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Microwave spectrum and gas phase structure of maleimide

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ABSTRACT

The rotational spectrum of maleimide was measured in the 5–12 GHz range using a Flygare–Balle type, pulsed-beam Fourier transform microwave spectrometer. Rotational transitions were measured for the parent, all unique singly substituted ^{13}C isotopologues, and an —ND, deuterium substituted isotopologue. The parent (or normal isotopologue) rotational constants, centrifugal distortion constants, and quadrupole coupling constants are $A = 6815.3251(12)$ MHz, $B = 2361.85011(64)$ MHz, $C = 1754.32750(64)$ MHz, $D_J = 0.232(24)$ kHz, $D_{JK} = 0.546(54)$ kHz, $1.5\chi_{aa} = 2.4227(53)$ MHz, and $0.25(\chi_{bb}-\chi_{cc}) = 1.3679(15)$ MHz. A best fit gas phase structure was determined using the experimental rotational constants of the isotopologues and some parameters from calculations. The inertial defect is $\Delta = -0.054$ amu Å^2, indicating a planar structure for maleimide, with no large amplitude motions observed on the —NH hydrogen atom. Calculations using B3LYP/aug-cc-pVTZ provided rotational constants which are much closer (within 1–2%) to the experimental values compared to the MP2/aug-cc-pVTZ calculated values.

1. Introduction

Maleimide (Mal), or 2,5-pyrroledione (IUPAC), and its derivatives are important compounds in biological chemistry, biotechnology and organic synthesis. Fluorescent Mal derivatives were used to study the *in vivo* processes of intracellular trafficking, membrane association, and auto toxicity [1,2]. These Mal compounds are also the backbone of some enzyme inhibitors [3]. In organic synthesis, Mal and its derivatives play an important role in the protection of amino groups [4]. Bismaleimide resins are important in industrial applications due to the high temperature performance, toughness, and low cost in products such as tires [2,5–7]. Polyethylene glycol (PEG)-Mal compounds are often used to attach proteins to surfaces or PEG to different amino acid residues [8,9]. Synthesis of Mal is achieved with copolymers of styrene and maleic anhydride and reacting with gaseous NH_3 at elevated temperature under vacuum conditions [10]. Mal can also be prepared from dimethyl maleate through the Rinkes method [11].

Mal has a planar structure and slight yellow crystalline appearance. The melting point is 92–95 °C [12] and the vapor pressure at 70 °C is sufficient to measure the pure rotational spectrum by pulsed-beam microwave spectroscopy. Mal has been studied by X-ray diffraction [13], electron diffraction [14], and IR spectroscopy [15]. Microwave spectroscopy is the preferred method to obtain accurate gas phase structural parameters of Mal. Other techniques, such as X-ray crystallography, can yield distorted structures caused by crystal packing effects in the solid state. This study extends the structural parameters of Mal to provide the gas phase microwave measurements and the gas phase structure.

2. Microwave measurements

The Mal sample was purchased from Sigma Aldrich (99%) and was used without further purification. All measurements were made in the 5–12 GHz range using a Flygare–Balle type pulsed-beam Fourier transform microwave spectrometer that has been described previously [15,16]. Prior to the molecular beam pulse, the pressure inside the vacuum cavity was maintained at 10^{-6} to 10^{-7} Torr. Ne was used as the carrier gas and the backing pressure was maintained at ~1 atm. In order to obtain sufficient vapor pressure of the solid Mal sample, the pulsed valve and sample cell were heated to ~70 °C, as this temperature provided a strong parent test signal that can be seen in one pulsed beam cycle.

The measured rotational transitions for the parent isotopologue are shown in Table 1. The singly substituted ^{13}C isotopologues were measured under natural abundance concentrations, using the same method as was used to measure the parent transitions. A —ND deuterium substituted isotopologue sample was prepared and its transitions were also measured. The —ND isotopologue was prepared by dissolving equimolar amounts of both Mal and D_2O and allowing them to exchange for several days. Most of the

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Table 1
Measured rotational transitions of the parent isotopologue of Mal, shown in MHz. The ν_{o-c} values are the differences between the observed and calculated values from the fit.

J′	Ka′	Kc′	F′	J″	Ka″	Kc″	F″	ν_{obs}	ν_{o-c}
1	1	0	1	1	0	1	1	5059.705	−0.002
1	1	0	1	1	0	1	2	5060.191	−0.000
1	1	0	2	1	0	1	1	5060.769	−0.001
1	1	0	1	1	0	1	0	5060.917	−0.001
1	1	0	2	1	0	1	2	5061.257	0.002
1	1	0	0	1	0	1	1	5062.367	0.003
2	1	1	2	2	0	2	2	5725.561	0.003
2	1	1	2	2	0	2	3	5726.190	0.005
2	1	1	3	2	0	2	3	5726.808	0.003
2	1	1	1	2	0	2	1	5727.498	−0.001
3	1	2	3	3	0	3	3	6827.303	0.002
3	1	2	4	3	0	3	3	6827.774	0.004
3	1	2	2	3	0	3	3	6827.938	0.002
3	1	2	3	3	0	3	4	6828.111	−0.002
3	1	2	3	3	0	3	2	6828.403	0.005
3	1	2	4	3	0	3	4	6828.586	0.003
3	1	2	2	3	0	3	2	6829.038	0.005
3	0	3	2	2	1	2	2	8214.566	0.003
3	0	3	3	2	1	2	2	8215.661	0.000
3	0	3	4	2	1	2	3	8215.991	0.005
3	0	3	2	2	1	2	1	8216.337	0.002
3	0	3	3	2	1	2	3	8216.799	−0.001
4	1	3	4	4	0	4	4	8466.040	−0.005
4	1	3	5	4	0	4	5	8467.432	−0.007
4	1	3	3	4	0	4	3	8467.795	−0.002
1	1	1	0	0	0	0	1	8568.683	−0.004
1	1	1	2	0	0	0	1	8569.553	−0.001
1	1	1	1	0	0	0	1	8570.125	−0.007
5	2	3	5	5	1	4	5	11862.727	0.002
5	2	3	6	5	1	4	6	11862.762	−0.004
4	0	4	4	3	1	3	3	12726.967	−0.002
4	0	4	5	3	1	3	4	12727.283	−0.003
4	0	4	3	3	1	3	2	12727.493	0.001
4	2	2	3	4	1	3	3	12191.258	0.004
4	2	2	5	4	1	3	5	12191.292	0.005
4	2	2	4	4	1	3	4	12191.410	−0.007

remaining water was removed under vacuum by pumping on the —ND sample for several hours at ~30 °C. All of the measured isotopologue transitions are listed in Table 2. The labeling scheme for each of the substituted atoms is shown in the best fit structure shown in Fig. 1. There was a small amount of line broadening observed for the —ND isotopologue transitions. This is most likely caused by the D quadrupole coupling, but there was no attempt to assign the D quadrupole splitting as these hyperfine splittings were not resolved.

3. Calculations

Ab initio calculations were performed to predict an optimized equilibrium structure of Mal using the Gaussian 09 suite [17], on the HPC system at the University of Arizona. We used the MP2 method with the aug-cc-pVTZ basis and also the B3LYP method with the aug-cc-pVTZ basis and these results are shown in Table 3. The predicted equilibrium rotational and quadrupole coupling constants were used in Pickett's SPCAT [18] program to predict the b-type transitions expected to be observed, as the calculated equilibrium structure had a large b-dipole moment component of 1.6 D. To predict the isotopologue rotational constants, a set of scale factors – the ratios between the experimental rotational constants of the parent and their corresponding *ab initio* values, were used to provide reasonable predictions. From the *ab initio* parent isotopologue molecular structure, the mass of the substituted atom was changed and the moments of inertia and corresponding rotational constants were recalculated using Kisiel's PMIFST [19] program. These calculated rotational constants were multiplied by the scale factors obtained from the parent to obtain corrected rotational constants for each of the singly substituted isotopologues. These scaled rotational constants were used in the SPCAT program, along with the experimentally determined quadrupole coupling constants of the parent, to predict the isotopologue rotational transitions. The experimental results agreed with those scaled values very well, within 1%.

4. Rotational constants

The rotational constants, quadrupole coupling constants and centrifugal distortion constants were all determined from the measured rotational transitions using Pickett's SPFIT program and all the fit values are shown in Table 3, along with the calculated equilibrium values. During the fits of the isotopologue rotational and quadrupole coupling constants, the centrifugal distortion constants were held fixed to what was obtained from the parent. The rotational constants obtained from the best fit gas phase structure are shown with the experimentally fit values, along with their observed−calculated differences (O−C) in Table 4. The calculated rotational constants from the best fit structure had a standard deviation of 0.285 MHz from the experimental values.

5. Molecular structure

A best fit gas phase structure was obtained for Mal using a nonlinear least squares fitting program with the measured rotational constants from each of the isotopologues. The fitting program varies the Cartesian coordinates of the atoms within the molecule and a "best fit" structure is determined. This best fit structure yields calculated moments of inertia closest to the experimentally obtained values (smallest rms error). From the *ab initio* calculations, the structure is predicted to be planar with C_{2v} symmetry. The inertial defect calculated using the experimental parent rotational constants is $\Delta = -0.0536$ amu Å^2, confirming that the actual structure of Mal is indeed planar. The slight negative value of the inertial defect is due to Mal experiencing out of plane vibrations [20]. The Kraitchman determined *c*-coordinates of H6 are small (Table 5) further supporting a planar structure of Mal, and indicating no large amplitude motions of H6.

In the structure fit, there were a total of 4 varied parameters representing small changes in the carbon atoms Cartesian coordinates in the *x*–*y* plane. With the Mal structure being planar, confirmed with the experimental value of the inertial defect, all *z*-coordinates were set to zero. We assume that the C_{2v} symmetry is maintained within the molecule and so the varied coordinates in the fit were the same for corresponding atoms on each side of the line of symmetry (through the N_5—H_6 bond), with the exception of the varied parameters in the *x*-direction which were opposite sign for each corresponding atom to account for the symmetry. The only fixed atoms in the fit were the N and H atoms forming the imide group, so the N—H bond length was fixed to the calculated equilibrium value. The H and O atoms bonded to the C atoms in the ring were varied using the same deviations of *x* and *y* as the carbons atoms they were bonded to, resulting in the C—H and C=O bond lengths also held fixed to calculated B3LYP equilibrium values. With these constraints and varied parameters, the standard deviation of this nonlinear least squares structure fit was 0.285 MHz.

A Kraitchman analysis was also performed on all isotopically substituted atoms using the Kisiel KRA [21] program. The best fit structure coordinates, as well as the Kraitchman determined coordinates for each substituted atom, is shown in Table 5. The coordinates from the best fit structure and Kraitchman analysis seem to agree very well with the exception of the *a*-coordinate of H6, shown as an imaginary value. This substituted atom lies on the