerization rates at different cloud depths, the expected \textit{trans-}to-\textit{cis} HCOOH abundance ratio at equilibrium, and the time needed to reach the equilibrium ratios (neglecting photodissociation).

The use of constant dust grain properties through the PDR is likely the most important simplification for the calculation of the photoisomerization rates \( \xi_{dc} \) and \( \xi_{cd} \). Grain populations are known to evolve in molecular clouds, especially in PDRs where the sharp attenuation of a strong FUV field results in a stratification of the dust and PAH properties with \( A_V \) \( \text{(Draine 2003).} \) Therefore, although the varying optical properties of grains are difficult to quantify and include in PDR models, they likely play

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**Fig. A.1.** One-dimensional potential energy surfaces of HCOOH as function of the OH torsional angle \( \phi_1 \). \textit{Top panel:} ground \( S_0 \) electronic state. \textit{Bottom panel:} excited \( S_1 \) state. One-dimensional cuts were obtained from the two-dimensional grid (see text) by setting \( \phi_2 = 180^\circ \) and \( \phi_3 = 300^\circ \) for \( S_0 \) and \( S_1 \), respectively. We also show the vibrational-wave functions obtained from a one-dimensional model. The different geometrical structures of the HCOOH molecule in each energy minimum are shown.
Table B.1. Photosomerization rates for the irradiation conditions in the Orion Bar.

| Cloud depth | \(N_A\) (2300 – 2800 Å) | \(\xi_{\text{inc}}\) | \(\xi_{\text{cis}}\) | \(\text{trans}/\text{cis}-\text{HCOOH}\) ratio at equilibrium | Time [years] |
|-------------|-------------------------|----------------|----------------|--------------------------------------------------------|-------------|
| 0           | 1.96 \times 10^{12}    | 5.45 \times 10^{-11} | 1.27 \times 10^{-10} | 2.3                                                   | 1.7 \times 10^{2} |
| 1           | 1.80 \times 10^{11}    | 3.41 \times 10^{-12} | 9.89 \times 10^{-12} | 2.9                                                   | 2.4 \times 10^{5} |
| 2           | 2.84 \times 10^{10}    | 3.79 \times 10^{-13} | 1.31 \times 10^{-12} | 3.5                                                   | 1.9 \times 10^{6} |
| 3           | 4.93 \times 10^{9}     | 4.62 \times 10^{-14} | 1.87 \times 10^{-13} | 4.1                                                   | 1.3 \times 10^{7} |
| 5           | 1.69 \times 10^{8}     | 7.83 \times 10^{-16} | 4.29 \times 10^{-15} | 5.5                                                   | 6.2 \times 10^{8} |

A role on how FUV photons of different energies are differentially absorbed as a function of \(A_V\) (Goicoechea & Le Bourlot 2007). For the particular case of HCOOH, the strength and width of the 2175 Å extinction bump (Cardelli et al. 1989) naturally divides the range of photons producing HCOOH photodissociation (those with \(E > 5\) eV) from those producing fluorescence (\(E < 5\) eV). The extinction bump has been related with the absorption of FUV photons by PAH mixtures and small carbonaceous grains (Joblin et al. 1992; Draine 2003). Although it is not known how the bump evolves with \(A_V\), it clearly determines how the lower-energy FUV photons are absorbed. In Fig. 3 (bottom panel) we show different extinction curves for different PAH abundances (Goicoechea & Le Bourlot 2007). Optical properties are taken from Li & Draine (2001) and references therein. In addition, and as in most PDR models, our predicted FUV spectrum does not include the absorption produced by hundreds of molecular electronic transitions blanketing the FUV spectrum (other than H\(_2\) and CO lines). All together, our assumption that the detected cis-HCOOH arises from PDR layers in which the flux of photons with \(\lambda > 2500\) Å dominates over the higher-energy photodissociating photons is very plausible.

Appendix C: Alternative mechanisms for trans-to-cis isomerization in the ISM

Searching for further support to the photoswitching scenario, we qualitatively explored other possibilities that may apply in interstellar conditions. In the laboratory, trans-to-cis isomerization has been observed in molecular ices irradiated by near-IR photons (Maçôas et al. 2004, Obert-Majkat et al. 2008). Hence, isomerization of solid HCOOH and subsequent desorption to the gas-phase might also be responsible of the cis-HCOOH enhancement. However, owing to the short lifetime of the cis conformer observed in ices (a few minutes if the irradiation is stopped, Maçôas et al. 2004), a very strong flux of IR photons would be needed to maintain significant abundances of solid cis-HCOOH. In addition, near-IR photons penetrate molecular clouds much deeper than FUV photons, and one would have expected to detect cis-HCOOH in all positions of the Bar, and towards the Orion hot core, a region irradiated by intense IR fields. Alternatively, the trans-to-cis isomerization might be triggered by collisions with electrons. Electrons are relatively abundant in FUV-irradiated environments (with ionisation fractions up to about \(n_e/n_H \approx 10^{-4}\) compared to shielded cloud interiors (\(n_e/n_H \approx 10^{-9}\)). Simple calculations show that electrons with energies of about 0.5 eV would be needed to overcome the energy barrier to HCOOH isomerization, and to produce a trans-to-cis abundance ratio of about 3. Such suprathermal electrons could be provided by the photoionisation of low ionisation potential atoms (C, S, Si...), but their abundance sharply decrease with \(A_V\) (Hollenbach & Tielens 1999). We estimate that at a cloud depth of \(A_V = 2\) mag, HCOOH collisional isomerization, if effective, could compete with photoswitching only if the elastic collisional rate coefficients were very high, of the order of \(>10^{-6}\) cm\(^3\) s\(^{-1}\) for a typical electron density of \(n_e < 1\) cm\(^{-3}\) in PDRs. However, the detection of trans-HCOOH, but not cis-HCOOH, towards other PDRs such as the Horsehead (Guzmán et al. 2014), with similar electron densities but much lower FUV photon flux (\(>100\) times less than the Bar), supports a photoswitching mechanism in the Orion Bar (i.e. high \(\xi_{\text{inc}}\) and \(\xi_{\text{cis}}\) rates), but makes it too slow for the Horsehead and other low FUV-flux sources. Either way, we encourage laboratory and theoretical studies of the possible role of electron collisions, as well as of a more detailed investigation of the HCOOH, and other species, photoswitching mechanism.

Appendix D: Rotational diagrams and column density calculation

Owing to the large number of detected HCOOH lines, we calculated rotational temperatures (\(T_{\text{rot}}\)) and column densities (\(N\)) from rotational population diagrams. The standard relation for the rotational diagram (Goldsmith & Langer 1999) is:

\[
\ln \frac{N_u}{g_u} = \ln N - \ln Q_{\text{rot}} - \frac{E_u}{kT_{\text{rot}}},
\]

with \(N_u/g_u\) given by

\[
\frac{N_u}{g_u} = \frac{8\pi k}{h c^2} \cdot \frac{\nu^3}{A_u \cdot g_u} \cdot \nu_d^{-1} \cdot \int T_{MB} dv [\text{cm}^{-2}].
\]

In the above relation, \(N_u\) is the column density of the upper level in the optically thin limit [cm\(^{-2}\)], \(N\) is the total column density [cm\(^{-2}\)], \(q_u\) is the statistical weight of the upper state of each level, \(Q_{\text{rot}}\) is the rotational partition function evaluated at a rotational temperature \(T_{\text{rot}}\), \(A_u\) is the Einstein coefficient \([\text{s}^{-1}]\), \(E_u/k\) is the energy of the upper level of the transition [K], \(\nu_d\) is the frequency of the \(u \to l\) transition [s\(^{-1}\)], \(\int T_{MB} dv\) is the velocity-integrated line intensity corrected from beam efficiency [K km s\(^{-1}\)], and \(\theta_d\) is the beam filling factor. Assuming that the emission source has a 2D Gaussian shape, \(\theta_d\) is equal to \(\theta_d = \theta_\text{HPBW}^2 / (\theta_\text{maj}^2 + \theta_\text{min}^2)\), with \(\theta_\text{HPBW}\) the HPBW of the telescope [arcsec] and \(\theta_\text{maj}\) the diameter of the Gaussian source [arcsec]. The values for \(\nu_d\), \(E_u/k\), \(g_u\), and \(A_u\) are taken from the MADEX spectral catalogue.

Rotational diagrams were built considering two limiting cases: (i) that the detected HCOOH emission is extended, with \(\theta_d = 1\); and (ii) that the emission is semi-extended, with \(\theta_d = 9''\) (Cuadrado et al. 2015). In a plot of \(\ln(N_u/g_u)\) versus the energy
A!

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assuming a Gaussian line profile (for a linewidth of 2 km s$^{-1}$) and line opacity (optically thin for the observed HCOOH lines) as-

grams). For a given column density $N$, the model computes each rotation transition, $E_u/k$, the population distribution roughly follows a straight line with a slope $-1/T_{rot}$. The total column density of the molecule, $N$, is obtained from the $y$-intercept and the partition function. Figure $C.1$ shows the resulting rotational diagrams assuming extended emission. The uncertainties shown in Table $C.1$ indicate the uncertainty obtained in the fit. The uncertainties obtained in the determination of the fit parameters with CLASS are included in the error bars at each point of the rotational diagram.

To crosscheck that the relative intensities of the detected cis- and trans-HCOOH rotational lines are those expected according to their inferred rotational temperatures (i.e. that the assigned lines are not blended with lines from other molecules), we carried out a simple excitation and radiative transfer calculation using MADEX. We assumed that the cis- and trans-HCOOH rotational levels are populated following a Boltzmann distribution at a single rotational temperature (obtained from the rotational di-

grams). For a given column density $N$, the model computes each line opacity (optically thin for the observed HCOOH lines) assuming a Gaussian line profile (for a linewidth of 2 km s$^{-1}$) and simulates the output mm spectrum at a given spectral resolution.

Fig. $C.1$. Rotational population diagrams from the observed HCOOH lines towards the Orion Bar, (+10''', -10'''') position. Left: Diagram for the cis conformer (measurements lie along a single component). Right: Diagram for the trans conformer showing how different $K_a$ rotational ladders split in different components. Fitted values of the rotational temperature, $T_{rot}$, and column density, $N$, are indicated in each panel (see also Table $C.1$).

Table $C.1$. Rotational temperatures ($T_{rot}$), column densities ($N$), and abundances towards the Orion Bar PDR, (+10''', -10'''') position.

|                      | Extended source |                     | Semi-extended source |                     |
|----------------------|-----------------|---------------------|----------------------|---------------------|
|                      | $T_{rot}$ [K]   | $N(X)$ [cm$^{-2}$] | $T_{rot}$ [K]        | $N(X)$ [cm$^{-2}$]  | Abundance$^*$       | Notes   |
| cis-HCOOH            | 23 (4)          | 4.6 (0.7) $\times$ 10$^{11}$ | 21 (4)               | 4.2 (0.6) $\times$ 10$^{12}$ |                   | a       |
| trans-HCOOH $K_a = 0$ | 12 (2)          | 3.5 (0.5) $\times$ 10$^{11}$ | 6 (1)                | 4.1 (0.6) $\times$ 10$^{12}$ | a, b     |
| trans-HCOOH $K_a = 1$ | 12 (3)          | 3.3 (1.3) $\times$ 10$^{11}$ | 6 (1)                | 3.6 (2.1) $\times$ 10$^{12}$ | a       |
| trans-HCOOH $K_a = 2$ | 13 (3)          | 6.3 (2.8) $\times$ 10$^{11}$ | 7 (1)                | 5.0 (2.4) $\times$ 10$^{12}$ | a       |
| [(cis+trans)-HCOOH]  | $\text{---}$    | 1.8 (0.3) $\times$ 10$^{12}$ | $\text{---}$         | 1.7 (0.3) $\times$ 10$^{13}$ | (0.3 - 2.7) $\times$ 10$^{-10}$ | c       |

Notes. $^*$ The abundance of each species with respect to H nuclei is given by $N(X)/N(H) = (N(X)/N(H_2)) * (N(H_2)/N(H))$, with $N(H_2) = 3 \times 10^{22}$ cm$^{-2}$ and $N(H) \approx 3 \times 10^{21}$ cm$^{-2}$ (Cuadrado et al. 2015, and references therein). (a) Rotational temperatures and column densities from rotational diagram analysis. (b) $\Delta N$ calculated assuming an error of 15%. (c) Total column densities calculated as the sum of the cis- and trans-HCOOH species.

Families [2] and [D.1] show the observed spectra (black histograms) and the modelled lines (red curves) for the $T_{rot}$ and $N$ values obtained assuming extended emission. The good agreement of the fits, and lack of any other candidate line from a different molecule in our catalogue, confirms that all detected lines belong to cis- and trans-HCOOH.

Appendix E: Non-detection of cis-HCOOH towards the Orion BN/KL hot core and Barnard-B1

We searched for cis-HCOOH in regions shielded from strong FUV radiation fields. We selected chemically rich sources for which we have also carried out deep mm-line surveys with the IRAM-30m telescope. In particular, we searched for HCOOH towards the hot core in Orion BN/KL (Tercero et al. 2010) and towards the quiescent dark cloud Barnard 1-b (B1-b; Cernicharo et al. 2012). Although we clearly detected lines from trans-HCOOH towards both sources, we did not find lines from cis-HCOOH above the detection limit of these deep surveys. Using the MADEX excitation code, we derived lower limits to the trans-to-cis abundance ratio towards these sources. Below we summarise the main results from these observations:

of the upper level of each rotational transition, $E_u/k$, the population distribution roughly follows a straight line with a slope $-1/T_{rot}$. The total column density of the molecule, $N$, is obtained from the $y$-intercept and the partition function. Figure $C.1$ shows the resulting rotational diagrams assuming extended emission. Table $C.1$ lists the $T_{rot}$ and $N$ obtained by linear least squares fits. The uncertainties shown in Table $C.1$ indicate the uncertainty obtained in the fit. The uncertainties obtained in the determination of the fit parameters with CLASS are included in the error bars at each point of the rotational diagram.

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trans-HCOOH line stacking

Fig. D.1. Detected trans-HCOOH rotational lines towards the edge of the Bar, (+10′′, -10′′) position. The ordinate refers to the intensity scale in main beam temperature units, and the abscissa to the LSR velocity. Line frequencies (in GHz) are indicated at the top of each panel together with the rotational quantum numbers (in blue). The red curve shows an excitation model that reproduces the observations. Cis-HCOOH lines are shown in Fig. 2.

Orion BN/KL hot core: the hot core is embedded in the Becklin-Neugebauer/Kleinmann-Low massive star-forming region, at ~4′ North-West from the Orion Bar, and ~0.5′ North-West from the Trapezium stars. Relatively narrow lines ($\Delta v_{FWHM} < 3 \text{ km s}^{-1}$) corresponding to a-type transitions of trans-HCOOH, with upper level energies up to $E_u/k \approx 300 \text{ K}$, are detected at a LSR velocity of ~8 km s$^{-1}$. The observed line parameters are consistent with emission from the hot core itself. This is dense, $n_H$ of a few $10^6$ cm$^{-3}$, and hot gas at about 200 K (Blake et al. 1987; Tercero et al. 2010), and also from the more extended warm gas (about 60 K) in the ambient molecular cloud, so-called the extended ridge (Blake et al. 1987; Tercero et al. 2010). Using MADEX and our accumulated knowledge of the source structure (see Tercero et al. 2010; Cernicharo et al. 2016 and references therein), we determine $T_{rot}(trans) = 100 \pm 35 \text{ K}$ and $N(trans) = (1.0 \pm 0.3) \times 10^{15} \text{ cm}^{-2}$ in the hot core, and $T_{rot}(trans) = 40 \pm 15 \text{ K}$ and $N(trans) = (1.0 \pm 0.3) \times 10^{14} \text{ cm}^{-2}$ in the extended ridge. We note that the extended ridge is the main responsible for the observed trans-HCOOH line emission in the 3 mm band. Although we obtain much higher trans-HCOOH column densities compared to the Orion Bar, lines from cis-HCOOH are not detected towards the hot core. Assuming $T_{rot}(trans) = T_{rot}(cis)$, we compute a lower limit to the trans-to-cis abundance ratio of >100 in the hot core, and >30 in the extended ridge.

B1-b cold cloud: Barnard 1 is a low mass star-forming region located in the Perseus cloud. The cold core B1-b harbours two submillimetre continuum sources (B1-bN and B1-bS) identified as first hydrostatic core candidates (Gerin et al. 2015), and B1b-W, an infrared source detected with Spitzer (Jørgensen et al. 2006). Complex organic molecules such as CH$_3$COOH, CH$_3$OH, and CH$_2$O have been identified (Marcelino 2007; Oberg et al. 2010; Cernicharo et al. 2012). We detect nine lines from trans-HCOOH in the 3 mm band. A rotational diagram provides $T_{rot}(trans) = 12 \pm 4 \text{ K}$ and $N(trans) = (1.5 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$. Figure E.1 shows the detected lines together with our best model fit (red curve). Lines are very narrow ($\Delta v_{FWHM} < 0.5 \text{ km s}^{-1}$), consistent with emission from quiescent cold gas (about 20 K) shielded from FUV radiation. Although the inferred trans-HCOOH column density is similar to that obtained towards the Orion Bar, we do not detect lines from cis-HCOOH at the noise level of the B1-b data. Assuming $T_{rot}(trans) = T_{rot}(cis)$, we determine a lower limit to the trans-to-cis abundance ratio of >60. This is similar to that of the extended molecular Ridge of Orion, but significantly higher than towards the Bar.
Appendix F: Detected cis- and trans-HCOOH lines towards the Orion Bar PDR
### Table F.1. Line parameters for cis-HCOOH towards the Orion Bar, (+10″, -10″) position.

| Transition  | Frequency  | $E_a$  | $A_{ul}$ | $S_{ul}$ | $g_u$ | $\int T_{MB} \, dv$ | $v_{LSR}$ | $\Delta v$ | $T_{MB}$ | S/N |
|-------------|------------|--------|----------|----------|-------|-------------------|-----------|----------|--------|-----|
| $(J_{K_a,K_c})_h \rightarrow (J_{K_a,K_c})_l$ | [MHz] | [K] | [s$^{-1}$] | | | [mK km s$^{-1}$] | [km s$^{-1}$] | [km s$^{-1}$] | [mK] |
| $4_{1,3} \rightarrow 4_{0,4}$ | 82740.491 | 14.5 | $2.32 \times 10^{-3}$ | 4.3 | 9 | 18.9(2.3) | 10.5(0.2) | 1.8(0.4) | 8.7 | 4.7 |
| $4_{1,4} \rightarrow 3_{1,3}$ | 85042.744 | 13.8 | $2.10 \times 10^{-3}$ | 3.7 | 9 | 15.3(3.5) | 10.6(0.3) | 2.1(0.5) | 6.6 | 3.5 |
| $5_{1,4} \rightarrow 5_{0,5}$ | 86566.490 | 19.9 | $2.59 \times 10^{-3}$ | 5.1 | 11 | 26.3(3.5) | 10.0(0.2) | 2.4(0.4) | 10.1 | 5.6 |
| $4_{0,4} \rightarrow 3_{0,3}$ | 87694.689 | 10.5 | $2.45 \times 10^{-3}$ | 4.0 | 9 | 26.6(2.3) | 10.6(0.1) | 2.0(0.2) | 12.7 | 9.6 |
| $4_{1,3} \rightarrow 3_{1,2}$ | 90661.090 | 14.5 | $2.54 \times 10^{-3}$ | 3.7 | 9 | 21.2(2.4) | 10.3(0.1) | 1.8(0.3) | 11.2 | 4.8 |
| $7_{0,7} \rightarrow 6_{1,6}$ | 90910.082 | 29.4 | $1.50 \times 10^{-3}$ | 3.5 | 15 | 10.9(2.4) | 10.1(0.2) | 1.5(0.4) | 6.9 | 3.9 |
| $6_{1,5} \rightarrow 6_{0,6}$ | 91291.549 | 26.5 | $2.95 \times 10^{-3}$ | 5.9 | 13 | 20.1(3.5) | 10.3(0.2) | 2.5(0.6) | 7.5 | 5.7 |
| $7_{1,6} \rightarrow 7_{0,7}$ | 97025.449 | 34.1 | $3.42 \times 10^{-3}$ | 6.6 | 15 | 15.5(2.4) | 10.5(0.1) | 1.8(0.3) | 7.0 | 4.4 |
| $8_{1,7} \rightarrow 8_{0,8}$ | 103845.157 | 42.8 | $4.02 \times 10^{-3}$ | 7.1 | 17 | 20.5(3.6) | 10.0(0.2) | 1.6(0.2) | 12.2 | 5.2 |
| $5_{1,5} \rightarrow 4_{1,4}$ | 106266.589 | 18.9 | $4.28 \times 10^{-3}$ | 4.8 | 11 | 22.2(2.4) | 10.7(0.1) | 1.8(0.3) | 11.0 | 4.5 |
| $5_{0,5} \rightarrow 4_{0,4}$ | 109470.705 | 15.8 | $4.87 \times 10^{-3}$ | 5.0 | 11 | 35.7(3.6) | 10.3(0.1) | 1.8(0.2) | 18.6 | 7.1 |
| $5_{1,4} \rightarrow 4_{1,3}$ | 113286.704 | 19.9 | $5.19 \times 10^{-3}$ | 4.8 | 11 | 39.6(5.3) | 10.7(0.2) | 1.9(0.3) | 19.7 | 6.0 |

### Table F.2. Line parameters for trans-HCOOH towards the Orion Bar, (+10″, -10″) position.

| Transition  | Frequency  | $E_a$  | $A_{ul}$ | $S_{ul}$ | $g_u$ | $\int T_{MB} \, dv$ | $v_{LSR}$ | $\Delta v$ | $T_{MB}$ | S/N |
|-------------|------------|--------|----------|----------|-------|-------------------|-----------|----------|--------|-----|
| $(J_{K_a,K_c})_h \rightarrow (J_{K_a,K_c})_l$ | [MHz] | [K] | [s$^{-1}$] | | | [mK km s$^{-1}$] | [km s$^{-1}$] | [km s$^{-1}$] | [mK] |
| $4_{1,4} \rightarrow 3_{1,3}$ | 86546.180 | 13.6 | $6.35 \times 10^{-6}$ | 3.7 | 9 | 23.8(3.5) | 10.4(0.1) | 1.8(0.3) | 13.7 | 7.0 |
| $4_{0,4} \rightarrow 3_{0,3}$ | 89579.168 | 10.8 | $7.51 \times 10^{-6}$ | 4.0 | 9 | 27.9(4.7) | 10.3(0.1) | 1.8(0.2) | 14.9 | 5.3 |
| $4_{1,3} \rightarrow 3_{2,2}$ | 89861.473 | 23.5 | $5.69 \times 10^{-6}$ | 3.0 | 9 | 26.4(7.0) | 10.0(0.4) | 2.2(0.7) | 11.3 | 3.0 |
| $4_{1,3} \rightarrow 3_{1,2}$ | 93098.350 | 14.4 | $7.91 \times 10^{-6}$ | 3.7 | 9 | 26.3(2.4) | 10.0(0.1) | 2.2(0.2) | 9.9 | 6.2 |
| $5_{1,5} \rightarrow 4_{1,4}$ | 108126.709 | 18.8 | $1.30 \times 10^{-3}$ | 4.8 | 11 | 28.7(2.4) | 10.2(0.1) | 1.5(0.2) | 14.0 | 8.3 |
| $5_{0,5} \rightarrow 4_{0,4}$ | 111746.771 | 16.1 | $1.49 \times 10^{-3}$ | 5.0 | 11 | 27.9(3.6) | 10.2(0.1) | 1.7(0.3) | 16.2 | 5.2 |
| $5_{1,4} \rightarrow 4_{2,3}$ | 112287.131 | 28.9 | $1.27 \times 10^{-3}$ | 4.2 | 11 | 32.2(3.6) | 10.7(0.1) | 2.1(0.2) | 14.2 | 6.1 |
| $5_{1,3} \rightarrow 4_{3,2}$ | 112459.608 | 44.8 | $9.73 \times 10^{-6}$ | 3.2 | 11 | 9.1(3.6) | 11.2(0.1) | 0.5(0.4) | 16.5 | 5.2 |
| $5_{3,2} \rightarrow 4_{3,1}$ | 112466.993 | 44.8 | $9.73 \times 10^{-6}$ | 3.2 | 11 | 14.0(3.6) | 10.1(0.3) | 1.8(0.5) | 7.3 | 2.8 |
| $5_{1,2} \rightarrow 4_{4,1}$ | 112432.278 | 67.1 | $5.47 \times 10^{-6}$ | 1.8 | 11 | 24.9(6.1) | 10.2(0.2) | 1.6(0.4) | 14.4 | 3.1 |
| $5_{1,1} \rightarrow 4_{4,0}$ | 112432.305 | 67.1 | $5.47 \times 10^{-6}$ | 1.8 | 11 | 24.9(6.1) | 10.2(0.2) | 1.6(0.4) | 14.4 | 3.1 |
| $5_{2,3} \rightarrow 4_{2,2}$ | 112891.429 | 28.9 | $1.29 \times 10^{-3}$ | 4.2 | 11 | 29.2(3.6) | 10.6(0.1) | 2.0(0.2) | 17.6 | 7.3 |