Widespread deuteration across the IRDC G035.39-00.33

A. T. Barnes\textsuperscript{1,2,}\textsuperscript{†}, S. Kong\textsuperscript{3}, J. C. Tan\textsuperscript{3,4}, J. D. Henshaw\textsuperscript{1}, P. Caselli\textsuperscript{5}, I. Jiménez-Serra\textsuperscript{6} and F. Fontani\textsuperscript{7}

\textsuperscript{1}Astrophysics Research Institute, Liverpool John Moores University, 146 Brownlow Hill, Liverpool L3 5RF, UK
\textsuperscript{2}School of Physics and Astronomy, University of Leeds, LS2 9JT, Leeds, UK
\textsuperscript{3}Department of Astronomy, University of Florida, Gainesville, FL 32611, USA
\textsuperscript{4}Department of Physics, University of Florida, Gainesville, FL 32611, USA
\textsuperscript{5}Max-Planck-Institute for Extraterrestrial Physics (MPE), Giessenbachstrasse 1, 85748 Garching, Germany
\textsuperscript{6}University College London, Department of Physics and Astronomy, 132 Hampstead Road, London NW1 2PS, UK
\textsuperscript{7}INAF - Osservatorio Astrofisico di Arcetri, L.go E. Fermi 5, I-50125, Firenze, Italy

Accepted 2016 February 18. Received 2016 February 15; in original form 2015 October 19.

ABSTRACT

Infrared Dark Clouds (IRDCs) are cold, dense regions that are usually found within Giant Molecular Clouds (GMCs). Ongoing star formation within IRDCs is typically still deeply embedded within the surrounding molecular gas. Characterising the properties of relatively quiescent IRDCs may therefore help us to understand the earliest phases of the star formation process. Studies of local molecular clouds have revealed that deuterated species are enhanced in the earliest phases of star formation. In this paper we test this towards IRDC G035.39-00.33. We present an 80'' by 140'' map of the $J = 2 \rightarrow 1$ transition of N$_2^+D^+$, obtained with the IRAM-30m telescope. We find that N$_2^+D^+$ is widespread throughout G035.39-00.33. Complementary observations of N$_2^+$ are used to estimate the deuterium fraction, $D_{\text{frac}}^{N_2H^+} = N(N_2^+D^+)/N(N_2H^+)$. We report a mean $D_{\text{frac}}^{N_2H^+} = 0.04 \pm 0.01$, with a maximum of $D_{\text{frac}}^{N_2H^+} = 0.09 \pm 0.02$. The mean deuterium fraction is $\sim 3$ orders of magnitude greater than the interstellar [D]/[H] ratio. High angular resolution observations are required to exclude beam dilution effects of compact deuterated cores. Using chemical modelling, we find that the average observed values of $D_{\text{frac}}^{N_2H^+}$ are in agreement with an equilibrium deuterium fraction, given the general properties of the cloud. This implies that the IRDC is at least $\sim 3$ Myr old, which is $\sim 8$ times longer than the mean free-fall time of the observed deuterated region.

Key words: stars: formation: high-mass; ISM: clouds; ISM: individual (G035.39-00.33); ISM: molecules.

1 INTRODUCTION

Infrared Dark Clouds (IRDCs) are regions of cold (T $< 25$K; e.g. Ragan et al. 2011) and dense (n(H$_2$) $\geq 10^3-4$ cm$^{-3}$; e.g. Hernandez et al. 2011; Butler & Tan 2012) gas, the most massive and dense of which have the potential to host the earliest stages of massive star and star cluster formation (Tan et al. 2014). Thus to understand these processes it is important to study the physical and chemical properties of IRDCs.

In such cold and dense environments, some molecules “freeze-out” onto the surfaces of dust grains forming icy mantles. Most notably CO is found to be highly depleted towards dense clouds within IRDCs (e.g. Fontani et al. 2012b; Gianetti et al. 2014), with line of sight CO depletion factors, $f_D$, of a few being reported towards the IRDC, G035.39-09.33 (i.e. the observed gas phase abundance of CO is a few times smaller than expected in the case of no depletion; Hernandez et al. 2011).

Unlike CO, N-bearing species, in particular NH$_3$ and N$_2$H$^+$, better trace dense and cold gas (e.g. Caselli et al. 1999; Bergin et al. 2002; Bergin & Tafalla 2007; di Francesco et al. 2007; Fontani et al. 2012a,c). This is due to the fact that CO, largely frozen out, is unable to
effectively destroy their molecular ion precursors (such as NH$_2$ and H$_2$), and hence less efficiently convert N$_2$H$^+$ into HCO$^+$. CO depletion, therefore, can boost the formation of nitrogen-bearing species. Furthermore, in the cold and dense environments of molecular clouds, abundances of deuterated nitrogen-bearing molecules are enhanced, as the formation rates of the deuterated forms of H$_2$ also increase with CO freeze-out (e.g. Dalgarno & Lepp 1984; Walmsley et al. 2005). These molecules are produced mainly by the exothermic proton-deuteron exchange reaction (for para-state reactants and products; Pagani et al. 1992):

$$\text{H}_2^+ + \text{HD} \rightarrow \text{H}_2^2D^+ + \text{H}_2 + \Delta E,$$

(1)

where $\Delta E = 232$ K (Millar et al. 1989). For significant CO depletion, temperatures below 30 K, and for an ortho-para H$_2$ ratio less than $\sim 0.1 - 0.01$ (e.g. Sipilä et al. 2013; Kong et al. 2015), this reaction proceeds from left to right, producing an excess of H$_2$D$^+$ and an abundance ratio ([H$_2$D$^+$]/[H$_2$]) orders of magnitude larger than the interstellar [D]/[H] ratio ($\sim 1.5 \times 10^{-5}$; e.g. Oliveira et al. 2003). Once the deuterated isotopologues of H$_2^+$ have formed, they can easily cede a deuteron to other neutral species and enhance their abundances. For example, the reactions of deuterated isotopologues of H$_2^+$ with N$_2$ can produce N$_2$D$^+$ increasing the deuteration fraction of N$_2$H$^+$. D$_n^+$\textsuperscript{2H$^+$} (we adopt the notation used by Kong et al. 2015, where the non-deuterated counterpart is shown in superscript).

Measurements of D$_n^+$\textsubscript{2H$^+$} towards low-mass cores range between $\simeq 0.1 - 0.7$ (e.g. Crapsi et al. 2004; Belloche et al. 2006; Friesen et al. 2010, 2013; Crapsi et al. 2005; Pagani et al. 2007; Bourke et al. 2012). For a sample of potential high mass star forming regions, Fontani et al. (2006) found D$_n^+$\textsubscript{2H$^+$} $\simeq 0.015$. Miettinen et al. (2011) found D$_n^+$\textsubscript{2H$^+$} $\simeq 0.002-0.028$ toward massive clumps within several IRDCs, while deuterium fractions as high as in low-mass prestellar cores have been observed toward massive starless clumps/cores embedded in quiescent IRDCs (Fontani et al. 2011).

This paper focuses on the massive (17,000 $\pm$ 5000 $M_\odot$; Kainulainen & Tan 2013), filamentary IRDC, G035.39-00.33 which resides at a distance of 2.9 $\pm$ 0.5 kpc (Simon et al. 2006)$^1$. This IRDC was first identified as having the potential to host massive cluster formation by Rathborne et al. (2006). The extinction mapping of Butler & Tan (2012) found several high mass surface density “cores” within G035.39-00.33, most notably the “H6” region which contains $\sim 70M_\odot$ of material within a radius of $\sim 0.25$ pc.

In recent years this IRDC has been the subject of an in-depth analysis, which has focussed on: large-scale shocks traced by SiO emission (Jiménez-Serra et al. 2010, Paper I), widespread CO depletion (Hernandez et al. 2011, Paper II), the virial state of the cloud (Hernandez et al. 2012, Paper III) and the kinematics of the low and high density gas and the excitation conditions in the cloud at varying scales (Henshaw et al. 2013; Jiménez-Serra et al. 2014; Henshaw et al. 2014, Paper IV; Paper V, Paper VI, respectively). As widespread CO depletion has been found in G035.39-00.33, this cloud is a ideal candidate to also exhibit widespread deuteration. This paper presents IRAM-30m N$_2$D$^+$ (2 - 1) observations of G035.39-00.33, with the aim of estimating the column density and deuteration fraction, and ultimately finding the evolutionary state of the cloud.

2 OBSERVATIONS

The N$_2$D$^+$ (2 - 1) observations were carried out through August 2009 with the Institut de Radioastronomie Millimétrique 30-m telescope (IRAM-30m) at Pico Veleta, Spain. The large-scale images were obtained in the On-The-Fly (OTF) mapping mode. The central coordinates of the maps are $\alpha(J2000)=18^h57^m08^s$, $\delta(J2000)=02^\circ10'39''$ ($l=35.51^\circ$, $b=-0.27^\circ$). The off-source position used was (300$''$, 0$''$; in relative coordinates). The EMIR receivers were used. The VERSatille SPectrometer Assembly (VESPA) provided a spectral resolution at 156 kHz (equivalent to 0.3 km s$^{-1}$) at the frequency of the N$_2$D$^+$ (2 - 1) line (main hyperfine component frequency 154217.1805 MHz; Dore et al. 2004). The data were converted into main beam brightness temperature, T$_{\text{MB}}$, from antenna temperature, T$_{\text{A}}$, by using the beam and forward efficiencies shown in Table 1.

---

Table 1. Frequency (MHz), Velocity Resolution, Beam Size, and Beam & Forward Efficiency for the observed transitions. Note that the Forward and Beam Efficiencies have been extrapolated from the telescope specified values to the transition frequencies$^1$.

| Transition | $\nu$ (MHz) | $\Delta \nu_{\text{res}}$ | Beam Size$^2$ | Beam$^3$ | Forward$^4$ |
|------------|-------------|--------------------------|----------------|----------|-------------|
| N$_2$D$^+$ (2 - 1) | 154217.18$^a$ | 0.31 | 16 | 0.66 | 0.93 |
| N$_2$H$^+$ (1 - 0)$^b$ | 93176.25$^c$ | 0.61 | 26 | 0.74 | 0.95 |
| C$^{18}$O (1 - 0) | 109782.17$^d$ | 0.053 | 22 | 0.73 | 0.97 |

---

$^1$ Following Hernandez et al. (2011), we adopt the kinematic distances of Simon et al. (2006), who assumed the Clemens (1985) rotation curve. This leads to a distance of 2.9 kpc for G035.39-00.33. The uncertainties in this distance are likely to be of order 0.5 kpc, which could result, for example, from line-of-sight non-circular motions of $\sim 8$ km s$^{-1}$.
urn was observed to calculate the focus, and pointing was checked every ~2 hours on G34.3+0.2. The data were calibrated with the chopper-wheel technique (Kutner & Ulich 1981), with a calibration uncertainty of ~20%. Information on the beam sizes, frequencies, velocity resolutions are summarised in Table 1.

GILDAS\textsuperscript{2} packages CLASS and MAPPING were used to post-process the data. This included subtracting a single-order polynomial function to produce a flat baseline, and convolving the OTF-data with a Gaussian kernel, increasing the signal-to-noise ratio, and allowing us to resample the data onto a regularly spaced grid. The absolute angular resolution of the IRAM-30m antenna at the frequency of the J = 2 → 1 transition of N$_2$D$^+$ is ~16′′. Throughout this work, all line data are spatially smoothed to achieve an effective angular resolution of ~27′′, with a pixel spacing of 13.5′′, to allow comparison with the N$_2$H$^+$ data.

We utilise the N$_2$H$^+$ (1 − 0) map from Paper IV (see this paper for more information on the N$_2$H$^+$ observations), CO depletion map of Paper III, and the mass surface density map from Kainulainen & Tan (2013).

3 RESULTS

Figure 1 presents the averaged spectrum for the mapped region, and some example spectra taken at positions of high integrated intensity (see Figure 2). All emission above a 3σ level of ~0.21 K km s$^{-1}$ ($\sigma = \sigma_{\text{RMS}} \Delta \nu_{\text{res}} \sqrt{N_a}$; where $\sigma_{\text{RMS}}$ is the root mean square noise of the spectrum in K, $N_a$ is the number of channels and $\Delta \nu_{\text{res}}$ is the velocity resolution in km s$^{-1}$), is seen within a velocity range of 40 − 50 km s$^{-1}$. This range is comparable to that found by the previously mentioned works on this cloud, and therefore we can be confident that the observed N$_2$D$^+$ emission is associated with G305.39-00.33.

Each spectrum has been inspected by-eye for the presence of multiple velocity components previously identified in N$_2$H$^+$ and C$^{13}$O emission (Paper IV; with mean N$_2$H$^+$ emission velocities of 42.95 ± 0.17 km s$^{-1}$, 45.63 ± 0.03 km s$^{-1}$, and 46.77 ± 0.06 km s$^{-1}$). However, evidence of only one component, centred at ~46 km s$^{-1}$ was found in the N$_2$D$^+$ data. Unlike the N$_2$H$^+$ (1 − 0) line, where one of the seven hyperfine components is isolated, N$_2$D$^+$ (2 − 1) possesses no isolated hyperfine components; the line is a blend of 40 hyperfine components, spread across a velocity range of 14.6 km s$^{-1}$ (as shown in Figure 1, upper panel). This, as well as linewidths of ~1 km s$^{-1}$ (i.e. similar to those of N$_2$H$^+$ (1 − 0); Paper IV), makes the identification of multiple velocity components very difficult.

Figure 2 presents a map of the N$_2$D$^+$ (2 − 1) emission integrated between 40 − 50 km s$^{-1}$. The integrated intensity contours are overlaid on the mass surface density map of Kainulainen & Tan (2013), and superimposed are the positions of the massive cores first identified by Rathborne et al. (2006) in millimetre continuum emission, which have been repositioned to the mid-infrared extinction peaks by Butler & Tan (2012). In Figure 2 we also show the location and strength of the 4.5 μm emission (‘green fuzzies’; Chambers et al. 2009), and the 8 μm and 24 μm (Carey et al. 2009). The N$_2$D$^+$ emission is concentrated towards the “H6” region, and the south, near H2, H3, H4 and H5 “core” regions. However, when considering the 2σ emission level there is evidence to suggest that the emission is extended across a large portion of the cloud.

4 ANALYSIS

4.1 Column density

The column densities are calculated from the integrated intensity of the N$_2$D$^+$ (2 − 1) line, following the procedure

\footnote{see https://www.iram.fr/IRAMFR/GILDAS/}
4.2 Deuterium fraction

The $N_2D^+$ to $N_2H^+$ column density ratio is used to define the deuterium fraction across the mapped region. Figure 3 shows the deuterium fraction for positions where the emission of both $N_2D^+$ and $N_2H^+$ is detected above a $2\sigma$ (cross hatched), above a $2.5\sigma$ (hatched), and above a $3\sigma$ (no hatch) level. We find values of the deuteration fractions larger than 0.01 widespread throughout the cloud, with the highest values found towards the north.

Taking into account only the emission above $3\sigma$, the mean beam-averaged deuterium fraction across G035.39-00.33 is $D_{\text{frac}}^{N_2H^+} = 0.04 \pm 0.01$. The maximum value is found north of the “H6” region (at $\alpha(J2000) = 18^h 57^m 09^s$, $\delta(J2000) = 02^\circ 11' 39''$), with a value of $D_{\text{frac}}^{N_2H^+} = 0.09 \pm 0.02$. Note that varying the excitation temperature for both $N_2H^+$ and $N_2D^+$ between 4-20 K would cause a change of $D_{\text{frac}}^{N_2H^+} = +15\%$ to $-55\%$.
To investigate how the \( \text{N}_2\text{H}^+ \) and \( \text{N}_2\text{D}^+ \) emission and the deuterium fraction vary within \( \text{G035.39-00.33} \), we plot them as a function of mass surface density in Figure 5. If we consider only the positions above a 3\( \sigma \) error threshold, the column density of \( \text{N}_2\text{D}^+ \) remains relatively constant with increasing mass surface density (dynamical range of \( \sim 1.5 \), which is similar to the scale of the uncertainties). However, for the same positions, the column density of \( \text{N}_2\text{H}^+ \) shows a significant positive gradient with increasing mass surface density (dynamical range of \( \sim 3 \)). This is reflected in the plot of deuterium fraction as a function of mass surface density, which shows an overall negative correlation. This is consistent with a picture in which the \( \text{N}_2\text{D}^+ \) is more spatially concentrated in cores than the \( \text{N}_2\text{H}^+ \), which is also present in the clump envelope (that dominates the mass).

Observations show that the deuterium fraction is highly sensitive to the level of CO freeze-out (e.g. Caselli et al. 2002a), where the CO depletion factor, \( f_D \), can be expressed as the ratio of the observed mass surface density to mass surface density derived from CO emission, assuming a reference CO fractional abundance with respect to H\(_2\). Paper III calculated the CO depletion averaged along each line-of-sight (i.e. each pixel) throughout \( \text{G035.39-00.33} \), \( f_D \), which is normalised such that on average pixels with mass surface densities of 0.01 g cm\(^{-2} \) \(< \Sigma < 0.03 \) g cm\(^{-2} \) are unity. Figure 5 displays the deuterium fraction as a function of normalised CO depletion factor, for which we do not see a positive correlation, but rather again an anti-correlation. This is contrary to what is expected, that level of deuteration is elevated in dense, CO depleted cores; but it is reminiscent of the results recently obtained toward the Ophiuchus low-mass star forming region (Punanova et al. 2015). These authors suggest that the highly deuterated but CO-rich cores may be recently formed, centrally concentrated starless cores.

These results could indicate that along the line-of-sight, high mass surface density and CO depleted positions have enhanced \( \text{N}_2\text{H}^+ \), but the \( \text{N}_2\text{D}^+ \) is only tracing a portion of this in the 3rd dimension. We, therefore, suggest that measurements of the deuterium fraction in massive star-forming regions could be limited by low spatial resolution observations (beam dilution), and/or the relatively unknown evolutionary stage of the gas (whether or not it has reached chemical equilibrium or is being influenced by the presence of YSOs). These are discussed in more detail in the following section.

### 5.2 Comparison with chemical models

To determine if the observed levels of deuteration are consistent with the current evolutionary stage of the G035.39-00.33, we have conducted a series of chemical models (Kong et al. 2015). The model consists of the Nahoon code and a reduced network extracted from KIDA database (Wakelam et al. 2012), including the elements H, D, He, C, N, O. The chemical species traced by the code contain up to 3 atoms in size, except for \( \text{H}_2\text{O}^+ \) and its deuterated isotopologues, which significantly improve the consistency with a more complete network (Sipilä et al. 2013). Spin states of \( \text{H}_2\text{H}^+ \) and their deuterated isotopologues are included, and the formation of \( \text{H}_2\text{H}^+ \) and \( \text{H}_2\text{D}^+ \) on dust grain surface are considered following Le Petit et al. (2002). We follow Pagani et al. (2009a) in calculating the dissociative
Figure 5. Shown in the panels are the $N_2H^+$ (upper left) and $N_2D^+$ (upper right) column densities as a function of mass surface density, deuterium fraction as a function of mass surface density (lower left), and deuterium fraction as a function of normalised CO depletion factor (lower right). Average errors for $N_2D^+$ column density and $D_{N_2H^+}$ are displayed in the upper right of each plot. Not shown are the errors on the mass surface density and CO depletion, which are $\sim 30\%$ (Kainulainen & Tan 2013) and $\sim 50\%$ (Paper III), respectively. The solid and transparent points represent positions where both the $N_2H^+$ and $N_2D^+$ emission is above a 3$\sigma$ and 2$\sigma$ error threshold, respectively.

recombination rates of all forms of $H_2^+$. The initial elemental abundances are listed in table 2 in Kong et al. (2015). In this paper, we treat the depletion of neutral species by reducing the initial elemental abundances of C, N, O by the depletion factor, $f_D$, and consider a broad combination of physical conditions appropriate for IRDC G035.39-00.33.

We explore a grid of models with $A_v = [5, 10, 20, 30]$ mag, $n_H = [0.1, 1, 2, 10] \times 10^4$ cm$^{-3}$, $T_{\text{kin}} = [10, 15, 20]$ K, $f_D = [1, 2, 3, 5, 10]$, to check the equilibrium $D_{N_2H^+}$ and timescale. We adopt a constant radiation field four times stronger than the standard Habing field ($G_0$), however because of high visual extinction values considered here, small changes of $G_0$ do not affect the chemistry. We also explore initial ortho-to-para $H_2$ ratios of $\text{OPR}_{H_2} = 0.001-3$. A $\text{OPR}_{H_2} = 3$ represents the high temperature statistical ratio limit, as ortho- and para-$H_2$ are formed at high temperatures on dust grains in the ratio of their nuclear spin state statistical weights (3:1; Flower 2003). $\text{OPR}_{H_2} = 0.1-1$
are values close to those deduced by Crabtree et al. (2011) in translucent clouds with \( T = 50-70 \) K: 0.8-0.3. Recently, Xu et al. (2016) made some rough constraints on the \( \text{H}_2 \) ortho-to-para ratio for the low density gas within Taurus. These authors estimate \( \text{OPR}_{\text{H}_2} \sim 0.2 \). Lower values are expected in dark molecular clouds (see Sipilä et al. 2013). Therefore, our \( \text{OPR}_{\text{H}_2} \) exploration covers typical values observed in molecular clouds.

Table 2 presents the results of a subset of models with input parameters which best represent the global properties of G035.39-00.33. Shown are the equilibrium deuterium fraction, \( \text{D}_{\text{eq}}^{\text{N}_2\text{H}^+} \), the time taken to achieve 90% of this value. Variation of the extinction is not displayed in the Table, as ranging \( A_v \) between \([10, 20, 30]\) mag does not significantly effect the results, however an extinction of 5 mag tends to decrease the \( \text{D}_{\text{eq}}^{\text{N}_2\text{H}^+} \), and the time by a factor of a few. This is not thought to be an issue as the mapped region of G035.39-00.33 has an average extinction of \( \sim 20 \) mag (Kainulainen & Tan 2013).

The observed deuterium fractions within G035.39-00.33 are generally similar with the model equilibrium values, for kinetic temperatures of 10 K and 15 K. If we assume that the cloud has a mean global density \( n_\text{H} \sim 10^4 \text{cm}^{-3} \) (Paper III), a mean CO depletion of \( f_D = 3 \), and assume the mean kinetic temperature is comparable to the \( \sim 15 \) K dust temperature found by Nguyen Luong et al. (2011), the model predicted equilibrium value is \( \text{D}_{\text{eq}}^{\text{N}_2\text{H}^+} \approx 0.048 \), remarkably close to the average observed value of \( \text{D}_{\text{eq}}^{\text{N}_2\text{H}^+} = 0.04 \pm 0.01 \).

Figure 6 shows how the ortho-to-para ratio of \( \text{H}_2 \) and

\[
\begin{align*}
\text{Figure 6.} & \quad \text{Time evolution of the OPR}_{\text{H}_2} \quad \text{(upper panel)} \quad \text{and} \quad \text{D}_{\text{eq}}^{\text{N}_2\text{H}^+} \quad \text{(lower panel)} \quad \text{under different assumptions of the initial OPR}_{\text{H}_2}, \quad \text{for} \quad n_\text{H} = 10^4 \text{cm}^{-3}, \quad f_D = 3, \quad T_{\text{kin}} = 15 \text{K} \quad \text{and} \quad A_v = 20 \text{mag. We explore OPR}_{\text{H}_2} \quad \text{from} \quad 3 \quad \text{down to} \quad 0.001. \\
\text{Figure 7.} & \quad \text{Time to reach the observed deuterium fraction} \quad \text{(D}_{\text{eq}}^{\text{N}_2\text{H}^+} = 0.04) \quad \text{from a given initial ortho-to-para ratio of \( \text{H}_2 \) (shown on the top axis) versus the time to reach this initial ortho-to-para ratio if starting from statistical equilibrium ratio of 3. The solid blue line shows this result for the fiducial model parameters, e.g. of density, temperature, depletion factor, cosmic ray ionisation rate. Grey dotted lines show contours of the sum of the deuteration timescale and ortho-to-para ratio decay timescale to equal 0.3, 1, 3, 10 Myr, as labelled. The dashed blue line (upper panel) shows the time to reach \( \text{D}_{\text{eq}}^{\text{N}_2\text{H}^+} = 0.02 \) for the fiducial model. The dashed and dot-dashed lines (lower panel) show the effect of varying several of the model parameters, as labelled. }
\end{align*}
\]
\[ D_{25}^{N_2H^+} \] vary as a function of time, for the model parameters of \( n_1 = 10^5 \text{ cm}^{-3}, f_D = 3, T_{\text{kin}} = 15 \text{ K} \) and \( A_e = 20 \text{ mag} \). For these properties which best describe G035.39-00.33, we find the time reached the observed deuteron fraction vary between \( \sim 0.2 - 8 \) Myrs, where the shortest times are for low initial ortho-to-para ratios (e.g. \( \text{OPR}_{\text{kin}}^+ = 0.001 \); also see Table 2).

Figure 7 displays the time needed to reach the observed deuteron fraction of \( D_{25}^{N_2H^+} = 0.04 \) from a given initial ortho-to-para ratio of \( H_2 \) (shown on the top axis) versus the time needed to reach this initial ortho-to-para ratio if starting from the high temperature statistical ratio limit of 3 (Kong et al. 2015). The solid blue line shows this result for the fiducial model parameters, e.g. of density, temperature, depletion factor, cosmic ray ionisation rate. The dashed blue line shows the time to reach \( D_{25}^{N_2H^+} = 0.02 \) for the fiducial model.

An estimate of the total age of the molecular cloud, i.e., from the time when the molecules formed with an assumed high temperature statistical ratio limit of 3 until the time they achieve the observed deuteron level, is the sum of the ortho-to-para ratio decay timescale and deuteron timescale: example contours of this sum for 0.3, 1, 3, 10 Myr are shown by the dotted black lines. The astrochemical model results indicate that a timescale of at least 3 Myrs is needed for the cloud to evolve from its initial state to the present observed deuterated state. Adopting values of CO depletion factor and density of a factor two higher \( (f_D = 6 \text{ and } n_1 = 2 \times 10^6 \text{ cm}^{-3}) \) or a cosmic ionisation rate of a factor two lower \( (\zeta = 1.25 \times 10^{-17} \text{ s}^{-1}) \) would imply cloud ages of at least 3-7 Myrs, shown in lower panel of Figure 7. We note that decreasing the CO depletion or density, or increasing the cosmic ionisation rate would cause the models to never reach an equilibrium deuteron fraction of 0.04, hence these are not plotted on Figure 6. We thus conclude that the age of IRDC G035.39-00.33 is at least \( \sim 3 \) Myr. This is a lower limit, since the current observed deuteron level is consistent with astrochemical equilibrium.

A lower limit of 3 Myr is equivalent to \( \sim 8 \) local free-fall timescales, assuming an average density of \( 10^3 \text{ cm}^{-3} \) (with spherical geometry \( \sim 4 \times 10^7 \text{ yrs} \)). This indicates the cloud is dynamically “old” and is thus likely to have had time to achieve approximate virial equilibrium (as was concluded in Paper III). This timescale is consistent with that estimated from a kinematic analysis in Paper IV. We note that future studies will involve comparison with models of evolving density (i.e. an evolving free-fall time).

Given that much of the complex structure observed in the mass surface density plot is not seen in the \( N_2D^+ \) and \( N_2H^+ \) emission maps, it is interesting to question if we are resolving all the dense sub-structures. Core diameters extracted from 3.2 mm continuum observations of G035.39-00.33 with the PdBI are typically 0.1 pc (Henshaw et al. in preparation). This implies an approximate beam dilution factor of \( \sim 0.07 \) (i.e. the square of the core-to-beam size ratio). To check this, we input typical core properties in the model. Assuming the cores have densities of \( \sim 10^5 \text{ cm}^{-3} \) (average “core”; e.g. Butler & Tan 2012), temperatures of \( \sim 10 \text{ K} \), and CO depletions of \( \sim 5-10 \), we find model predicted \( D_{25}^{N_2H^+} \approx 0.011-0.17 \) (see Table 2), which are closer to the deuteron values found in high-mass prestellar cores (Fontani et al. 2011). Applying the beam dilution factor to the predicted values, we find deuterium fractions of \( \sim 0.007 - 0.01 \). Although these values are slightly below what is observed, this could be a plausible explanation for the low observed deuteron fractions in the IRDCs, where unresolved dense cores are present. The timescales to reach these deuteron levels in gas at these higher densities of \( 10^5 \text{ cm}^{-3} \) are shorter: \( \sim 1 \) Myr (see also Punanova et al. 2015). However, this is still long compared to the local free-fall time of \( \sim 0.1 \) Myr.

Higher angular resolution observations of \( N_2D^+ \) are needed to disentangle if G035.39-00.33 has reached a deuteron fraction equilibrium in its diffuse, \( \sim 10^5 \text{ cm}^{-3} \) bulk density, or if the observed deuteration is dominated by a population of denser, currently unresolved cores.

6 SUMMARY

In this work, we have presented \( N_2D^+ (2 - 1) \) data towards G035.39-00.33. The main results are summarised below:

i) The emission from \( N_2D^+ \) is extended across G035.39-00.33, and from this emission we calculate a mean beam-averaged column density of \( N (N_2D^+) = 6.2 \pm 1.4 \times 10^{13} \text{ cm}^{-2} \).

ii) We report an average deuteron fraction of \( D_{25}^{N_2H^+} (N_2D^+/N_2H^+) = 0.04 \pm 0.01 \), which is three orders of magnitude higher than the interstellar [D]/[H] ratio, and within the range quoted for other IRDCs (e.g. Miettinen et al. 2011; Gerner et al. 2015), yet it is significantly smaller than the values found toward massive starless cores within quiescent IRDCs (Fontani et al. 2011).

iii) We have conducted chemical modelling of the deuteron, and find that the observed values of the deuteron fraction are consistent with those of chemical equilibrium. Such an equilibrium would have taken at least \( \sim 3 \) Myr to be established. This scenario places a lower limit on the cloud age of \( \sim 8 \) local free-fall times, which indicates that the IRDC filament is dynamically “old”, with sufficient time to relax to a quasi-equilibrium virialized state. This is consistent with the previous age estimates based on the kinematics (Henshaw et al. 2013). Future studies will involve comparison with models of evolving density (i.e. an evolving free-fall time).

iv) To test if beam dilution of denser unresolved substructure is causing the low deuteron fraction, we input typical core properties in the model. We find that these would reach equilibrium faster (in about 1 Myr) and have a higher equilibrium value. Using estimates for the cores size, of \( \sim 0.1 \) pc, we determine that a beam dilution factor of \( \sim 0.07 \) is needed to reproduce the observed deuteron fractions, i.e. dense cold cores only occupy 7% of the cloud volume. Note that, irrespective of this, the cloud is still dynamically old.

In light of the results, we propose that higher angular resolution observations are needed to further investigate the nature of the deuteron fraction measured across G035.39-00.33.
ACKNOWLEDGEMENTS

We would like to thank the anonymous referee for their constructive comments. Furthermore, we would like to thank Michael Butler and Jouni Kainulainen for providing us with the mass surface density map, and Audra Hernandez for the CO depletion factor map. This research has made use of NASA's Astrophysics Data System. A.T.B would like to acknowledge the funding provided by Liverpool John Moores University, Max-Plank-Institute for Extraterrestrial Physics, and the University of Leeds. P.C acknowledges the financial support of the European Research Council (ERC; project PALs 320620). I.J.-S. acknowledges the funding received from the STFC through an Ernest Rutherford Fellowship (proposal number ST/L004801/1). J.C.T. acknowledges NASA grant ADAP10-0110.

REFERENCES

Belloche A., Parise B., van der Tak F. S. J., Schilke P., Leurini S., Güsten R., Nymann L.-Å., 2006, A&A, 454, L51

Bergin E. A., Tafalla M., 2007, ARA&A, 45, 339

Bergin E. A., Alves J., Huard T., Lada C. J., 2002, ApJL, 570, L101

Bourke T. L., Myers P. C., Caselli P., Di Francesco J., Belloche A., Plume R., Wilner D. J., 2012, ApJ, 745, 117

Butler M. J., Tan J. C., 2012, ApJ, 754, 5

Carey S. J., et al., 2009, PASP, 121, 76

Caselli P., Walmsley C. M., Tafalla M., Dore L., Myers P. C., 1999, ApJL, 523, L165

Caselli P., Walmsley C. M., Zucconi A., Tafalla M., Dore L., Myers P. C., 2002a, ApJ, 565, 344

Caselli P., Benson P. J., Myers P. C., Tafalla M., 2002b, ApJ, 572, 238

Cazzoli G., Puzzarini C., Lapinov A. V., 2003, ApJ, 592, L19

Chambers E. T., Jackson J. M., Rathborne J. M., Simon R., 2009, ApJS, 181, 360

Clemens D. P., 1985, ApJ, 295, 422

Crabtree K. N., Indriolo N., Kreckel H., Tom B. A., McCall B. J., 2011, ApJ, 729, 15

Crapsi A., Caselli P., Walmsley C. M., Tafalla M., Lee C. W., Bourke T. L., Myers P. C., 2004, A&A, 420, 597

Crapsi A., et al., 2005, A&A, 439, 1023

Dalgarano A., Lepp S., 1984, ApJL, 287, L47

Dore L., Caselli P., Beninati S., Bourke T., Myers P. C., Cazzoli G., 2004, A&A, 413, 1177

Flower D., 2003, Molecular Collisions in the Interstellar Medium

Fontani F., Caselli P., Crapsi A., Cesaroni R., Molinari S., Testi L., Brand J., 2006, A&A, 460, 709

Fontani F., et al., 2011, A&A, 529, L7+

Fontani F., Palau A., Busquet G., Isella A., Estalella R., Sanchez-Monge A., Caselli P., Zhang Q., 2012a, MNRAS, 423, 1691

Fontani F., Giannetti A., Beltrán M. T., Dodson R., Rioja M., Brand J., Caselli P., Cesaroni R., 2012b, MNRAS, 423, 2342

Fontani F., Caselli P., Zhang Q., Brand J., Busquet G., Palau A., 2012c, A&A, 541, A32

Friesen R. K., Di Francesco J., Myers P. C., Belloche A., Shirley Y. L., Bourke T. L., André P., 2010, ApJ, 718, 666

Friesen R. K., Kirk H. M., Shirley Y. L., 2013, ApJ, 765, 59

Gerner T., Shirley Y., Beuther H., Semenov D., Linz H., Aberson T., Henning T., 2015, preprint, (arXiv:1503.06594)

Giannetti A., et al., 2014, A&A, 570, A65

Henshaw J. D., Caselli P., Fontani F., Jiménez-Serra I., Tan J. C., 2013, ApJ, 778, 11

Hernandez A. K., Tan J. C., Kainulainen J., Caselli P., Butler M. J., Jiménez-Serra I., Fontani F., 2012, ApJL, 756, L13

Jiménez-Serra I., Caselli P., Tan J. C., Hernandez A. K., Fontani F., Butler M. J., van Loo S., 2010, MNRAS, 406, 187

Jiménez-Serra I., Caselli P., Fontani F., Tan J. C., Henshaw J. D., Kainulainen J., Hernandez A. K., 2014, MNRAS, 439, 1996

Kainulainen J., Tan J. C., 2013, A&A, 549, A53

Kong S., Caselli P., Tan J. C., Wakelam V., Sipilä O., 2015, ApJ, 804, 98

Kong S., et al., 2016, ApJ

Kutner M. L., Ulrich B. L., 1981, ApJ, 258, 479

Le Petit F., Roueff E., Le Bourlot J., 2002, A&A, 399, 369

Miettinen O., Hennemann M., Lim H., 2011, A&A, 534, A134

Millar T. J., Bennett A., Herbst E., 1989, ApJ, 340, 906

Nguyen Luong Q., et al., 2011, A&A, 535, A76

Olivera C. M., Hébrard G., Howk J. C., Krui J. W., Chayer P., Moos H. W., 2003, ApJ, 587, 235

Pagan L., Salez M., Wannier P. G., 1992, A&A, 258, 479

Pagan L., Baczmann A., Cabrit S., Vastel C., 2007, A&A, 467, 179

Pagan L., et al., 2009a, A&A, 494, 623

Pagan L., Daniel F., Dubernet M., 2009b, A&A, 494, 719

Punanova A., Caselli P., Pon A., Belloche A., André P., 2015, preprint, (arXiv:1512.02966)

Ragan S. E., Bergin E. A., Wilner D., 2011, ApJ, 736, 163

Rathborne J. M., Jackson J. M., Simon R., 2006, ApJ, 641, 389

Simon R., Rathborne J. M., Shah R. Y., Jackson J. M., Chambers E. T., 2006, ApJ, 653, 1325

Sipilä O., Caselli P., Harju J., 2013, A&A, 554, A92

Tan J. C., Beltrán M. T., Caselli P., Fontani F., Fuente A., Krumholz M. R., McKee C. F., Stolte A., 2014, Protostars and Planets VI, pp 149–172

Wakelam V., et al., 2012, ApJS, 199, 21

Walmsley C. M., Flower D. R., Pineau des Forêts G., 2004, A&A, 418, 1035

Xu D., Li D., Yue N., Goldsmith P. F., 2016, preprint, (arXiv:1601.03165)

di Francesco J., Evans II N. J., Caselli P., Myers P. C., Shirley Y., Aikawa Y., Tafalla M., 2007, Protostars and Planets V, pp 17–32

This paper has been typeset from a T EX/L TEX file prepared by the author.
Table 2. Equilibrium deuterium fractions for models with an extinction of $A_v = 20$ mag, number densities, $n_H$, of $10^4$ and $10^5$ cm$^{-3}$, and initial ortho-to-para H$_2$ ratios of 0.001, 0.01, 0.1, and 1. Columns show the model inputs of gas kinetic temperature, $T_{\text{kin}}$, CO depletion, and model outputs of equilibrium value of $D_N^2H_2^+$ and the time taken to achieve 90% of this value, $t_{\text{eq,90}}$.

| $T_{\text{kin}}$ (K) | $f_D$ | $D_N^2H_2^+$ frac | $t_{\text{eq,90}}$ (Myr) | $n_H = 10^4$ cm$^{-3}$ ($t_{\text{ff}} = 4.4 \times 10^5$ yrs) | | $n_H = 10^5$ cm$^{-3}$ ($t_{\text{ff}} = 1.4 \times 10^5$ yrs) |
|----------------------|-------|-------------------|--------------------------|--------------------------------------------------------|------|--------------------------------------------------------|
| 10.0                 | 1.0   | 0.021             | 0.73                     | 3.24                                                   | 6.19 | 8.36                                                   |
| 10.0                 | 3.0   | 0.044             | 0.29                     | 2.10                                                   | 3.61 | 4.73                                                   |
| 10.0                 | 5.0   | 0.057             | 0.24                     | 1.79                                                   | 3.01 | 3.92                                                   |
| 10.0                 | 10.0  | 0.076             | 0.26                     | 1.50                                                   | 2.45 | 3.16                                                   |
| 15.0                 | 1.0   | 0.022             | 0.71                     | 3.32                                                   | 6.32 | 8.50                                                   |
| 15.0                 | 3.0   | 0.048             | 0.27                     | 2.06                                                   | 3.52 | 4.60                                                   |
| 15.0                 | 5.0   | 0.062             | 0.20                     | 1.73                                                   | 2.90 | 3.76                                                   |
| 15.0                 | 10.0  | 0.083             | 0.19                     | 1.43                                                   | 2.32 | 2.99                                                   |
| 20.0                 | 1.0   | 0.015             | 0.39                     | 2.91                                                   | 6.48 | 8.72                                                   |
| 20.0                 | 3.0   | 0.025             | 0.03                     | 1.90                                                   | 3.57 | 4.65                                                   |
| 20.0                 | 5.0   | 0.029             | 0.003                    | 1.61                                                   | 2.91 | 3.76                                                   |
| 20.0                 | 10.0  | 0.034             | 0.0005                   | 1.32                                                   | 2.32 | 2.96                                                   |

$OPR_0^{H_2} = 0.001$ | $OPR_0^{H_2} = 0.01$ | $OPR_0^{H_2} = 0.1$ | $OPR_0^{H_2} = 1$