New Spectral Characterization of Dimethyl Ether Isotopologues CH$_3$OCH$_3$ and $^{13}$CH$_3$OCH$_3$ in the THz Region

J. M. Fernández$^{1}$, G. Tejeda$^{1}$, M. Carvajal$^{2,3}$, and M. L. Senent$^{4}$

$^1$Laboratory of Molecular Fluid Dynamics, Instituto de Estructura de la Materia IEM-CSIC, Unidad Asociada GIFMAN, CSIC-UHU; E-28006 Madrid, Spain
$^2$Dpto. Ciencias Integradas, Centro de Estudios Avanzados en Física, Matemática y Computación, Facultad de Ciencias Experimentales, Universidad de Huelva; Unidad Asociada GIFMAN, CSIC-UHU; E-21071 Huelva, Spain
$^3$Instituto Universitario Carlos I de Física Teórica y Computacional, Universidad de Granada, Granada, Spain
$^4$Theoretical Chemistry and Physics Department, Instituto de Estructura de la Materia IEM-CSIC, Unidad Asociada GIFMAN, CSIC-UHU; E-28006 Madrid, Spain

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Abstract

The torsional Raman spectra of two astrophysically detected isotopologues of dimethyl ether (DME, $^{12}$CH$_3$O$^{12}$CH$_3$ and $^{13}$CH$_3$O$^{13}$CH$_3$) have been recorded at room temperature and cooled in a supersonic jet and interpreted with the help of highly correlated ab initio calculations. DME displays excited torsional and vibrational levels at low energy that can be populated at the temperatures of the star-forming regions, obliging to extend the analysis of the rotational spectrum over the ground state. Its spectrum in the THz region is rather complex due to the coupling of the torsional overtones $2\nu_{11}$ and $2\nu_{15}$ with the COC-bending mode and the presence of many hot bands. The torsional overtones are set here at $2\nu_{11} = 385.2$ cm$^{-1}$ and $2\nu_{15} = 482.0$ cm$^{-1}$ for $^{12}$CH$_3$O$^{12}$CH$_3$ and $2\nu_{11} = 385.0$ cm$^{-1}$ and $2\nu_{15} = 481.1$ cm$^{-1}$ for $^{13}$CH$_3$O$^{13}$CH$_3$. The new assignment of $2\nu_{11}$ is downshifted around $\sim 10$ cm$^{-1}$ with respect to the literature. All the other (hot) bands have been reassigned consistently. In addition, the infrared-forbidden torsional fundamental band $\nu_{11}$ is observed here at 197.8 cm$^{-1}$. The new spectral characterization in the THz region reported here provides improved values of the Hamiltonian parameters to be used in the analysis of the rotational spectra of DME isotopologues for further astrophysical detections.

Key words: astrochemistry – ISM: lines and bands – ISM: molecules – methods: laboratory: molecular – molecular data – techniques: spectroscopic

1. Introduction

Dimethyl ether (DME, CH$_3$OCH$_3$) is a relevant astrophysical molecule that was first detected in the interstellar medium (ISM) by Snyder et al. (1974) and later on was identified as an abundant species in star-forming regions (Schilke et al. 2001). DME is mainly formed in the gas phase via the radiative association reaction of methoxy and methyl radicals, and it presents a correlation with methyl formate (Carvajal et al. 2010; Favre et al. 2014), via the oxidation of CH$_3$OCH$_2$, in cold objects (Balucani et al. 2015).

In addition to works prior to its detection in the ISM (Taylor & Vidale 1957; Kasai & Myers 1959; Fateley & Miller 1962; Blukis et al. 1963; Durig et al. 1976; Groner & Durig 1977), the astrophysical interest for the complete description of the spectrum in the millimeter and submillimeter regions of DME and its isotopologues, such as $^{13}$CH$_3$OCH$_3$ ($^{13}$C-DME) and CH$_3$OCH$_2$D (d-DME), has brought about many laboratory studies of its rotational spectrum and of a few vibrational bands (Lovas et al. 1979; Neustock et al. 1990; Groner et al. 1998; Coudert et al. 2002; Niide & Hayashi 2003; Endres et al. 2009; Kutzer et al. 2016). In turn, the analysis of an extensive number of spectral lines in astronomical observations has given rise to the identification of DME in Orion-KL (Brouillet et al. 2013) and the detection of the first excited torsional states lines in a high-mass star-forming region (Bisschop et al. 2013). Furthermore, the ground state rotational lines corresponding to the monosubstituted isotopologues $^{13}$C-DME and d-DME were first observed in a high-mass star-forming region (Koerber et al. 2013; Richard et al. 2013).

DME is a nonrigid asymmetric top with two methyl internal rotors that splits each rovibrational level into nine components (Groner & Durig 1977; Senent et al. 1995a, 1995b), some of them degenerate. Hence, the high-resolution spectrum of DME is quite dense, and its analysis is challenging. Furthermore, because the first and the second excited torsional levels lie at relatively low energy, they can be populated at the temperatures of the hot core regions, obliging to extend the spectral analysis to the two torsional fundamentals and their overtones. The spectral region of the torsional overtones is further complicated due to their coupling with the COC-bending mode (Senent et al. 1995b) and the presence of many hot bands. The following notation will be used throughout the paper: $\nu_{11}$ is the “anti-geared” torsion, $\nu_{15}$ is the “geared” torsion, and $\nu_7$ is the COC-bending mode; vib-torsional energy levels will be denoted as ($\nu_{11}$ $\nu_{15}$ $\nu_7$), where $\nu_i$ is the number of torsional or vibrational quanta in the corresponding mode.

The torsional spectrum of DME was investigated experimentally at room temperature by Groner & Durig (1977), using Raman and infrared techniques. The torsional fundamental $\nu_{15}$ was observed at 241.0 cm$^{-1}$. The other torsional fundamental $\nu_{11}$ is forbidden in the absorption spectrum and was estimated between 199 and 202 cm$^{-1}$. The two torsional overtones were assigned to the peaks observed at $2\nu_{11} = 395.5$ cm$^{-1}$ and $2\nu_{15} = 481.2$ cm$^{-1}$. The lack of an accurate value for the $\nu_{11}$ torsional mode prevented the determination of some of the interaction parameters of the effective Hamiltonian needed for a further analysis.

In this paper, the torsional Raman spectra of DME and of $^{13}$C-DME have been recorded at room temperature and of cooled DME in a supersonic jet. The spectrum of cooled DME allowed us to assign unequivocally the torsional overtones and their first hot bands, amending some of the previous assignments. In turn,
the new frequencies have been used to refine 3D quantum calculations, employing a state-of-the-art coupled-cluster theory with single and double substitutions (CCSD(T)) ab initio calculations (Villa et al. 2011) and a torsion–torsion-bending Hamiltonian (Senent et al. 1995b; Carvajal et al. 2012). The new characterization provides improved values of the Hamiltonian parameters for the analysis of DME and $^{13}$C-DME rotational spectra and future astrophysical detections.

2. New Experimental Raman Measurements

Two sets of Raman spectra of DME were recorded in this work: (i) at room temperature and (ii) jet cooled. The sample of DME was supplied by Praxair, with nominal purity of 99.8%, while that of $^{13}$C-DME was synthesized in the University of Kassel, Germany (Kutzer et al. 2016); the latter sample was distilled by liquid nitrogen to remove residual H$_2$ from the synthesis. Raman spectra of DME and of $^{13}$C-DME were recorded at room temperature under static conditions (pressure 550 mbar and 380 mbar, respectively). In addition, supersonic jets of mixtures of DME diluted in He were produced to cool the DME. Raman shifts were calibrated against Hg and Ne emission lines and are accurate to $\pm 0.1$ cm$^{-1}$. Raman scattering was excited by 10 W of linearly polarized radiation at 532 nm from a Coherent Verdi V10 laser, which was sharply focused down to a 15 $\mu$m beam waist on the sample by a $f = 35$ mm lens. Scattered radiation perpendicular to both laser propagation and polarization was collected by an $f = 55$ mm photographic objective (Nikon, $f/1.8$) and projected, with a total magnification $\times 10$, onto the entrance slit of the spectrograph. This is a Jobin-Yvon double monochromator, equipped with two 2400 groove/mm gratings, and a CCD detector with $13 \times 13 \mu$m$^2$ pixels, which is refrigerated by liquid nitrogen. The entrance slit was 75 and 150 $\mu$m, yielding a spectral resolution of 0.36 and 0.72 cm$^{-1}$, respectively. Several scans were spike filtered and averaged.

Raman spectroscopy can be an invaluable tool to investigate the torsional modes of symmetric molecules like ethane (Fantoni et al. 1986; Fernández-Sánchez et al. 1989), propane (Engeln et al. 1990), or butane (Compton et al. 1980; Engeln & Reuss 1991). In such symmetric molecules, some of the torsional modes are forbidden in infrared (IR) or microwave (MW) absorption, while the torsional overtones give rise to weak Q-branches in Raman spectrum, often accompanied by a rich structure of hot bands. In the case of DME, the $\nu_{11}$ torsional mode is silent in IR-MW; on the contrary, the two torsional modes are Raman allowed, as well as their overtones. The Raman spectra of DME and $^{13}$C-DME in this latter region are shown in Figure 1. This region is dominated by the COC-bending mode $\nu_7$, which yields the peak at $\sim 410$ cm$^{-1}$. In addition to that, a rich structure of peaks due to hot bands can be seen, which hinders the safe assignment of the two torsional overtones. The spectrum of $^{13}$C-DME is rather similar to that of DME, with some of the peaks shifted toward lower wavenumbers, due to the mass increase, as discussed below. The lowest panel shows the spectrum of jet-cooled DME in a supersonic expansion diluted in helium. As can be clearly seen, only three peaks survive at low temperature, which can be assigned unambiguously to the two torsional overtones plus the COC-bending modes. Actually, the $2\nu_{11}$ torsional overtone had been wrongly assigned (Groner & Durig 1977) to the peak at 395.5 cm$^{-1}$ in the room temperature spectrum, which disappears when the molecule is jet cooled, while the peak at 385.2 cm$^{-1}$ remains at low temperature.

The Raman spectrum of the jet-cooled DME in the region of the torsional fundamentals is shown in Figure 2. These Raman bands are extremely weak and had not been reported before. The faint Q branch at 241.4 cm$^{-1}$ is the $\nu_{15}$ mode, which was observed previously in IR (Fateley & Miller 1962; Groner & Durig 1977). The broad band with the comb-like rotational structure can be assigned to the unobserved $\nu_{11}$ torsional

![Figure 1. Raman spectra of CH$_3$OCH$_3$ and $^{13}$CH$_3$OCH$_3$ in the region of the torsional overtones. For band numbering, refer to Table 2.](image-url)
fundamental. A simulation with PGOPHER (Western 2016), with the selection rules $\Delta K_z = \pm 1$ and $\Delta K_c = \pm 1$, corresponding to a Raman band of $A_2$ symmetry in the $C_2v$ point group, allows us to locate the band origin at 197.8 cm$^{-1}$, although it could be downshifted by one unit of the peak spacing (1.9 cm$^{-1}$).

3. Theoretical Model for the Spectral Analysis

In previous papers on DME (Villa et al. 2011) and its isotopologues CH$_3$OCD$_3$, CD$_3$OCD$_3$ (Senent et al. 2012), $^{13}$CH$_3$OCH$_3$ (Carvajal et al. 2012), and CH$_3$OCH$_2$D (Carvajal et al. 2014), we used a 3D model for the analysis of their far-IR spectra. Assuming that the three low-frequency vibrational modes can be treated separately from the remaining “high-frequency” vibrations, the 3D Hamiltonian can be written as

$$
\hat{H}(\alpha, \theta_1, \theta_2) = -\sum_{i=1}^{3} \sum_{j=1}^{3} \frac{\partial}{\partial \theta_i} B_{ij}(\alpha, \theta_1, \theta_2) \frac{\partial}{\partial \theta_j} + V^{\text{eff}}(\alpha, \theta_1, \theta_2).
$$

In this equation, $q_i, q_j = (\alpha, \theta_1, \theta_2)$ represent the three independent variables: the COC-bending $\alpha$ and the two torsional coordinates, $\theta_1$ and $\theta_2$. The first term, which depends on the $B_{ij}$ parameters (the G-matrix elements in cm$^{-1}$), is a 3D-kinetic energy operator. The second term, the effective potential energy $V^{\text{eff}}$, is the sum of three contributions:

$$
V^{\text{eff}}(\alpha, \theta_1, \theta_2) = V(\alpha, \theta_1, \theta_2) + V'(\alpha, \theta_1, \theta_2) + V^{\text{ZPVE}}(\alpha, \theta_1, \theta_2)
$$

where $V(\alpha, \theta_1, \theta_2)$ is the ab initio potential energy, $V'(\alpha, \theta_1, \theta_2)$ is the Podolsky pseudopotential, and $V^{\text{ZPVE}}(\alpha, \theta_1, \theta_2)$ is the zero-point vibrational energy correction. The ab initio potential energy $V$ is isotopically invariant, whereas $V'$ and $V^{\text{ZPVE}}$ (and thus the effective potential $V^{\text{eff}}$) depend on the nuclear masses, as well as, of course, the kinetic energy parameters $B_{ij}$.

All of the terms in Equations (1) and (2) can be determined from energies, geometries, and harmonic frequencies from accurate ab initio calculations, as described elsewhere (Senent 1998a, 1998b). In the present paper, we used the previous ab initio calculations by Villa et al. (2011), performed with the Gaussian 09 code (Frisch et al. 2009). CCSD (Scuseria & Schaefer 1989) was employed for the geometry optimizations. To improve the energies, single point calculations were performed, adding a perturbative treatment of triple excitations (CCSD(T); Pople et al. 1987) on the CCSD geometries. Long range effects are well described because the augmented aug-cc-pVTZ basis set was employed in all of the computations (Woon & Dunning 1993).

Ab initio energies $V(\alpha, \theta_1, \theta_2)$ were calculated at 126 configurations for selected values of the three $(\alpha, \theta_1, \theta_2)$ coordinates: $\alpha = (104^\circ \pm 676 \rightarrow 119^\circ \pm 676, \Delta \alpha = 3^\circ)$, and $\theta_1, \theta_2 = 0^\circ, \pm 30^\circ, \pm 90^\circ, \pm 150^\circ, 180^\circ$. In all of the 126 configurations, the remaining $3N - 9$ internal coordinates were allowed to relax. The other terms of the Hamiltonian, $B_{ij}$, $V'$, and $V^{\text{ZPVE}}$, were also computed for the same 126 configurations; the $V^{\text{ZPVE}}$ correction, which was needed to obtain reliable results (Smeyers et al. 1996), was computed within the harmonic approximation. Analytical 3D effective potential energy surfaces $V^{\text{eff}}(\alpha, \theta_1, \theta_2)$ for DME and $^{13}$C-DME were then obtained by fitting their values at the 126 configurations to a series of the form:

$$
V^{\text{eff}}(\alpha, \theta_1, \theta_2) = \sum_{l=0}^{3} \sum_{m=-l}^{l} \sum_{n=-m}^{m} \alpha^l \cos(3m\theta_1) \cos(3n\theta_2) + B_{l|m} \alpha^l \sin(3m\theta_1) \sin(3n\theta_2)
$$

For DME, $A_{l|m} = A_{l|m}$ and $B_{l|m} = B_{l|m}$, while for the less symmetric $^{13}$C-DME, the $|A_{l|m} - A_{l|m}|$, and $|B_{l|m} - B_{l|m}|$
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differences are found to be lower than 0.0001 cm\(^{-1}\). Formally identical fits were carried out for each of the kinetic energy operators \(B_g(\alpha, \theta_1, \theta_2)\).

The original code ENEDIM (Senent 2001) was used to carry out the calculations and fits of the \(V_{\text{eff}}(\alpha, \theta_1, \theta_2)\) and \(B_g(\alpha, \theta_1, \theta_2)\) surfaces and then to compute variationally the torsional and bending energy levels of the 3D Hamiltonian. To reduce the computational expenses and for the classification of the levels, the molecular symmetry properties were taken into consideration. The two isotopologues studied here, \(^{12}\text{CH}_3\text{O}^{13}\text{CH}_3\) (DME) and \(^{13}\text{CH}_2\text{O}^{12}\text{CH}_3\) (\(^{13}\text{C}\)-DME), can be classified in the \(G_{36}\) and \(G_{18}\) Molecular Symmetry Groups (Bunker & Jensen 1989), respectively. \(G_{36}\) contains nine irreducible representations: four nondegenerate \(A_1, A_2, A_3, \) and \(A_4,\) four doubly-degenerate \(E_1, E_2, E_3, \) and \(E_4\) and one four-fold degenerate \(G\). \(G_{18}\) contains two nondegenerate representations, \(A_1\) and \(A_2,\) and two double-degenerate ones, \(E_1, E_2, E_3, \) and \(E_4\). The correlation between \(G_{36}\) and \(G_{18}\) representations was detailed previously (Carvajal et al. 2012; Villa et al. 2013).

In our previous papers (Villa et al. 2011; Carvajal et al. 2014), the parameters of the ab initio potential energy surfaces and the ab initio kinetic parameters calculated in our previous works on DME (Villa et al. 2011) and \(^{13}\text{C}\)-DME (Carvajal et al. 2012).

Those ab initio calculations provided a reasonable description of the torsional features but failed to reproduce the bending fundamental \(\nu_7\) (421.64 cm\(^{-1}\) ab initio versus 412.35 cm\(^{-1}\), as observed by Kutzer et al. 2016). The ab initio Hamiltonian was then refined in this work following three steps: (i) the adjustment of the bending fundamental close to the experimental value, (ii) the reassignment of the two torsional fundamentals and their overtones according to the new Raman spectra, and (iii) the assignment of the other observed bands and the subsequent global fit of the Hamiltonian. The main difference between the old Hamiltonians from Villa et al. (2011) and Carvajal et al. (2012) and the present one involves the second step. These three steps are detailed next.

(i) The main weakness of the ab initio potential energy surface (Villa et al. 2011) concerns the employed definition of the COC-bending coordinate, which was set to the COC angle \(\alpha\), missing the contribution of other coordinates, such as the in-plane HCO angles. Therefore, for a more realistic description of the COC bending, a new \(\alpha'\) coordinate was introduced:

\[
\alpha' = \alpha (1 + F/100),
\]

where \(F\) is a factor that corrects the contribution of the curvilinear internal coordinate angle to the normal COC-bending coordinate. Hence, the \(B_{\alpha',\alpha}\) kinetic parameter was also corrected in all of the conformations. For DME and \(^{13}\text{C}\)-DME, \(F\) was optimized to be 1.954 (Villa et al. 2011; Carvajal et al. 2012) to reproduce the experimental bending energy term values. This represents a coordinate correction lower than 2%.

(ii) The ab initio torsional overtones of DME (Villa et al. 2011), when compared with the experimental data by Groner & Durig (1977), yielded the differences (obs-calc) \(\Delta = 395.5 - 388.61 = +6.89\) cm\(^{-1}\) for \(2\nu_{11}\) and \(\Delta = 481.2 - 487.22 = -6.02\) cm\(^{-1}\) for \(2\nu_{15}\). One torsional overtone seemed to be underestimated by the calculations whereas the other one appeared overestimated. In the subsequent adjustment (Villa et al. 2011), the potential term \(B_{\nu_{11}}\) in Equation (3), one of the main responsible for the gap between

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Table 1
Energies (in cm\(^{-1}\)) of the Lowest Torsional and Bending Levels of DME and \(^{13}\)C-DME

| (v11, v15, v7) | Symm. | \(^{12}\)CH3O\(^{12}\)CH3 | Symm. | \(^{13}\)CH3O\(^{12}\)CH3 |
|---------------|-------|-----------------|-------|-----------------|
|               | OLD\(^{a}\) | NEW\(^{a}\) |      | OLD\(^{a}\) | NEW\(^{a}\) |
| 0 0 0         | A1    | 0.000           | A1    | 0.000           |
|               | G     | 0.000           | E1    | 0.000           |
|               | E1    | 0.001           | E2    | 0.001           |
|               | E3    | 0.001           | E3    | 0.001           |
| 1 0 0         | A3    | 201.611         | A2    | 200.912         |
|               | G     | 201.602         | E1    | 200.903         |
|               | E2    | 201.593         | E2    | 200.904         |
|               | E3    | 201.593         | E3    | 200.895         |
| 0 1 0         | A2    | 241.783         | A2    | 241.607         |
|               | G     | 241.774         | E1    | 241.598         |
|               | E1    | 241.765         | E2    | 241.598         |
|               | E4    | 241.765         | E3    | 241.589         |
| 2 0 0         | A1    | 391.094         | A1    | 389.609         |
|               | G     | 391.225         | E1    | 389.732         |
|               | E1    | 391.358         | E2    | 389.734         |
|               | E3    | 391.358         | E3    | 389.859         |
| 0 0 1         | A1    | 412.086         | A1    | 409.170         |
|               | G     | 412.086         | E1    | 409.173         |
|               | E1    | 412.087         | E2    | 409.173         |
|               | E3    | 412.087         | E3    | 409.176         |
| 1 1 0         | A4    | 422.176         | A1    | 421.629         |
|               | G     | 422.393         | E1    | 421.846         |
|               | E2    | 422.609         | E2    | 421.838         |
|               | E4    | 422.609         | E3    | 422.053         |
| 0 2 0         | A1    | 480.889         | A1    | 479.987         |
|               | G     | 480.960         | E1    | 480.059         |
|               | E1    | 481.031         | E2    | 480.057         |
|               | E3    | 481.031         | E3    | 480.129         |
| 3 0 0         | A3    | 569.642         | A2    | 568.029         |
|               | G     | 567.967         | E1    | 566.480         |
|               | E2    | 566.614         | E2    | 566.406         |
|               | E3    | 566.615         | E3    | 565.145         |
| 2 1 0         | A2    | 590.656         | A2    | 589.896         |
|               | G     | 588.364         | E1    | 587.584         |
|               | E1    | 585.795         | E2    | 587.703         |
|               | E4    | 585.797         | E3    | 585.152         |
| 1 0 1         | A3    | 613.117         | A2    | 610.202         |
|               | G     | 613.206         | E1    | 610.290         |
|               | E2    | 613.294         | E2    | 610.291         |
|               | E3    | 613.294         | E3    | 610.379         |
| 0 1 1         | A2    | 636.395         | A2    | 634.044         |
|               | G     | 636.449         | E1    | 634.095         |
|               | E1    | 636.506         | E2    | 634.090         |
|               | E4    | 636.507         | E3    | 634.144         |
| 1 2 0         | A3    | 648.652         | A2    | 646.719         |
Table 1
(Continued)

| (v_{11}, v_{15}, v_{3}) | Symm. | $^{12}$CH$_3$O$^{13}$CH$_3$ | Symm. | $^{13}$CH$_2$O$^{12}$CH$_3$ |
|-------------------------|-------|-----------------------------|-------|-----------------------------|
|                         |       | OLD$^a$ | NEW$^b$ | OLD$^c$ | NEW$^b$ | OLD$^a$ | NEW$^b$ |
| G                       | 647.493 | 646.185 | E1 | 645.527 | 644.432 | |
| E2                      | 646.295 | 644.894 | E2 | 645.564 | 644.471 | |
| E3                      | 646.286 | 644.884 | E3 | 644.328 | 643.140 | |
| E4                      | 644.319 | 643.129 | E4 | 644.319 | 643.129 | |
| A1                      | 706.250 | 703.223 | A1 | 705.812 | 702.388 | |
| G                       | 708.488 | 705.787 | E1 | 707.928 | 704.883 | |
| E1                      | 727.726 | 723.674 | E2 | 708.391 | 705.332 | |
| E3                      | 726.577 | 722.224 | E3 | 726.116 | 722.212 | |
|                         |        |        | E4 | 725.509 | 720.574 | |
| A2                      | 717.917 | 718.784 | A2 | 716.038 | 718.141 | |
| G                       | 717.442 | 718.122 | E1 | 715.594 | 717.483 | |
| E1                      | 716.716 | 716.717 | E2 | 715.601 | 717.481 | |
| E4                      | 717.059 | 717.671 | E3 | 714.923 | 715.883 | |
|                         |        |        | E4 | 715.225 | 717.040 | |
| A4                      | 711.733 | 709.884 | A1 | 711.676 | 709.692 | |
| G                       | 731.779 | 728.819 | E1 | 731.382 | 728.093 | |
| E2                      | 735.657 | 733.397 | E2 | 730.719 | 727.475 | |
| E4                      | 736.031 | 733.928 | E3 | 735.199 | 732.699 | |
|                         |        |        | E4 | 735.531 | 732.219 | |
| A1                      | 785.149 | 779.346 | A1 | 783.614 | 777.555 | |
| G                       | 784.508 | 779.640 | E1 | 783.133 | 778.089 | |
| E1                      | 783.988 | 779.822 | E2 | 783.084 | 778.032 | |
| E3                      | 783.912 | 779.724 | E3 | 782.666 | 778.371 | |
|                         |        |        | E4 | 782.595 | 778.274 | |
| A1                      | 805.550 | 806.600 | A1 | 800.434 | 802.112 | |
| G                       | 805.861 | 806.826 | E1 | 800.978 | 802.594 | |
| E1                      | 806.194 | 807.097 | E2 | 800.964 | 802.564 | |
| E3                      | 806.105 | 806.966 | E3 | 801.516 | 803.083 | |
|                         |        |        | E4 | 801.443 | 802.962 | |
| A4                      | 810.976 | 810.464 | A1 | 809.108 | 808.658 | |
| G                       | 809.429 | 808.742 | E1 | 807.652 | 807.050 | |
| E2                      | 807.515 | 806.719 | E2 | 807.701 | 807.095 | |
| E4                      | 807.579 | 806.834 | E3 | 805.916 | 805.227 | |
|                         |        |        | E4 | 805.970 | 805.333 | |
| A1                      | 823.691 | 824.164 | A1 | 819.009 | 819.193 | |
| G                       | 822.370 | 822.840 | E1 | 818.451 | 818.710 | |
| E1                      | 821.995 | 822.630 | E2 | 818.364 | 818.633 | |
| E3                      | 821.689 | 822.259 | E3 | 818.138 | 818.488 | |
|                         |        |        | E4 | 817.920 | 818.254 | |
| Unlabeled energy levels |        |        |        |        |        | |
| 0 2 1$^d$               | A1     | 858.148 | 860.357 | A1 | 855.085 | 858.393 | |
| G                       | 857.950 | 860.106 | E1 | 854.896 | 858.156 | |
| E1                      | 857.832 | 859.899 | E2 | 854.913 | 858.173 | |
| E3                      | 857.778 | 859.845 | E3 | 854.795 | 857.961 | |
|                         |        |        | E4 | 854.746 | 857.914 | |

Notes.

$^a$ Calculated with the adjusted Hamiltonian of Villa et al. (2011).

$^b$ Calculated with the refined Hamiltonian of this work.

$^c$ Calculated with the adjusted Hamiltonian of Carvajal et al. (2012).

$^d$ Tentative label.
Table 2
Experimental and Calculated Wavenumbers (cm$^{-1}$) of the Raman Transitions of DME and $^{13}$C-DME

| Band # | (v$_{11}$ v$_{15}$ v$_{17}$) $\rightarrow$ (v$_{11}$ v$_{15}$ v$_{17}$)$_f$ | Symm. | $^{12}$CH$_3$O$^{13}$CH$_3$ | $^{13}$CH$_3$O$^{13}$CH$_3$ |
|--------|-------------------------------------------------|--------|--------------------------|--------------------------|
|        |                                                 |        | Calc.$^a$ Exp.$^b$ Symm. | Calc.$^a$ Exp.$^b$ Symm. |
| 1      | 0 0 0 $\rightarrow$ 1 0 0                         | A3     | 198.34 197.8 ± 0.2       | A2 197.36                |
|        |                                                  | G      | 198.33 E1                | 197.35                   |
|        |                                                  | E2     | 198.32 E2                | 197.35                   |
|        |                                                  | E3     | 198.32 E3                | 197.34                   |
|        |                                                  | E4     | 197.34                    |                          |
| 2      | 0 0 0 $\rightarrow$ 0 1 0                         | A2     | 242.60 241.4 ± 0.4       | A2 242.69 241.4 ± 0.5    |
|        |                                                  | G      | 242.59 E1                | 242.68                   |
|        |                                                  | E1     | 242.58 E2                | 242.68                   |
|        |                                                  | E4     | 242.58                    | 242.67                   |
| 3      | 0 0 0 $\rightarrow$ 2 0 0                         | A1     | 386.53 385.2 ± 0.2       | A1 384.83 385.0 ± 0.2    |
|        |                                                  | G      | 386.66 E1                | 384.95                   |
|        |                                                  | E1     | 386.79 E2                | 384.96                   |
|        |                                                  | E3     | 386.79                    | 385.08                   |
| 4      | 1 0 0 $\rightarrow$ 3 0 0                         | A3     | 365.79 362.6 ± 0.2       | A2 364.68 362.3 ± 0.2    |
|        |                                                  | G      | 364.28 E1                | 363.30                   |
|        |                                                  | E2     | 363.03 E2                | 363.24                   |
|        |                                                  | E3     | 363.03                    | 362.08                   |
| 5      | 0 0 1 $\rightarrow$ 2 0 1                         | A1     | 411.12 411.1 ± 0.2       | A1 408.76 409.3 ± 0.2    |
|        |                                                  | G      | 409.80                    | 408.28                   |
|        |                                                  | E1     | 409.59                    | 408.20                   |
|        |                                                  | E3     | 409.22                    | 408.06                   |
| 6      | 0 0 0 $\rightarrow$ 0 2 0                         | A1     | 481.94 482.0 ± 0.2       | A1 481.65 481.1 ± 0.2    |
|        |                                                  | G      | 482.02                    | 481.73                   |
|        |                                                  | E1     | 482.10                    | 481.73                   |
|        |                                                  | E3     | 482.10                    | 481.81                   |
| 7      | 1 0 0 $\rightarrow$ 1 2 0                         | A3     | 449.10 450.2 ± 0.4       | A2 448.36 449.2 ± 0.5    |
|        |                                                  | G      | 447.85                    | 447.08                   |
|        |                                                  | E2     | 446.57                    | 447.12                   |
|        |                                                  | E3     | 446.56                    | 445.80                   |
|        |                                                  | E4     |                           | 445.79                   |
| 8      | 0 1 0 $\rightarrow$ 0 3 0                         | A2     | 476.18 480.7 ± 0.2       | A2 475.46 479.0 ± 0.3    |
|        |                                                  | G      | 475.53                    | 474.81                   |
|        |                                                  | E1     | 474.13                    | 474.81                   |
|        |                                                  | E4     | 475.09                    | 473.22                   |
| 9      | 0 0 0 $\rightarrow$ 0 0 1                         | A1     | 413.04 412.5 ± 0.2       | A1 410.43 410.0 ± 0.2    |
|        |                                                  | G      | 413.04                    | 410.43                   |
|        |                                                  | E1     | 413.04                    | 410.43                   |
|        |                                                  | E3     | 413.04                    | 410.43                   |
| 10     | 1 0 0 $\rightarrow$ 1 0 1                         | A3     | 413.23 413.2 ± 0.2       | A2 410.88 410.8 ± 0.2    |
|        |                                                  | G      | 413.28                    | 410.93                   |
|        |                                                  | E2     | 413.32                    | 410.94                   |
|        |                                                  | E3     | 413.32                    | 410.99                   |
| 11     | 0 1 0 $\rightarrow$ 0 1 1                         | A2     | 395.65 395.5 ± 0.2       | A2 394.13 393.9 ± 0.2    |
|        |                                                  | G      | 395.72                    | 394.19                   |
|        |                                                  | E1     | 395.79                    | 394.19                   |
|        |                                                  | E4     | 395.79                    | 394.26                   |
| 12     | 2 0 0 $\rightarrow$ 0 0 2                         | A1     | 420.07 424.2 ± 0.2       | A1 417.28 422.0 ± 0.3    |
\( \nu_{11} \) and \( \nu_{12} \) bands, had to be forced and strongly modified to reproduce the old data.

Here, with the new Raman reassignments, the discrepancies between experimental and ab initio values decrease significantly: \( \Delta = 385.2 - 388.61 = -3.41 \text{ cm}^{-1} \) for \( 2\nu_{11} \) and \( \Delta = 482.0 - 487.22 = -5.22 \text{ cm}^{-1} \) for \( 2\nu_{15} \). Thus, both overtones appear now at higher frequencies in the calculations, and gaps between torsional levels are described correctly without any refinement of the \( B_{011} \) parameter.

(iii) To reproduce the newly assigned experimental bands, just a few parameters of the Hamiltonian need to be optimized: one kinetic parameter and two potential parameters. In Table 3, the fitted effective potential coefficients \( (A_{200}, A_{020}) \) are indicated.

The new optimized Hamiltonians are more confidently used in the assignments of other bands of the two isotopologues and in future works. For example, the IR-forbidden torsional fundamental \( \nu_{11} \) of DME, calculated ab initio at 199.16 cm\(^{-1} \), is predicted now at 198.33 cm\(^{-1} \), which is much closer to the present experimental observation at 197.8 cm\(^{-1} \) (see Figure 2).

Table 1 lists the torsional-bending energies for DME and \( ^{13}\text{C}\)-DME up to \( \sim 860 \text{ cm}^{-1} \) calculated in this work and compares with those reported previously. It should be stressed that the calculated energy levels could be labeled within a \( (\nu_{11} \nu_{15} \nu_{7}) \) scheme up to \( \sim 825 \text{ cm}^{-1} \), as listed in Table 1. For higher energies, the large torsional splittings and mixing of the wavefunctions impedes the unambiguous assignment of such a \( (\nu_{11} \nu_{15} \nu_{7}) \) label to all of the computed levels, especially for the less symmetric \( ^{13}\text{C}\)-DME. The experimental Raman transition wavenumbers of DME and \( ^{13}\text{C}\)-DME, and their assignments, are listed in Table 2 to facilitate the understanding of Figures 1 and 2, along with the calculated wavenumbers from the fitted energies of Table 1.

### 5. Concluding Remarks

The spectrum of DME and isotopologues in the THz region is rather complex due to the high density of states, the torsional splittings, the coupling of the torsional overtones with the COC-bending mode, and the presence of many hot bands. Thus, a conclusive assignment of the far-IR spectrum is greatly facilitated by measurements at different temperatures to distinguish between cold and hot bands. This is one of the main results of the present work.

New laboratory measurements of the torsional Raman spectrum of DME and \( ^{13}\text{C}\)-DME, from room temperature down to 56 K, are reported. This has allowed us to observe the torsional band \( \nu_{11} = 197.8 \text{ cm}^{-1} \), which was not reported to date and to reassign its overtone at \( 2\nu_{11} = 385.2 \) and 385.0 cm\(^{-1} \) for DME and \( ^{13}\text{C}\)-DME, respectively. In due turn, this has also allowed us to assign all of the lowest energy levels correctly (see Table 1), which are those relevant for the analysis of the astronomical observations.

The new Raman measurements have been interpreted with the help of highly correlated ab initio calculations within a 3D torsional-vibrational model. The ab initio parameters of the 3D Hamiltonian have been refined using the new experimental data. In the past, such refinement highlighted some problems derived from the lack of experimental data corresponding to the \( \nu_{11} \) torsional mode, and the large density of states in the region of the torsional overtones, where the coupling with the COC bending occur. These problems have been fixed here, reaching a better agreement with the experiment. Eventually, the quantitative interpretation of the energy level structure in molecules with such large amplitude internal motions must rely on quantum chemical calculations validated by laboratory data.

### Table 2 (Continued)

| Band # | \((\nu_{11} \nu_{15} \nu_{7}) \rightarrow (\nu_{11} \nu_{15} \nu_{7})\) | Symm. | \(^{13}\text{CH}_{3}\)O\(^{13}\text{CH}_{3}\) | Symm. | \(^{13}\text{CH}_{3}\)O\(^{13}\text{CH}_{3}\) |
|--------|---------------------------------|-------|-----------------|-------|-----------------|
|        |                                 |       | Calc.\(^{a}\)  | Exp.\(^{b}\) | Calc.\(^{c}\)  | Exp.\(^{c}\) |
| 13     | 2 0 0 → 2 0 1                    | A1    | 437.64          | 437.5 ± 0.5 | A1    | 434.36          | 434.0 ± 0.2 |
|        |                                 | G     | 436.18          | E1     | 434.64          | 434.0 ± 0.2 |
|        |                                 | E1    | 435.84          | E2     | 433.68          | 433.41 |
|        |                                 | E3    | 435.47          | E3     | 433.17 |
| 14     | 0 0 1 → 0 0 2                    | A1    | 393.56          | 396.3 ± 0.3 | A1    | 391.68          | 394.7 ± 0.2 |
|        |                                 | G     | 393.79          | E1     | 392.16 |
|        |                                 | E1    | 394.06          | E2     | 392.13 |
|        |                                 | E3    | 393.93          | E3     | 392.66 |
|        |                                 | E4    | 392.53 |
| 15     | 0 2 0 → 0 2 1\(^{c}\)           | A1    | 378.42          | 381.0 ± 0.2 | A1    | 376.74          | 379.2 ± 0.2 |
|        |                                 | G     | 378.09          | E1     | 376.42 |
|        |                                 | E1    | 377.80          | E2     | 376.44 |
|        |                                 | E3    | 377.75          | E3     | 376.15 |
|        |                                 | E4    | 376.10 |

**Notes.**

\(^{a}\) Calculated with the refined Hamiltonian of this work.

\(^{b}\) Experimental.

\(^{c}\) Tentative assignment.
DME has been observed in excited torsional states in hot astrophysical environments. The present results can help to characterize the potential energy landscape in this gas phase, and to predict other yet unobserved bands, for future astrophysical detections of other isotopologues of DME in the ISM.

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**ORCID iDs**

J. M. Fernández [https://orcid.org/0000-0002-6636-7978](https://orcid.org/0000-0002-6636-7978)
G. Tejeda [https://orcid.org/0000-0003-0810-9652](https://orcid.org/0000-0003-0810-9652)
M. Carvajal [https://orcid.org/0000-0001-8743-129X](https://orcid.org/0000-0001-8743-129X)
M. L. Senent [https://orcid.org/0000-0003-1878-7377](https://orcid.org/0000-0003-1878-7377)

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