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Investigations into the millimeter and submillimeter-wave spectrum of perdeuterated methanol, CD₃OD, in its ground and first excited torsional states

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Abstract

The rotational spectrum of CD_3OD in its ground and first excited torsional states has been recorded in three frequency windows 78–119, 705–750, and 812–903 GHz in order to improve our model Hamiltonian [L.-H. Xu, H.S.P. Müller, F.F.S. van der Tak and S. Thorwirth, J. Mol. Spectrosc. 228 (2004) 220–229] that had been developed for searching for CD_3OD in the interstellar medium. In the present study, 103 transitions for $v_t = 0$ and 82 transitions for $v_t = 1$ have been assigned, reaching J and K quantum numbers of 25 and 14, respectively. The observed and calculated transition frequencies in the ground and first excited torsional states agree on the average to within ~ 100 and 200 kHz, respectively. Thus, the majority of the transitions, particularly those in the ground torsional state, could be reproduced within or close to their experimental uncertainties of 20–100 kHz. The reproduction of the data proved to be more challenging at higher J and K, particularly in the first excited torsional state, where the data set is more sparse than at lower quantum numbers.
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1. Introduction

Methanol is an important interstellar molecule, and transitions of CH_3OH are frequently used to identify and characterize star-forming regions [1]. In cold, dark clouds, only the lowest rotational levels of CH_3OH are populated, and the abundance is fairly low [2,3]. The molecule is much more prevalent in warm and dense clouds where higher excited rotational and torsional or vibrational states are populated, giving rise to a plethora of emission features [4–7]—some of which may show maser activity [8,9].

Exchange of one or more H atoms by D leads to much lower zero-point vibrational energies in the D containing species. This causes deuterated molecules, including methanol, to be enriched considerably over the interstellar atomic D/H ratio of $\sim 1.5 \times 10^{-5}$ in fairly dense molecular clouds that are very cold (~ 10 K) or have been very cold until quite recently. Not only mono-deuterated molecules have been detected in space, but also doubly deuterated ones, such as D_2CO [10], NHD_2 [11], CHD_2OH [12], D_2S [13], HD_2^+ [14], and D_2CS [15], and even the triply deuterated molecules ND_3 [16,17] and CD_3OH [18] have been identified in low-mass star-forming regions recently. When star-formation leads to heating up of such a molecular cloud the deuterium enrichment diminishes slowly through protonation of the molecule. Deuterated methanol is especially interesting in this respect because it offers two chemically very different sites for protonation: the methyl group and the hydroxyl group. As the latter is protonated much more easily than the former, CH_3OD is much less abundant in warmer low-mass star-forming regions than CH_2DOH. In fact, the abundance of CH_3OD towards the low-mass protostar IRAS 16293-2422 is between that of CHD_2OH and that of CD_3OH [18]. Similar differences in the column densities are expected to hold for the isotopic pairs CHD_2OH/CH_2DOD and CD_3OH/CHD_2OD. Hence, these isotopic pairs could be used as chemical clocks in low-mass star-forming regions. The interstellar observation of CD_3OD—or even the determination

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of sufficiently low upper limits—will broaden the picture considerably.

Methanol is not only an important molecule for astrochemistry and astrophysics, but the large amplitude CH_3-torsional motion causes methanol to be a very fascinating and challenging molecule from the spectroscopic point of view as well because the torsion perturbs the K-level structure considerably. In the ground vibrational state, it bears resemblance to a rigid-rotor K-level structure, with deviations arising from the interaction with the torsion leading to small A/E torsional splittings. However, the A/E energies of the first excited torsional state straddle the barrier to free rotation of the CH_3 group, and large A/E torsional splitting significantly disorders the rigid-rotor K-level structure. Hence, this state is difficult to describe. For higher excited torsional states, the energy level structure approaches that of a free rotor. Since torsion–rotation interactions cause additional complications, it is perhaps not surprising that, despite considerable efforts, the quantitative description of the rotational spectrum of CH_3OH in low torsional and other small amplitude vibrational states does not yet meet the needs of the astrophysical and astrochemical community.

The spectroscopic information available for isotopic species other than CH_3OH is generally more limited, especially for CD_3OD. Several spectroscopic investigations on CD_3OD have been published [19–23], but the early data [19,21] had a limited coverage whereas Refs. [22,23] were of limited use because no or only few transition frequencies with assignments and uncertainties were made available to the open literature. Starting from the results in Refs. [19,21], the CD_3OD data set was greatly extended in our previous study on the rotational spectrum of CD_3OD in its ground and first excited torsional states [24]. That work included 379 lines up to 233 GHz with J and K quantum numbers up to 20 and 10, respectively, with the majority of the transition frequencies being published for the first time. The overall unit-less weighted standard deviation of the fit was 1.06, meaning that the data were reproduced essentially within the very small experimental uncertainties of mostly 20–30 kHz.

In spite of the considerable number of energy levels accessed in the previous study, there were still some deficiencies of concern for the quality of the predicted frequencies. For example, only a small number of K-ladders was connected by transitions with $\Delta K \neq 0$ for $v_t = 1$. Moreover, in earlier investigations of the rotation–torsional spectra of various isotopic species of methanol it was found that far-infrared torsion–rotational transitions with moderate accuracy of 6 MHz had a profound stabilizing effect on fitting the more accurate (mostly 50–100 kHz) microwave to submillimeter-wave transitions. Therefore, we decided to test and improve our model Hamiltonian by extending the data set to higher frequencies and higher values in J and K and particularly by connecting more K-ladders in $v_t = 1$.

The torsion–rotation states of methanol transform according to the representations A_1, A_2, and E of the G_6 molecular symmetry group [25]. The traditional notation (A^+, A^-, E) [26] is used in this paper for convenience and consistency with previous work. The A^+ and A^- labels can be related to A_1 and A_2 representations of G_6 [27]. All E levels have the same symmetry and often are labeled for convenience as E_1 $(K \geq 0)$ or E_2 $(K < 0)$ according to the relative orientations of the torsional and K-rotational angular momenta [27].

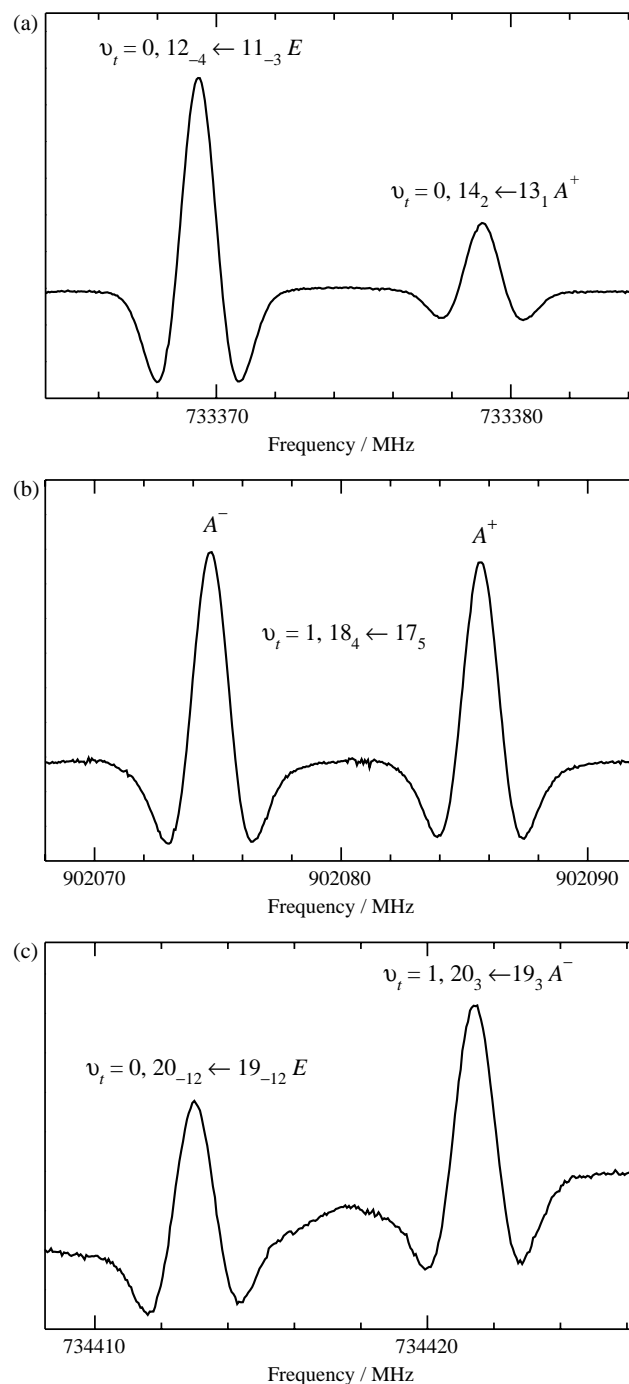Fig. 1. Section of the submillimeter wave absorption spectrum of CD_3OD, showing (a) the $v_t = 0$, $J_K = 12_{-4} \leftarrow 11_{-3}$ transition of E symmetry and the $14_2 \leftarrow 13_1$ transition of A symmetry and $+$ parity; (b) the $v_t = 1$, $J_K = 18_4 \leftarrow 17_5$ transition of A symmetry and $-$ and $+$ parity, respectively; and (c) the $J_K = 20_{-12} \leftarrow 19_{-12}$ transition of $v_t = 0$ and E symmetry as well as the $20_3 \leftarrow 19_3$ transition of $v_t = 1$, A symmetry and $-$ parity. Each line appears approximately as a second derivative of a Gaussian because of the $2f$-modulation employed to reduce noise and baseline effects.