Millimetre and submillimetre spectroscopy of isobutene and its detection in the molecular cloud G+0.693[*]

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ABSTRACT

Context. Isobutene ((CH_3)$_2$C=CH_2) is one of the four isomers of butene (C_4H_8). Given the detection of propene (CH_3CH=CH_2) toward TMC-1, and also in the warmer environment of the solar-type protostellar system IRAS 16293−2422, one of the next alkenes, isobutene, is a promising candidate to be searched for in space.

Aims. We aim to extend the limited line lists of the main isotopologue of isobutene from the microwave to the millimetre region in order to obtain a highly precise set of rest frequencies and to facilitate its detection in the interstellar medium.

Methods. We investigated the rotational spectrum of isobutene in the 35−370 GHz range using absorption spectroscopy at room temperature. Quantum-chemical calculations were carried out to evaluate vibrational frequencies.

Results. We determined new or improved spectroscopic parameters for isobutene up to a sixth-order distortion constant. These new results enabled its detection in the G+0.693 molecular cloud for the first time, where propene was also recently found. The propene to isobutene column density ratio was determined to be about 3:1.

Conclusions. The observed spectroscopic parameters for isobutene are sufficiently accurate that calculated transition frequencies should be reliable up to 700 GHz. This will further help in observing this alkene in other, warmer regions of the ISM.

Key words. Astrochemistry/ Techniques: spectroscopic/ Molecular data/ ISM: molecules/ Radio lines: ISM/ISM: individual objects: G+0.693-0.027

1. Introduction

Dense and cold molecular clouds in the interstellar medium (ISM) have been found to be a rich source of unsaturated species (McGuire et al. 2017; McGuire 2022). Most of these molecules are known to have large dipole moments, such as methylcyanopolyynes $CH_3C_{2n+1}N$ (n=1−4) (Solomon et al. 1971; Broten et al. 1984; Snyder et al. 1984; Siebert et al. 2022), cyanoallene CH_2CCHCN (Lovas et al. 2006), cyanopropenes C_3H_5CN (Cernicharo et al. 2022), cyanomethanimine HNCHCN (Rivilla et al. 2019), O-bearing species such as ethenediol (Rivilla et al. 2022a) and *n*-propanol (Jiménez-Serra et al. 2022), nitriles including cyanic acid (HOCN), and three C_4H_3N isomers (Rivilla et al. 2022c), and propargylimine (Bizzocchi et al. 2020). Some of the detected partially or nearly saturated molecules with low dipole moments are hydrocarbons, such as propene CH_2CHCH$_3$ (Marcelino et al. 2007; Manigand et al. 2021), butenyne CH_2CHCCH (Cernicharo et al. 2021), and methylpolyynes $CH_3C_{2n}H$ (n=1−3) (Hollis et al. 1981; Irvine et al. 1981; Walmsley et al. 1984; Remijan et al. 2006). An up-to-date list of detected molecules can be found in the Cologne Database for Molecular Spectroscopy (CDMS; Endres et al.

(2016)). Only a small number of the detected molecules have low dipole moments.

The detection of saturated or nearly saturated hydrocarbons —which have low or zero dipole moments— is important for our understanding of the chemistry of ISM. However, such detections are challenging or impossible owing to the dipole moments of these molecules. Propene is among the largest saturated or nearly saturated hydrocarbons that have been detected not only towards dark clouds, such as the Taurus Molecular Cloud-1 (TMC-1) (Marcelino et al. 2007), but also in the warmer environment of the solar-type protostellar system IRAS 16293−2422 (Manigand et al. 2021). An interesting open question in astrochemistry pertains to our understanding of the formation and abundance of hydrocarbons in the ISM (García de la Concepción et al. 2023). A number of chemical models have been developed to understand their formation. Different possibilities include ion–neutral molecular reactions followed by dissociative recombination, radiative association reactions of hydrocarbons with H_2, direct hydrogenation of atoms or simple molecules on grain surfaces, and radical association in a suitable network of reactions (Marcelino et al. 2007; Rawlings et al. 2013).

Following propene, one of the next nearly saturated hydrocarbons, isobutene, also known as 2-methylpropene, (CH_3)$_2$C=CH_2, contains one C and two H atoms more than propene and is therefore a promising molecule to be searched for in the ISM. If detected, isobutene will be the second molecule with a branched carbon backbone after propyl cyanide (Belloche et al. 2014). One of the possible formation mechanisms

of isobutene could be the addition of the CH_3 radical to propene. The rotational spectrum of isobutene was studied to a limited extent in the frequency region from 8 and 35 GHz (Laurie 1961; Scharpen & Laurie 1963; Demaison & Rudolph 1975; Gutowsky & Germann 1991). These works provided the rotational constants, the dipole moment value from Stark effect measurements, the internal rotation barrier height, the experimental structure from isotopic substitution, and analyses of the ground and the two lowest torsionally excited state splittings.

In the present article, we aim to extend the existing line list of the main isotopologue of isobutene using absorption spectroscopy at room temperature. We measured transition frequencies in the range 35−370 GHz in order to provide a list of rest frequencies that are sufficiently accurate for radio astronomical searches not only in cold (∼10 K) molecular clouds, but also in the warmer (≳ 100 K) environments of star-forming regions (see Section 2). Further, the obtained rest frequencies of isobutene are used to facilitate its first detection in the ISM towards the G+0.693−0.027 molecular cloud (G+0.693 hereafter) located in the Sagittarius (Sgr) B2 complex, close to Sgr B2(N), which in turn is close to the Galactic Centre (Section 3.2). In this work, we also searched for other low-dipole moment hydrocarbons for which rotational line lists exist in the CDMS, and report the detection of propene and the search for 1-butyne in the G+0.693 molecular cloud (Section 3.3 and 3.4).

2. Laboratory spectroscopy

2.1. Experimental details

The investigation of the rotational spectrum of isobutene (Sigma-Aldrich, 99% purity) shown in Fig. 1 was carried out with two different spectrometers. We employed two 7 m coupled glass cells, each with an inner diameter of 10 cm in a double-path arrangement, for measurements in the 70−120 GHz region, yielding an optical path length of 28 m. We used a 5 m double path cell with a 10 cm inner diameter for the 35−65 GHz, 170−250 GHz, and 250−370 GHz ranges. Other than the 35−65 GHz range, we used a tripler with in-house developed electronics to reach the desired frequency range of 70−120 GHz. For the 170−250 GHz and 250−370 GHz ranges, a commercial multiplier chain (Virginia Diodes Inc., WR2.8x3 and WR4.3x2) was used. The multipliers are driven by Rohde & Schwarz SMF 100A synthesisers as sources and Schottky diode detectors. Frequency modulation was employed to reduce baseline effects with 2f demodulation. This causes absorption lines to appear approximately as second derivatives of a Gaussian. Additional information on the spectrometers is available in Ordu et al. (2012) and Martin-Drumel et al. (2015), respectively.

We covered the entire 70−120 GHz and 170−250 GHz ranges in steps of 500 MHz and 1 GHz, respectively. In the 35−65 GHz and 250−370 GHz ranges, individual transition frequencies were recorded in 1.5 MHz steps focusing on the well-predicted lines. The difference in recording strategy is based on the available sensitivity and line density in each frequency range. The pressure was set to around 2.1 Pa in the 3 mm region as test measurements showed that peak intensity was best between ∼2.0 and ∼2.5 Pa. We refilled the cells after roughly five hours to avoid pressure broadening due to small leakages. The assigned uncertainties for the newly measured lines were around 10−35 kHz, where a Voigt line-profile fit was used to determine the centre frequency. Most of the lines had an uncertainty of less than 20 kHz. However, when neighbouring J transitions were overlapping, uncertainty values of 30-35 kHz were applied.

Fig. 1. Sketch of the isobutene molecule. The C atoms are shown in dark grey, the smaller H atoms in light grey. The a- and b-axes are shown, and the c-axis is perpendicular to the plane of the C atoms.

2.2. Spectroscopic background

Isobutene is an asymmetric rotor and with $\kappa = (2B - A - C)/(A - C) = 0.6673$ close to the oblate top limit of +1. Its dipole moment of 0.503 ± 0.009 D is along the b-inertial axis, which is aligned with the C=C bond; see Fig. 1 (Laurie 1961). The molecular symmetry group of isobutene is G_{36}. In the rigid rotor case, the molecule has C_{2v} symmetry with two equivalent methyl groups and two equivalent methylene hydrogens. Laurie (1961) and Demaison & Rudolph (1975) report the height of the three-fold barrier to internal rotation V_3 to be around 2.21 kcal mol^{-1} and 2.170(9) kcal mol^{-1} or ∼760 cm^{-1}, respectively, in good agreement with each other. The internal rotation of the methyl groups splits the energy levels into four substates, labelled AA, AE, EA, and EE. For consistency with previous works, we use the labels A_1A_1, A_1E, EA_1, and EE in this work (Demaison & Rudolph 1975), where A_1A_1 is non-degenerate, A_1E and EA_1 are doubly degenerate, and EE is quadruply degenerate. Only transitions within one symmetry species, that is, only the transition corresponding to $A_1A_1 \leftarrow A_1A_1$ and equivalent are allowed. Demaison & Rudolph (1975) calculated that for isobutene, which has eight symmetrically interchangeable protons, each transition should be observable as a quartet with spin-weight intensity ratios of $A_1A_1 : EE : A_1E : EA_1$, which depend on the parity of the K_aK_c labels. If $K_a + K_c$ is even, the transition intensities should be 36 : 64 : 20 : 16, and if $K_a + K_c$ is odd, these should be 28 : 64 : 12 : 16. Furthermore, Demaison & Rudolph (1975) suggest that the A_1E and EA_1 species collapse frequently when the internal rotation barrier is sufficiently high and when there is no near K degeneracy. Depending on the splitting width and the instrument resolution, most of the lines of isobutene measured between 8 and 35 GHz showed singlet and triplet splitting pattern. Only in a few cases were quartet patterns observed where the A_1E and EA_1 splitting was large enough to be resolved.

2.3. Spectroscopic results and discussion

We observed a b-type spectrum of isobutene. The strongest transitions of isobutene in our data are R-branch transitions ($\Delta J = +1$) with $\Delta K_a = \pm 1$ and $\Delta K_c = +1$. The Boltzmann peak at 300 K is near 280 GHz. Q-branch transitions with $\Delta K_a = \pm 1$ and $\Delta K_c = \mp 1$ are weak but observable.

As shown in Fig. 2, we observed unsplit lines and triplet line patterns for the most part. The triplet transitions of isobutene are expected to be in the intensity ratio of ∼1 : 2 : 1. The observed

Fig. 2. Part of the millimetre-wave spectrum of isobutene. All transitions are split due to the internal rotation (see text). However, most of the lines are observed as unresolved single lines (as shown for $4_{0,4} \leftarrow 3_{1,3}$ and $4_{1,4} \leftarrow 3_{0,3}$ transitions) or triplets (as shown for $26_{19,7} \leftarrow 26_{18,8}$ transition) because of the high barrier to the methyl internal rotation. The three components are assigned from left to right as A_1A_1, EE, and unresolved A_1E plus EA_1 with measured splitting $A_1A_1 - EE$ of 0.3 MHz.

Fig. 3. The $20_{19,1} \leftarrow 20_{18,2}$ and $20_{19,2} \leftarrow 20_{18,3}$ transitions of isobutene highlighting the 'normally' forbidden c-type transition resulting from the interation of the overall and internal rotation. We note that the EA_1 component of the $20_{19,2} \leftarrow 20_{18,2}$ was too weak to be observed.

fine structure due to methyl group internal rotors —which results in the triplet pattern— has been assigned as A_1A_1, EE, and blended $A_1E + EA_1$. The splitting width ($A_1A_1 - EE$) of the $26_{19,7} \leftarrow 26_{18,8}$ transition shown in Fig. 2 is 0.3 MHz. Most of the assigned R-branch transitions appeared as unresolved singlets, and triplet patterns are only observed in some cases with $J \leq 17$ transitions, where the maximum splitting width is 1 MHz. Triplet patterns have been observed for Q-branch transitions with $J \leq 58$ transitions, with a splitting width of 5.4 MHz.

We did not resolve the A_1E/EA_1 splitting except in a few more complex patterns in the spectrum of isobutene. As shown in Fig. 3, we not only observe the allowed $20_{19,1} \leftarrow 20_{18,2}$ b-type transition, but also the normally forbidden $20_{19,2} \leftarrow 20_{18,2}$ c-type transition. Mixing occurs in the A_1E and EE characters of the internal rotation components if the internal rotation splitting and the asymmetry splitting are of similar magnitude (Perrin et al. 2015; Demaison & Rudolph 1971). This results in six lines, where four (A_1A_1, EE, A_1E and EA_1) belong to the former and two (EA_1 and EE) to the latter transition. The positions and intensities of each component are different from the expected pattern of A_1A_1, EE, A_1E, and EA_1 with intensity ratios of 36 : 64 : 20 : 16 . Similar behaviour is observed for $20_{19,2} \leftarrow 20_{18,3}$ and $20_{19,1} \leftarrow 20_{18,3}$ transitions, as shown in Fig. 3. We observed a few additional transitions with irregular internal rotation patterns; all of them had low values of K_c and K_a values close to J.

We used the program ERHAM by Groner (1997, 2012) to calculate and fit the rotational spectrum of isobutene. Previously assigned transitions (Laurie 1961; Demaison & Rudolph 1975; Gutowsky & Germann 1991) were used for the determination of initial rotational parameters in Watson's A reduction. In total, transitions up to $J = 17$ and $K_c = 4$ have been reported up to 35 GHz. Newly measured transitions from 35–270 GHz were added step wise to improve the data set. We started with low J, K_c transitions and gradually included higher J and K transitions at higher frequencies. In each frequency range, the R-branches

were added first if the predicted intensities were sufficient to be observed to get a good-quality prediction of the distortion constants. This was followed by addition of predicted Q-branch transitions, which led us to introduce additional centrifugal distortion and tunnelling parameters. These iterations proceeded until a reasonable ERHAM fit was achieved. The new software, which is called LLWP and is based on Loomis-Wood plots, was used to assign the transitions (Bonah et al. 2022). In total, the final fit includes 1176 distinct transitions.

Transitions up to $J = 60$ and $K_c = 41$ were included in the fit. A total of 19 spectroscopic parameters were determined by the least-squares method and are listed in Table 1. The rotational parameters A, B, and C are compared with the previous work from Demaison & Rudolph (1975). We determined a complete set of quartic and sextic distortion parameters for the first time. In addition, two internal rotation parameters (ρ and β), one energy tunnelling parameter (ϵ_{10}), and one tunneling correction parameter $[(B - C)/4]_{10}$ were determined. The notation $[(B - C)/4]_{10}$ follows Groner (1997) and signals a tunnelling correction to $B - C$. This parameter can also be viewed as an asymmetry correction to the tunnelling and could then be labelled as ϵ_2. The weighted (dimensionless) standard deviation of the fit is 0.98, while the rms (for the unweighted frequencies) is 26.5 kHz.

The range of J and K_c quantum number and also the number of different transition frequencies for isobutene were greatly increased with respect to the previous investigations. The line list of the assigned transitions can be found in the CDMS[1], along with further related files.

A comparison of the observed distortion parameters with those from quantum-chemical calculations described in Appendix B is not straightforward. This is due to the fact that the output is reported in the III^r representation, which is because isobutene is an oblate rotor, whereas ERHAM employs the prolate I^r representation only. The A reduction in an oblate representation (III^r or III^l) has quite frequently turned out to be a poor choice, because of the slower convergence compared to other combinations of reduction and representation; see for example Müller et al. (2022). The work from Demaison & Rudolph

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[1] https://cdms.astro.uni-koeln.de/classic/predictions/daten/Isobutene/

(1975) reports a limited set of spectroscopic parameters $A - C$ as well as Δ_{JK}, Δ_K, δ_J, and δ_K for the ground state of isobutene from 37 Q-branch transitions in the III^r representation. We fit the complete set of previous data from $8-35$ GHz using ER-HAM for a comparison with our present values. The results of the previous data fit can be found in Table A.1 in Appendix A. Only the rotational constants, together with ρ, β, ϵ_{10}, and quartic distortion parameters, were allowed to float in the fit. As the number of transitions from previous data was limited, the sextic distortion constants were not well determined in trial fits. The obtained parameters are of the same order of magnitude as those of the present work. Some of the distortion parameters, Δ_{JK} and Δ_J, were not well determined and display discrepancies compared to our present values. The effect of the deviations can be seen in the rest frequencies calculated from these data, especially when going to transitions with higher J values. For example, the transition frequency of the relatively strong R-branch transition $9_{0,9} \leftarrow 8_{1,8}$ is found to be ~1 MHz higher than from our parameters. This difference increases further to around 12 MHz for transitions with higher J, as in the $20_{0,20} \leftarrow 19_{1,19}$ transition.

The V_3 barrier height of isobutene is known to be 760 cm^{-1}. However, for acetone and dimethyl ether (DME) this value is 251 cm^{-1} and 903 cm^{-1}, respectively, which also have two methyl tops equivalent to that of isobutene (Groner et al. 2002, 1998). Generally, the barrier height is inversely proportional to the size of the splitting $(A_1A_1 - EE)$. Another factor that becomes important for methyl top molecules is ρ. Isobutene and acetone have similar ρ values of 0.055 and 0.06, respectively. Whereas, the ρ value for DME is 0.2. Therefore, the change in the splitting size with increasing K is larger in DME compared to acetone and isobutene.

In the isobutene spectrum, some transitions pertaining to the two low-lying fundamental torsional states, $v_{15} = 1$ and $v_{21} = 1$ (Table B.1), of isobutene were identified in our room-temperature spectra. These states were investigated previously by Demaison & Rudolph (1975). The Boltzmann factor for these two excited states at 300 K are 0.4 and 0.36, respectively, compared to the ground state (see Table B.1). In cold sources, their population is negligible (see Table 2). Therefore, in the present work, we do not focus on the analysis of the torsional states as we are interested in searching for the ground state of isobutene in the ISM.

2.4. Considerations for generating an isobutene line list

The search for isobutene in the ISM requires the generation of a sufficiently accurate line list. The variance file generated from the fit of the spectroscopic parameters to the experimental data is one important ingredient. Another fairly obvious ingredient is the permanent dipole moment, which was determined experimentally as 0.503 ± 0.009 D by Laurie (1961). An additional one is the partition function. Traditionally, this was determined only for the ground vibrational state, but in the somewhat warmer $(T \gtrsim 100$ K$)$ and denser medium, excited vibrational states are frequently populated non-negligibly. The ideal solution to determine the partition function is to sum over all rovibrational states at a given temperature. However, spectroscopic parameters are rarely known extensively enough for molecules with more than three atoms. A usually good approximation is to express the total partition function Q_{tot} as a product of the rotational (Q_{rot}) and the vibrational partition function (Q_{vib}). The rotational partition function was calculated using SPCAT (Pickett 1991), which sums over the ground state energy levels up to sufficiently high values of J and K_a, which were taken as 185 and 125, respec-

Table 1. Present and previous experimental spectroscopic parameters (MHz) $^{(a)}$ of the main isotopologue of isobutene and details of the fits.

Parameters	
Previous work$^{(a)}$	
A /MHz	9133.31 (3)
B /MHz	8381.80 (3)
C /MHz	4615.97 (2)
This work$^{(b)}$	
A /MHz	9133.36452 (12)
B /MHz	8381.87456 (12)
C /MHz	4615.97690 (11)
Δ_K /kHz	9.09875 (12)
Δ_{JK} /kHz	-5.46233 (12)
Δ_J /kHz	4.57324 (14)
δ_K /kHz	1.585116 (57)
δ_J /kHz	1.971182 (29)
Φ_K /mHz	104.63 (11)
Φ_{KJ} /mHz	-101.68 (11)
Φ_{JK} /mHz	12.408 (74)
Φ_J /mHz	6.394 (60)
ϕ_K /mHz	-0.960 (40)
ϕ_{JK} /mHz	14.369 (38)
ϕ_J /mHz	3.280 (10)
ϵ_{10} /MHz	-3.2257 (12)
$[(B-C)/4]_{10}$ /kHz	0.0352 (15)
$\rho \times 10^{-3}$	55.8678 (23)
β / $^\circ$	29.506 (17)
no. of lines	3751
no. of transitions	1176
standard deviation$^{(c)}$	0.98
microwave rms /kHz	26.514

Notes. $^{(a)}$ Demaison & Rudolph (1975)
$^{(b)}$ Watson's A reduction in the I^r representation is used in ERHAM. Numbers in parentheses are one standard deviation in units of the least significant figures. The first block shows rotational and centrifugal distortion constants, and the second and third blocks show ERHAM tunnelling parameters and geometrical values, respectively. The bottom row contains general information about the fits.
$^{(c)}$ Weighted unitless value for the respective single state fit.

tively, for isobutene. We did not use ERHAM for this purpose because of limitations in J and K. The reduced spin weights were employed to overcome limitations in the upper state degeneracy (g_u) for the catalogue form. The spin weights $36 : 64 : 20 : 16$ for even states and $28 : 64 : 12 : 16$ for odd states were also reduced by a factor of four for generation of Q_{rot}.

It is quite common that vibrational energies are not known or only known approximately, in particular for low-lying vibrational and for overtone and combination states. A usually good approximation is the harmonic approximation, and in most cases better values can be obtained if the anharmonic fundamentals are employed.

The vibrational modes of isobutene can be found in Appendix B. Details of the calculation of vibrational frequencies

Table 2. Rotational Q_{rot} and vibrational partition functions Q_{vib} for isobutene at temperatures (K) implemented in the CDMS.

Temperature (K)	Q_{rot}	Q_{vib}
300.000	1493981.0421	2.278
225.000	970052.1240	1.787
150.000	527900.3030	1.351
75.000	186656.4270	1.046
37.500	66044.4178	1.001
18.750	23393.8153	1.000
15.000	16755.3941	1.000
9.375	8303.1944	1.000
5.000	3256.3920	1.000
2.725	1326.5615	1.000

Notes. See text for details.

Fig. 4. Local thermodynamic equilibrium spectrum of the molecule, assuming two temperatures of astronomical sources where the molecule can potentially be detected: 9.375 K (dark clouds or low-excitation T regions), and 150 K (representing the environment of hot cores or corinos). For comparison, a 300 K spectrum is also shown to stress the effect of temperature on the spectrum peak. We considered the total partition function Q_{tot} for the simulation.

can be found in Appendix B. The values of Q_{rot} and Q_{vib} at temperatures commonly employed in the CDMS catalogue are given in Table 2. A local thermodynamic equilibrium (LTE) spectrum simulated at 9.375 K, 150 K, and 300 K employing the corresponding Q_{tot} from Table 2 is shown in Figure 4. The shape of the spectrum and its peak at different temperatures can guide new observational searches.

3. Astronomical search

3.1. Observations of the G+0.693-0.027 molecular cloud

The molecular cloud G+0.693-0.027 (hereafter G+0.693) located in the Sgr B2 region at the centre of our Galaxy is one of the most chemically rich sources in the ISM (see e.g. Zeng et al. 2018; Bizzocchi et al. 2020; Rivilla et al. 2019, 2020,

2021a,b, 2022a,b,c; Rodríguez-Almeida et al. 2021a,b; Zeng et al. 2021; Jiménez-Serra et al. 2022). We searched for several hydrocarbons (isobutene, propene, and 1-butyne) using a high-sensitivity spectral survey towards G+0.693 carried out with the IRAM 30m telescope (Granada, Spain) and Yebes 40m telescope (Guadalajara, Spain). The observations were centred at α(J2000.0) = $17^h47^m22^s$, and δ(J2000.0) = $-28°21'27''$. The position switching mode was used in all the observations with the off position located at $\Delta\alpha = -885''$, $\Delta\delta = 290''$ from the source position. The line intensity of the spectra was measured in units of T_A^* as the molecular emission towards G+0.693 is extended over the beam (Requena-Torres et al. 2006, 2008; Zeng et al. 2018, 2020). For more detailed information about the observational survey, we refer to Rodríguez-Almeida et al. (2021a), Rivilla et al. (2021b) and Rivilla et al. (2022c).

3.2. Detection of isobutene ($(CH_3)_2C=CH_2$)

The Yebes 40 m observations cover a spectral range from 31.0 GHz to 50.4 GHz, while the IRAM 30 m observations cover the spectral ranges 71.77-116.72 GHz, 124.8–175.5 GHz, 199.8-222.3 GHz, and 223.3-238.3 GHz. We implemented the spectroscopic entry of isobutene from this work into the MADCUBA package[2]; version 21/03/2023; Martín et al. 2019). Using the SLIM (Spectral Line Identification and Modeling) tool of MADCUBA, we generated a synthetic spectrum of isobutene under the assumption of LTE, and compare with the observed spectra. Several groups of transitions of the molecule, which are shown in Figure 5, are detected in the G+0.693 spectral survey. Their spectroscopic information is listed in Table 4. We note that in Table 4, the upper state degeneracy, g_u, is divided by a factor of four. The reduced spin weight was employed to overcome limitation in the catalogue form. The group of transitions with $J = 8-7$ at 77.978 GHz, $9-8$ at 87.209 GHz, and $10-9$ at 96.440 GHz appears completely unblended, without any contamination from other species. The group of transitions at 41.048 and 41.058 GHz (Table 4) produces a doublet, which combined with emission from the ^{13}C isotopologue of ethanol nicely reproduces the spectral profile observed (upper left panel in Fig. 5). The $J = 9-8$ and $10-9$ groups of transitions at 95.459 and 96.440 GHz are detected with lower signal-to-noise ratio, but they are also compatible with the observed spectra. We note that no predicted transition by the LTE model is missing in the spectra.

We used the transitions shown in Fig. 5 (listed in Table 4) to derive the physical parameters of the isobutene emission. We used the SLIM-AUTOFIT tool of MADCUBA, which provides the best non-linear least-squares LTE fit to the data using the Levenberg-Marquardt algorithm. The parameters used in the LTE model are: molecular column density (N), excitation temperature (T_{ex}), velocity (V_{LSR}), and full width half maximum (FWHM) of the Gaussian line profiles. For the case of the isobutene fit, to allow the convergence of the AUTOFIT algorithm, we fixed the values of the velocity and the linewidth to V_{LSR}=69 km s^{-1} and FWHM=20 km s^{-1}, respectively, which are commonly found in other molecular tracers in G+0.693 (see Requena-Torres et al. 2006, 2008; Zeng et al. 2018), and we also used these to fit other hydrocarbons, such as propyne (Bizzocchi et al. 2020). The best fit provided by AUTOFIT, also taking into account the emission produced by other molecules already iden-

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Fig. 5. Unblended or slightly blended transitions of isobutene ($(CH_3)_2C=CH_2$) detected towards the G+0.693 molecular cloud. The black line and grey histogram show the observed spectrum. The LTE fit of isobutene is indicated with a red curve, while the emission of all the molecules identified in G+0.693, including isobutene, are indicated in purple.

Table 3. Derived physical parameters for the hydrocarbons analysed towards the G+0.693−0.027 molecular cloud. Values without uncertainties were fixed when performing the fit (see text).

Name	Formula	N ($\times 10^{13}$ cm^{-2})	T_{ex} (K)	V_{LSR} (km s^{-1})	FWHM (km s^{-1})	Abundance[a] ($\times 10^{-10}$)	Ref.[b]
Propene	$CH_2=CHCH_3$ (C_3H_6)	82±16	16±4	69	20	60	(1)
Isobutene	$(CH_3)_2C=CH_2$ (C_4H_8)	26±4	14±9	69	20	19	(1)
Propyne	CH_3CCH (C_3H_4)	170±2	19±1	69	20	126	(2)
1-butyne	C_2H_5CCH (C_4H_6)	< 2.7	19	69	20	< 2	(1)

Notes. [a] We adopted $N_{H_2}=1.35\times 10^{23}$ cm^{-2}, from Martín et al. (2008). [b] References: (1) This work; (2) Bizzocchi et al. (2020).

tified in the survey, is shown with a red curve in Figure 5. We found $T_{ex}=14\pm7$ K, and $N=(2.6\pm0.4)\times10^{14}$ cm^{-2}, which translates into a molecular abundance of 1.9×10^{-9} (Table 3).

3.3. Detection of propene (CH$_2$=CHCH$_3$)

We also report the detection of propene towards G+0.693 ($CH_2=CHCH_3$). The CDMS entry 42516 was used for this search. This entry is based on Craig et al. (2016) with most of the data coming from Pearson et al. (1994), and Wlodarczak et al. (1994). Multiple unblended or slightly blended transitions

Table 4. List of selected transitions of isobutene $((CH_3)_2C=CH_2)$ and propene $(CH_2=CHCH_3)$ detected towards G+0.693, whose spectra are shown in Figures 5 and 6, respectively. We provide the transition frequencies, quantum numbers, base 10 logarithms of the integrated intensity at 300 K (log I), the base 10 logarithm of Einstein coefficients (log A_{ul}), and upper state degeneracy (g_u). We note that g_u is calculated based on reduced spin weights by a factor of four. For isobutene, we have included all the hyperfine transitions that fall in the spectral ranges shown in Fig. 5. Some of them are weak and their contribution to the synthetic spectrum is negligible, but we have included them for completeness.

Species	Frequency (GHz)	Transition $(J'_{K_{a'},K_{c'}} \leftarrow J''_{K_{a''},K_{c''}}(\sigma_1\sigma_2))$	log I (nm^2 MHz)	log A_{ul} (s^{-1})	g_u	E_u (K)	Blending[b]
$(CH_3)_2C=CH_2$	41.0488473	$4_{0,4} - 3_{1,3}(12)$	-7.5883	-7.1083	45	5.22	$CH_3^{13}CH_2OH$
	41.0488473	$4_{0,4} - 3_{1,3}(11)$	-7.4914	-7.1083	36	5.22	$CH_3^{13}CH_2OH$
	41.0488769	$4_{0,4} - 3_{1,3}(01)$	-6.9863	-7.1083	144	5.22	$CH_3^{13}CH_2OH$
	41.0489065	$4_{0,4} - 3_{1,3}(00)$	-7.2361	-7.1082	81	5.22	$CH_3^{13}CH_2OH$
	41.0581587	$4_{1,4} - 3_{0,3}(11)$	-7.7130	-7.1080	36	5.22	$CH_3^{13}CH_2OH$
	41.0581587	$4_{1,4} - 3_{0,3}(12)$	-7.5881	-7.1079	27	5.22	$CH_3^{13}CH_2OH$
	41.0581894	$4_{1,4} - 3_{0,3}(01)$	-6.9860	-7.1079	144	5.22	$CH_3^{13}CH_2OH$
	41.0582201	$4_{1,4} - 3_{0,3}(00)$	-7.3450	-7.1079	63	5.22	$CH_3^{13}CH_2OH$
	77.9785914	$8_{0,8} - 7_{1,7}(12)$	-6.7124	-6.2134	85	17.54	-
	77.9785914	$8_{0,8} - 7_{1,7}(11)$	-6.6155	-6.2134	68	17.54	-
	77.9785915	$8_{1,8} - 7_{0,7}(11)$	-6.8373	-6.2133	51	17.54	-
	77.9785915	$8_{1,8} - 7_{0,7}(12)$	-6.7124	-6.2134	68	17.54	-
	77.9786193	$8_{0,8} - 7_{1,7}(01)$	-6.1103	-6.2133	272	17.54	-
	77.9786195	$8_{1,8} - 7_{0,7}(01)$	-6.1103	-6.2133	272	17.54	-
	77.9786473	$8_{0,8} - 7_{1,7}(00)$	-6.3602	-6.2133	153	17.54	-
	77.9786474	$8_{1,8} - 7_{0,7}(00)$	-6.4694	-6.2134	119	17.54	-
	87.2098252	$9_{0,9} - 8_{1,8}(11)$	-6.6912	-6.0612	57	21.72	-
	87.2098252	$9_{1,9} - 8_{0,8}(12)$	-6.5662	-6.0611	76	21.72	-
	87.2098252	$9_{0,9} - 8_{1,8}(12)$	-6.5662	-6.0611	95	21.72	-
	87.2098252	$9_{1,9} - 8_{0,8}(11)$	-6.4693	-6.0611	76	21.72	-
	87.2098526	$9_{1,9} - 8_{0,8}(01)$	-5.9642	-6.0612	304	21.72	-
	87.2098526	$9_{0,9} - 8_{1,8}(01)$	-5.9642	-6.0612	304	21.72	-
	87.2098801	$9_{0,9} - 8_{1,8}(00)$	-6.3232	-6.0612	133	21.72	-
	87.2098801	$9_{1,9} - 8_{0,8}(00)$	-6.2140	-6.0611	171	21.72	-
	94.4876421	$8_{2,6} - 7_{3,5}(12)$	-6.6924	-6.1025	85	23.07	-
	94.4876421	$8_{2,6} - 7_{3,5}(11)$	-6.5955	-6.1025	68	23.07	-
	94.4877915	$8_{2,6} - 7_{3,5}(01)$	-6.0904	-6.1026	272	23.07	-
	94.4879409	$8_{2,6} - 7_{3,5}(00)$	-6.3402	-6.1025	153	23.07	-
	94.4904265	$8_{3,6} - 7_{2,5}(11)$	-6.8173	-6.1025	51	23.07	-
	94.4904265	$8_{3,6} - 7_{2,5}(12)$	-6.6924	-6.1025	68	23.07	-
	94.4905764	$8_{3,6} - 7_{2,5}(01)$	-6.0903	-6.1025	272	23.07	-
	94.4907263	$8_{3,6} - 7_{2,5}(00)$	-6.4494	-6.1025	119	23.07	-
	95.4590035	$9_{1,8} - 8_{2,7}(11)$	-6.6748	-6.0010	57	25.09	-
	95.4590035	$9_{1,8} - 8_{2,7}(12)$	-6.5499	-6.0010	76	25.09	-
	95.4590057	$9_{2,8} - 8_{1,7}(12)$	-6.5499	-6.0010	95	25.09	-
	95.4590057	$9_{2,8} - 8_{1,7}(11)$	-6.4530	-6.0010	76	25.09	-
	95.4590922	$9_{1,8} - 8_{2,7}(01)$	-5.9478	-6.0010	304	25.09	-
	95.4590944	$9_{2,8} - 8_{1,7}(01)$	-5.9478	-6.0010	304	25.09	-
	95.4591808	$9_{1,8} - 8_{2,7}(00)$	-6.3068	-6.0009	133	25.09	-
	95.4591830	$9_{2,8} - 8_{1,7}(00)$	-6.1977	-6.0010	171	25.09	-
	96.4409266	$10_{1,10} - 9_{0,9}(11)$	-6.5616	-5.9249	105	26.35	-
	96.4409266	$10_{1,10} - 9_{0,9}(12)$	-6.4366	-5.9249	84	26.35	-
	96.4409266	$10_{0,10} - 9_{1,9}(12)$	-6.4366	-5.9249	63	26.35	-
	96.4409266	$10_{0,10} - 9_{1,9}(11)$	-6.3397	-5.9249	84	26.35	-
	96.4409536	$10_{1,10} - 9_{0,9}(01)$	-5.8346	-5.9249	336	26.35	-
	96.4409536	$10_{0,10} - 9_{1,9}(01)$	-5.8346	-5.9249	336	26.35	-
	96.4409805	$10_{1,10} - 9_{0,9}(00)$	-6.1936	-5.9249	189	26.35	-
	96.4409805	$10_{0,10} - 9_{1,9}(00)$	-6.0844	-5.9249	147	26.35	-
$CH_2=CHCH_3$	89.9972320	$5_{1,4} - 4_{1,3}(11)$	-5.9650	-6.3190	44	14.83	-
	89.9981740	$5_{1,4} - 4_{1,3}(00)$	-5.9650	-6.3190	44	14.83	-
	103.6891170	$6_{0,6} - 5_{0,5}(11)$	-5.7493	-6.1109	52	17.50	-
	103.6900200	$6_{0,6} - 5_{0,5}(00)$	-5.7493	-6.1109	52	17.50	-
	156.4469910	$9_{2,8} - 8_{2,7}(11)$	-5.2750	-5.5851	76	44.78	-
	156.4475110	$9_{2,8} - 8_{2,7}(00)$	-5.2750	-5.5851	76	44.78	-

(a) $(\sigma_1\sigma_2)$ refers to the ERHAM labelling of internal rotor components (Groner 1997),
where $00 = A_1A_1$, $01 = EE$, $11 = A_1E$, $12 = EA_1$.

Fig. 6. Selected clean transitions of propene (CH_2=$CHCH_3$) detected towards the G+0.693 molecular cloud. The black line and grey histogram show the observed spectrum. The LTE fit of propene is indicated with a red curve, while the emission from all the molecules identified in G+0.693 are indicated in purple.

of this species are detected in the survey, which we used to derive the physical properties of the emission. We show in Figure 6 some selected clean transitions, whose spectroscopic information is summarised in Table 4. We use the same procedure used to fit isobutene, obtaining T_{ex}=16±4 K, identical within uncertainties to that derived for isobutene, and N=(8.2±1.6)×10^{14} cm^{-2}, which translates into a molecular abundance of 6.0×10^{-9} (Table 3). Thus, the abundance ratio between propene and isobutene, CH_2=$CHCH_3$/(CH_3)$_2$C=CH_2, is ~3.

3.4. Non-detection of 1-Butyne (C_2H_5CCH)

Following the detection of propene and isobutene (C_3H_6 and C_4H_8 isomers, respectively), we also searched for 1-butyne, C_2H_5CCH (C_4H_6). This species was tentatively detected using a stacking technique towards the TMC-1 dark cloud by Cernicharo et al. (2021). We employed the CDMS entry 54519 (version 1; March 2017). In this entry, the data are obtained from Steber et al. (2012), which also comprise frequencies from Demaison et al. (1983) and Landsberg & Suenram (1983). The species is not detected in the G+0.693 spectral survey. We used the brightest transitions —according to the simulated LTE model— that are not strongly blended with brighter transitions of other molecules to derive the upper limit to the column density. We applied the excitation temperature, velocity, and linewidth derived for the simpler member of its family, propyne (Table 3): T_{ex}=19 K, V_{LSR}=69 km s^{-1} and FWHM=20 km s^{-1}. To derive the upper limit of the column density, we used the highest value that produces a LTE model compatible with the observed spectrum. We obtained $N < 2.7$×10^{13} cm^{-2}, which means an upper limit to its abundance compared to H_2 of < 2×10^{-10}. This gives a ratio of CH_3CCH/$C_2H_5CCH > 63$ which is in good agreement with that found in the dark cloud TMC-1 of >133. The TMC-1 ratio is calculated using the abundances derived from the tentative detection of C_2H_5CCH by Cernicharo et al. (2021), and the detection of CH_3CCH (Gratier et al. 2016; Cabezas et al. 2021). However, this methy-/ethyl- ratio is significantly higher than those found in other families towards G+0.693, such as alcohols, thiols, aldehydes, and isocyanates, which are in the range 7−24 (Rodríguez-Almeida et al. 2021a,b; Sanz-Novo et al. 2022; Jiménez-Serra et al. 2022).

4. Conclusion

We extended the isobutene line list to 370 GHz applying absorption spectroscopy. Transitions up to $J_{max} = 60$ and $K_{c,max} = 41$ were included in the fit, which led to the determination of a complete set of quartic and sextic distortion parameters for the first time. The rest frequencies resulting from this fit enabled us to search for isobutene in the G+0.693 molecular cloud. Within this source, we also successfully found propene and determined a propene to isobutene abundance ratio of 3. We also searched for 1-butyne.

Our final parameters for isobutene are good up to 700 GHz, and possibly higher with J extending to about 70. Therefore, a search for isobutene in other molecular clouds such as TMC-1 and the warm parts of star-forming regions, such as in IRAS 16293−2422, could be promising. Molecular clouds, such as G+0.693 and TMC-1, are a rich source of atomic carbon available in the gas phase, which drives a rich chemistry in hydrocarbon species. Therefore, the detection of isobutene could help us to understand the chemistry of the formation of saturated hydrocarbon species within these molecular clouds.

Isobutene is one of four butene isomers, along with 1-butene, **syn**-2-butene, and **anti**-2-butene. The latter does not have a rotational spectrum because of its C_i symmetry, which leads to a zero dipole moment. Limited microwave data are available for both conformers of 1-butene (Kondo et al. 1968) and for **syn**-2-butene (Sarachman 1968; Meyer et al. 1991). It will be interesting to search for these isomers in the ISM because branched molecules, such as isobutene, have so far been found to be less abundant than their unbranched isomers. The known examples are propyl cyanide (Belloche et al. 2014) and propanol (Jiménez-Serra et al. 2022; Belloche et al. 2022). A detection of 1-butene or **syn**-2-butene will present another pair of isomers that can be used to improve existing astrochemical models (Belloche et al. 2014; Garrod et al. 2017; Belloche et al. 2022).

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Table A.1. Experimental spectroscopic parameters (MHz) of the main isotopologue of isobutene obtained by fitting all the previous available data between 8–35 GHz.

Parameters	
A /MHz	9133.3642 (13)
B /MHz	8381.8739 (13)
C /MHz	4615.9765 (13)
Δ_K /kHz	8.888 (74)
Δ_{JK} /kHz	−5.16 (10)
Δ_J /kHz	4.28 (32)
δ_K /kHz	1.452 (43)
δ_J /kHz	2.014 (15)
ϵ_{10} /MHz	−3.201 (24)
$\rho \times 10^{-3}$	56.37 (25)
β / °	29.53 (10)
no. of lines	472
no. of transitions	118
standard deviation[a]	0.89
microwave rms /kHz	34

Notes. [a] Weighted unit-less value for the respective single state fit.

Appendix A: Rotational parameters from previous data set

Laurie (1961), Demaison & Rudolph (1975), and Gutowsky & Germann (1991) published rotational data for isobutene; although the latter two publications did not consider earlier data in their analyses. We fit these data together for a comparison of the parameter values and the predictive power compared to our more extensive results. The data are sufficient to determine rotational and quartic centrifugal distortion parameters, which are given in Table A.1.

Appendix B: Vibrational spectrum of isobutene

Isobutene has 30 vibrational modes. The vibrational representation under C_{2v} symmetry is $10A_1 + 5A_2 + 6B_1 + 9B_2$. We note that the B_1 and B_2 representations are interchanged from the previous representations used in Pathak & Fletcher (1969), Harris & Levin (1971b), and Harris & Levin (1971a). In recent representations, B_1 and B_2 accounts for vibrations along xz and yz planes, respectively. Therefore, we report B_1 and B_2 in their current representations.

As we do not know how reliable and how complete the reported vibrational data are, we carried out quantum-chemical calculations at the Regionales Rechenzentrum der Universität zu Köln (RRZK) using the commercially available program Gaussian 09 (Frisch et al. 2013). We applied the B3LYP hybrid density functional (Becke 1993; Lee et al. 1988). We employed the correlation consistent basis set augmented with diffuse basis functions aug-cc-pVTZ (Dunning, Jr. 1989).

A list of the observed infrared and Raman frequencies in the gas and solid phases compared with calculated harmonic and anharmonic frequencies at the B3LYP level of theory is reported in Table B.1 (Gordy & Cook 1970). All 30 vibrational fundamentals were observed in solid state Raman spectra, whereas in the gas phase Raman spectrum only 22 bands were identified. In infrared experiments, 17 modes were observed, where in some cases *PQR* band shapes were also observed, which are useful for the assignment of a vibrational mode to the symmetry class. The experimental frequencies are within 6% and 4% of the calculated harmonic and anharmonic frequencies, respectively.

The two lowest vibrational modes, ν_{15} and ν_{21}, of isobutene are both Raman active, but only the ν_{21} mode is infrared active. Both vibrational modes were reported from Raman experiments in the solid phase (Harris & Levin 1971b,a). A value for ν_{21} was determined in addition in a gas phase infrared spectroscopic study (Durig et al. 1977). Additional insight into the fundamental torsional modes of isobutene could not be extracted from the Raman spectrum in the gas phase in this last work by Durig et al. (1977).

The study of the torsional vibrations of isobutene were useful in determining the internal rotation barrier height. From gas phase measurements, the effective barrier was derived to be 728±3 cm^{-1} (2.08±0.01 kcal mol^{-1}) (Durig et al. 1977). This value is similar to the microwave study, where the barrier was determined to be 2.21 kcal mol^{-1} (Demaison & Rudolph 1975). Interestingly, from the solid phase measurements, a higher barrier height was evaluated (979 cm^{-1} or 2.8 kcal mol^{-1}) (Harris & Levin 1971a). As mentioned by Demaison & Rudolph (1975), this difference suggests that large intermolecular forces exist in the solid phase, which result in a higher barrier in the condensed phase. Therefore, this could further indicate that the torsional fundamentals in the gas phase are lower than those measured in the liquid or solid phase by Raman spectroscopy.

Table B.1. Quantum-chemically calculated harmonic and anharmonic vibrational frequencies (cm^{-1}) of isobutene and experimental data (cm^{-1}).

Symmetry	Normal modes	Harmonic frequency	Anharmonic frequency	Observed in Infrared	Observed in Raman	
				gas phase[a] R/Q/P	gas phase[a]	solid phase[b]
A_1	ν_1	3130.1	2987.2	2990/2980.4/2968	2989	2988
	ν_2	3102.4	2962.5	2940.8	2930	2942
	ν_3	3013.6	2911.5	—	2911	2916
	ν_4	1713.3	1666.6	1661.1	1655	1653
	ν_5	1502.4	1466.8	1469.6	1462	1458
	ν_6	1444.3	1413.5	—	1416	1421
	ν_7	1414.8	1377.4	1392/1381.2/1370	1366	1376
	ν_8	1085.2	1070.2	1075/1063.9/1054	1058	1058
	ν_9	814.4	797.5	—	803	809
	ν_{10}	379.3	393.6	—	383	389
A_2	ν_{11}	3048.1	2908.0	—	2970	2956
	ν_{12}	1471.6	1438.3	—	1459	1438
	ν_{13}	1022.2	998.2	—	—	969
	ν_{14}	703.4	694.0	—	—	685
	ν_{15}	168.6	185.2	—	—	209[d]
B_1	ν_{16}	3050.8	2909.0	2944.9	—	2956
	ν_{17}	1489.5	1445.4	-/1443.7/1426	1439	1458
	ν_{18}	1108.6	1081.1	1079	—	1085
	ν_{19}	923.1	906.8	906/889.7/873	883	889
	ν_{20}	442.3	445.0	445/429.1/412	431	438
	ν_{21}	210.0	213.9	197.6[c]	—	239[d]
B_2	ν_{22}	3207.1	3064.7	3096/3086.0/3074	3079	3077
	ν_{23}	3100.8	2960.9	—	2970	2968
	ν_{24}	3008.0	2893.1	2892.9/2882	2892	2898
	ν_{25}	1483.4	1457.0	1458.4	1439	1430
	ν_{26}	1409.5	1377.0	—	1386	1386
	ν_{27}	1296.4	1267.3	1292/1281.9/1270	1281	1271
	ν_{28}	987.3	975.0	—	—	996
	ν_{29}	961.2	951.6	973.7	972	958
	ν_{30}	439.2	444.1	—	—	438

Notes. [a] Pathak & Fletcher (1969) [b] Harris & Levin (1971b) [c] Durig et al. (1977) [d] Harris & Levin (1971a)