Rotational spectrum of *trans–trans* diethyl ether in the ground and three excited vibrational states

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Abstract

We report the results of a comprehensive reinvestigation of the rotational spectrum of diethyl ether based on broadband milli-metre-wave spectra recently recorded at The Ohio State University and in Warsaw, covering the frequency region 108–366 GHz. The data set for the ground vibrational state of *trans–trans* diethyl ether has been extended to over 2000 lines and improved spec-troscopic constants have been determined. Rotational spectra in the first excited vibrational states of the three lowest vibrational modes of *trans–trans*-diethyl ether, v_{20}, v_{39}, and v_{12} have been assigned. The $v_{20} = 1$ and $v_{39} = 1$ states are near 100 cm^{-1} in vibra-tional term value and are coupled by a strong *c*-axis Coriolis interaction, which gives rise to many spectacular manifestations in the rotational spectrum. All of these effects have been successfully fitted for a dataset comprising over 3000 transitions, leading to precise determination of the energy difference between these states, $(\Delta E/hc)=10.400222(5)$ cm^{-1}. A newly developed software package for assignment and analysis of broadband spectra is described and made available.
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1. Introduction

Diethyl ether is a well-known compound, with notable uses as an early anaesthetic and a currently popular chem-ical solvent. It is also of potential interstellar relevance since the smaller member of this series, dimethyl ether, has been found to possess high abundance in hot-core type sources within dense interstellar clouds [1]. The rota-tional spectrum of diethyl ether has recently been record-ed almost continuously over the frequency range 108–366 GHz by means of the FASSST technique [2,3]. This spectrum formed the basis for a considerable improvement in the spectroscopic constants for the

ground state of *trans–trans* (*tt*) diethyl ether [4], which is the most abundant isomer of this molecule. In addition, the rotational spectrum of the less abundant *trans–gauche* (*tg*) diethyl ether was assigned for the first time [3], and the room-temperature percentage of diethyl ether in this form was determined to be 30.5(13)%. The *tg* isomer has been estimated to be about 450 cm^{-1} less stable than the *tt* form [3]. It can be expected, therefore, that rotational transitions in the lowest vibrationally excited states of *tt*-diethyl ether will give rise to stronger features in the rotational spectrum than those of the *tg* form, even when the differences in dipole moments and transition types for the two forms are accounted for. This was indeed confirmed by the presence of many strong satellite branches in the vicinity of the known Q-branch of the ground state. Nevertheless, the same survey showed that

Table 1
The low wavenumber normal modes of *tt*-diethyl ether

Normal mode	$\omega_{calc.}$ [a] (cm^{-1})	$\nu_{obs.}$ [b] (cm^{-1})	Symmetry species	Mode specification [c]
ν_{11}	927	935	B_1	CC stretch
ν_{10}	837	848	A_1	CO stretch
$\{\nu_{37}$	809	825	B_2	Methyl rocking
ν_{18}	796	811	A_2	Methylene rock
$\{\nu_{11}$	426	438	A_1	$\angle$COC bend
ν_{31}	417		B_1	$\angle$OCC bend
$\{\nu_{38}$	260		B_2	Methyl torsion
ν_{19}	254		A_2	Methyl torsion
ν_{12}	186		A_1	$\angle$COC bend
$\{\nu_{39}$	104.7		B_2	CC torsion
ν_{20}	89.9		A_2	CC torsion

[a] Evaluated from the MP2/6-31G(d,p) harmonic force field obtained with PC-GAMESS [5,6], which was scaled with a factor of 0.9 (0.95 in vibrational frequency).
[b] Ref. [7].
[c] Approximate description based on the internal coordinate which is the dominant contributor to the normal mode [7].

the positions and shapes of these Q-branches are highly irregular, so much so that even an unambiguous identification of a single band sequence was difficult.

The reason for this behaviour becomes apparent on consideration of the wavenumbers of the lowest normal modes of *tt*-diethyl ether, listed in Table 1. The molecule is of C_{2v} symmetry and mode numbering has been made in the standard way, from highest to lowest wavenumber, in the order of modes belonging to A_1, A_2, B_1, and B_2 representations, respectively. Even though the information on the six lowest-frequency modes is limited to that from ab initio calculation, the reliability of the calculation is confirmed by good agreement between the experiment and calculation for quartic centrifugal distortion constants [4], the values of which depend primarily on the several lowest frequency modes. In addition, for ν_{11} and modes higher than this in term value, the calculation is in good agreement with the experimental wavenumbers and assignment reached in [7]. Inspection of Table 1 leads to the conclusion that practically all of the vibrational satellites in the rotational spectrum might be anticipated to participate in some sort of interstate interaction. Most of the vibrational modes below 1000 cm^{-1} appear to be grouped into pairs with a rather small wavenumber separation. Also, while the third mode from the bottom, ν_{12}, is fairly isolated in wavenumber, its first excited state, $\nu_{12} = 1$, is expected to be rather close in energy to that for $\nu_{20} = 2$, $(\nu_{20} = 1, \nu_{39} = 1)$, and possibly even $\nu_{39} = 2$. It is perhaps fortunate that this picture was not completely apparent to us at the commencement of this work, since it might have not been attempted at all on the grounds of anticipated difficulties in the analysis of strongly coupled states. As a result we are able to report the analysis and spectroscopic constants for the three of the lowest excited vibrational states of *tt*-diethyl ether.

2. Experimental details

The present analysis was carried out on the basis of the same spectra that were used in the identification of *tg*-diethyl ether [3]. Those consisted of an almost continuous 108–366 GHz spectrum recorded with the FASSST spectrometer at Ohio State [2,3], and less extensive, but somewhat better resolved spectra recorded at 253–342 GHz with the PLL spectrometer in Warsaw [3,8].

Analysis of such broadband spectra poses a considerable challenge to data reduction and management. This is a relatively new phenomenon in pure rotational spectroscopy, in which instrumental constraints tended to limit the sizes of data sets. In the frequency range covered by the FASSST spectrum there are, however, several thousand lines available for even a single spectroscopic species. The actual spectrum is also a mixture of transitions from many spectroscopic species requiring efficient procedures for assigning, measurement and fitting of such data. This problem has already been addressed by some of the present authors in the form of the CAAARS package [9], where the acronym decodes as Computer Aided Assignment of Asymmetric Rotor Spectra. This package is implemented in the Igor Pro [10] software environment, which is also used in the recording and calibration of the FASSST spectrum.

The presently reported analysis of the rotational spectrum of diethyl ether was, however, performed with a new software package, written by the first-named author. This package, called Assignment and Analysis of Broadband Spectra (AABS), has been designed to provide an alternative to CAAARS. AABS is highly portable in that it does not require a proprietary software package, uses moderate computer resources, and ready to run executables are freely available from the PROSPE website [11]. This package is based on a pair of well tested programs, ASCP—a stick type previewer of spectral predictions, and SVIEW—a spectral viewing program. These programs have been in use in the Warsaw laboratory for many years [12], and new versions called ASCP_L and SVIEW_L have been developed to provide facilities for dealing with extremely broadband spectra. The programs can still work in standalone mode but, more importantly, they are now capable of linked operation. The main interface is illustrated in Fig. 1. The SVIEW_L module displays the experimental spectrum, while ASCP_L displays predictions, which can come either from the SPCAT [13,14], or the ASROT [11] program. It is possible to display predictions for many spectroscopic species simultaneously, and extensive user configurable features are available to aid in discrimination between different sets of lines of interest. Standard zooming/scrolling, as well as many other commands for easily navigating over the expanse of the spectrum are provided.

One of the more important features of the new package is the ability to highlight a sequence of predicted