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Pure Rotational Spectrum of Dibenzofuran in Range of 2–6 GHz†

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We report the observation and assignment of the rotational spectra of dibenzofuran measured in the range of 2–6 GHz with a newly constructed broadband chirped-pulse Fourier transform microwave (cp-FTMW) spectrometer. An analysis of the microwave spectra led to the assignment of 40 b-type transitions, resulting in the accurate determination of the rotational constants $A=2278.19770(38)$ MHz, $B=601.12248(10)$ MHz, and $C=475.753120(98)$ MHz.

Key words: Dibenzofuran, Polycyclic aromatic hydrocarbons, Broadband rotational spectroscopy

I. INTRODUCTION

The origin of ubiquitous unidentified infrared emission (UIR) features seen in the interstellar medium (ISM) remains a mystery. Although polycyclic aromatic hydrocarbons (PAHs) are widely believed to be the carriers for the UIR bands [1, 2], the molecular specific identification has been proven difficult using the commonly employed rotational spectroscopy in radio astronomy due to the often small or zero dipole moment that many PAHs possess. On the other hand, the search for simple aromatic molecules that are likely linked to the formation of PAHs but easier to observe, seems to be a valid approach to constrain models in interstellar chemistry. Dibenzofuran has been proposed to lead to PAH formation at temperatures above 800 °C through oxidation pathways [3]. In this context, as a simple oxygenated PAH with considerable dipole moment, it would serve as a candidate for the detection of PAHs in the ISM.

Dibenzofurans have been observed in ambient air [4] and its formation can be attributed to the same source as unsubstituted PAHs such as incomplete combustion in waste incineration [5, 6]. As an oxygenated PAH, dibenzofurans are produced through secondary oxidation of PAHs by chemical and microbiological processes [7, 8]. Higher toxicity such as mutagenicity and carcinogenicity has been shown over the parent PAHs in oxygenated PAHs [9]. Dibenzofuran in particular, undergoes oxidation reactions with OH radicals, NO3 radicals and O3 in the atmosphere [10], making the information pertaining to its gas-phase structure and spectroscopy of fundamental interest. Dibenzofuran can serve as a prototype of this class of substituted PAHs to be studied by spectroscopy as this tricyclic moiety is present in this family of compounds.

Up to date, dibenzofuran has been investigated by vibrational spectroscopy [11, 12] and rotationally-resolved electronic spectroscopy [13–15]. This work aims to extend the range of laboratory spectroscopy to support the astrophysical observation of potential precursor molecules for multi-ring PAHs through a microwave investigation of its pure rotational spectrum. We report the measurement and analysis of the observed spectra of dibenzofuran in the vibrational ground state in the range of 2–6 GHz.

II. METHODS

A. Experiments

The rotational spectra of dibenzofuran were recorded using a chirp-pulse Fourier Transform microwave (cp-FTMW) spectrometer working between 1 and 18 GHz recently developed at Nanjing University of Science and Technology (NJU) described in detail [16, 17]. In short, a chirped pulse is produced by mixing linear frequency sweeps generated by an arbitrary waveform generator (Tabor WX1281, 1.25 GS/s, 1 GHz) and the cw output of a microwave synthesizer (Anapico Apex420, 1–18 GHz). This broadband pulse is then amplified using a solid state amplifier (BONN, 5W) before being coupled to the custom-built vacuum chamber which contains a pair of high gain horn antenna for broadcasting and receiving the microwave signal. The vacuum chamber is pumped through a molecular pump with a background pressure around $1\times10^{-5}$ Pa. A gas mixture of noble gas seeded with sample molecules was allowed to enter the vacuum chamber through a pulsed solenoid valve with a diameter of 1.0 mm (Parker Se-
ab initio methods were employed to optimise the ground state (cc-pVnZ, ζ with the correlation consistent polarised valence n-tuple Parr (B3LYP) \cite{19, 20}, exchange-correlation functional turbation theory (MP2) \cite{18} while the DFT calculation carried out using the second order Møller-Plesset per-

B. Computation

Both \textit{ab initio} and density functional theory (DFT) calculations were employed to optimise the ground state structure of dibenzofuran. The \textit{ab initio} calculation was carried out using the second order Møller-Plesset perturbation theory (MP2) \cite{18} while the DFT calculation was performed using the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) \cite{19, 20}, exchange-correlation functional with the correlation consistent polarised valence n-tuple ζ (cc-pVnZ, n=D and T here) basis sets. The augmentation of such basis sets was not used as Treitel and co-workers concluded that the inclusion of diffuse functions does not improve the calculated geometrical parameters for PAH anions significantly \cite{21}. All geometric optimisations were carried out using the Gaussian 09 package \cite{22}, and the calculated rotational constants and dipole moment are shown in Table I. The Cartesian coordinates of the optimised structures calculated using each level of theory and basis set can be found in supplementary materials.

III. ASSIGNMENT AND RESULTS

A. Effective Hamiltonian

The analyses of the pure rotational spectra in the GHz and THz regions were carried out using Watson’s A-reduced effective Hamiltonian \cite{23} in the $I^r$ representation, which is shown here including up to sextic centrifugal distortion constants:

\[
\hat{H}_{\text{tot}}^{I^r} = A^r J_z^2 + B^r J_z^2 + C^r J_z^2 - \Delta_J^r J_z^4 - \Delta_K^r J_z^2 J_z^2 + \Delta_{JK}^r J_z^4 - \frac{1}{2} \left[ \left( \delta_J J_z^2 + \delta_K J_z^2 \right), \left( J_z^2 + J_z^2 \right) \right]_+ + \phi_J^r J_y J_z^4 + \phi_{JK}^r J_z^2 J_z^2 + \phi_K^r J_z^2 J_z^2 + \phi_{JK}^r J_z^4 + \frac{1}{2} \left[ \left( \eta_J^r J_z^4 + \eta_K^r J_z^4 \right), \left( J_z^2 + J_z^2 \right) \right]_+ (1)
\]

where with i=\(\sqrt{-1}\), we have the angular momentum operators:

\[
\hat{J}^2 = J_x^2 + J_y^2 + J_z^2, \quad \hat{J}_\pm = \hat{J}_x \pm i \hat{J}_y
\]

All observed transitions were fitted using the $I^r$ representation in the Pickette’s SPFIT/SPCAT spectral fitting programme\cite{24}.

![FIG. 1 An overview of the microwave spectrum of dibenzofuran between 4.5 and 5.5 GHz measured with 1,000,000 FIDs.](image1)

![FIG. 2 A zoomed-in spectrum of the microwave spectrum of dibenzofuran with three assigned transitions.](image2)
TABLE I Computational results for dibenzofuran ($\Delta^a=0$).

<table>
<thead>
<tr>
<th></th>
<th>MP2</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/MHz</td>
<td>B/MHz</td>
<td>C/MHz</td>
</tr>
<tr>
<td>cc-PVDZ</td>
<td>2246.5932</td>
<td>594.1975</td>
</tr>
<tr>
<td>cc-PVTZ</td>
<td>2283.6884</td>
<td>603.4914</td>
</tr>
</tbody>
</table>

B. Assignment of the pure rotational spectra in the ground state

Dibenzofuran is an asymmetric rotor of $C_{2v}$ symmetry. Its permanent electric dipole moment is expected to lie along the $b$-axis allowing transitions to obey $b$-type selection rules ($ee$ and $oee$, $e$ for even and $o$ for odd values of the quantum numbers $K_a$ and $K_c$) [25]. The principal axis system for dibenzofuran is given in FIG. 3.

The assignment of the observed spectra in the range of 2–6 GHz was assisted by a simulation of the spectrum using the calculated rotational constants at MP2/cc-pVZT level. A total of 40 $b$-type transitions were assigned using the PGOPHER programme [26, 27] in the range of 2–6 GHz with $J_{\text{max}}=19$ and $K_{a,\text{max}}=5$. The assigned transitions were fitted and the resulting spectroscopic parameters are given in Table II. The root-mean-square deviation $d_{\text{rms}}$ of the fit is 4 kHz, with the typical linewidths (full-width at half-maximum) of about 80 kHz. A full list of the assigned transitions is provided in supplementary materials.

IV. DISCUSSION

Pure rotational transitions were measured and assigned from 2 GHz to 6 GHz, providing the first study in the microwave range. This allowed for an accurate determination of the rotational constants. Comparing the rotational constants with values obtained from reported high resolution electronic spectroscopy studies [14, 15], the accuracy of our values is improved by at least two orders of magnitude as shown in Table II, reflecting the high resolution of Fourier transform microwave (FTMW) over techniques in the optical range. The root-mean-square deviations ($\sigma_{\text{rms}}$) of the fit of 4.6 kHz is considerably less than one-tenth of the ~80 kHz observed linewidths, suggesting the effective Hamiltonian employed here provides an accurate description of observed spectral features in this range. As a result, the spectroscopic parameters reproduce the experimental spectrum very well. In comparison, the $\sigma_{\text{rms}}$ values in Ref. [14] and Ref. [15] are a few MHz. It is worth mentioning that such an agreement was achieved by including only three rotational constants in the fit while centrifugal distortion constants were found not sensitive to the observed transitions in this study.

All calculations in this study show a planar structure for dibenzofuran with $C_{2v}$ symmetry, indicating the only non-zero dipole moment being along the $C_2$ axis which coincides with the $b$-axis through the oxygen atom as shown in FIG. 3. This is consistent with the experimental findings that only $b$-type transitions were observed. Although the experimentally obtained rotational constants alone were not enough for accurate structural determination, one can determine the inertial defect to verify the expected planar cyclic structure. Dibenzofuran with a $C_{2v}$ is expected to have a zero inertial defect as it is planar (see Table II). However, our value of the inertial defect calculated using the experimental rotational constants is $-0.285652$. As it is a slightly negative number, we can attribute it to the averaging of vibrational levels of the out-of-plane, low-lying, large amplitude motions that are often associated with PAHs. In particular, the “butterfly” motions are ubiquitous in tricyclic molecules and the fundamental of such motion in dibenzofuran is at only ~100 cm$^{-1}$ [28].

V. CONCLUSION

In the current study, we presented the first spectroscopic study of dibenzofuran in the microwave region. It has been demonstrated that cp-FTMW is capable of measuring such a non-volatile molecule in a supersonic jet. The results from this work have the potential to guide the astrophysical and atmospheric searches for this molecule via remote sensing. It has been observed that the equilibrium structure of this tricyclic...
molecule has coupled with the low-lying, out-of-plane modes and our accurately determined rotational constants can provide the basis for the rovibrational studies of such modes in the far-infrared region.

Supplementary materials: The line list of assigned transitions as well as the theoretical geometric parameters of dibenzofuran is included in the electronic supplementary data.

VI. ACKNOWLEDGMENTS

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TABLE II Spectroscopic constants for the ground state of dibenzofuran.

<table>
<thead>
<tr>
<th></th>
<th>A/MHz</th>
<th>B/MHz</th>
<th>C/MHz</th>
<th>N</th>
<th>σ/kHz</th>
<th>Δ/(amu·Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>2278.19770(38)</td>
<td>601.12248(10)</td>
<td>475.753120(98)</td>
<td>40</td>
<td>4.616</td>
<td>–0.285652</td>
</tr>
<tr>
<td>Ref.[14]</td>
<td>2278.104(23)</td>
<td>601.003(33)</td>
<td>475.675(30)</td>
<td>3138</td>
<td>14333</td>
<td>–0.288523</td>
</tr>
<tr>
<td>Ref.[15]</td>
<td>2278.2(1)</td>
<td>601.1(1)</td>
<td>475.8(1)</td>
<td>2140</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: values in parenthesis provide statistical 1σ uncertainties in units of the last specified digits.