

A COMPUTER SIMULATION OF THE RING PUCKERING AND OXYGEN WAGGING DYNAMICS IN THE S_0 STATE OF CYCLOBUTANONE.

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Abstract

The satisfactory modelling of the ring puckering displacements in small ring molecules has been difficult to achieve since the equilibrium structure of the ring atoms depends on the balance between the ring strain and the torsional repulsion forces. Ring strain forces result from the compression of the C-C-C bond angles to 90 degrees to form the square ring and favour the planar conformation, whereas, the torsional repulsion forces between the C-H bonds prefer a puckered conformation. Information about the equilibrium structure and the balance between these forces comes from the sequence bands observed in the far infrared spectrum. A two dimensional study of the ring puckering and oxygen wagging vibrational modes was used to simulate the far infrared spectrum and test the balance between these forces.

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1. INTRODUCTION

In 1945, Bell pointed out that the out-of-plane displacement of the diagonal atoms of a four membered system would result in a potential function that would be described by a single quartic term.[1] This prediction was based on a model where the puckering internal coordinate was assumed to be derived from a linear combination of bending coordinates of the ring atoms. With an out-of-plane displacement of the ring atoms, the quadratic force terms describing the bending displacements cancel each other, leaving a residual force constant term that is quartic in the ring displacements. In the case of cyclobutanone, C_4H_6O , the three ring carbons of nominally sp^3 hybridization (bond angle = 109.5°) and the sp^2 carbonyl atom (bond angle = 120.0°) are compressed into a ring with angles close to 90.0° . The so-called ring strain generated by this compression stabilizes the ring into a planar conformation. The other major factor that determines the ring stability is the torsional repulsion between the four C-H bonds. In the planar conformation, these C-H bonds eclipse each other when viewed along the C-C bond direction and they create repulsions that distort the ring into a nonplanar conformation. In the prototype cyclobutanone system, CB, the torsional repulsions and the ring strain forces are closely balanced with the result that the equilibrium structure of the ring is pseudo-planar with the central barrier in the puckering potential lying well below the vibrational zero point energy.

It is possible to model the molecular potential for the puckering dynamics by a potential function containing two terms. The effect of the strain energy is represented by the quartic oscillator expression, $A(z)^4$ where z is an internal coordinate that measures the puckering displacement. The tendency towards nonplanarity can be measured by height of the central barrier that is described by a quadratic term $-B(z)^2$. While the resulting double minimum function, $V(z) = A(z)^4 - B(z)^2$ is too limited to model the dynamics at higher energies, it is useful for separating out the twin effects of ring strain and torsional repulsion.

Information about the Q_{20} ring puckering normal mode has been mainly drawn from the far-infrared region of the gas phase vibrational spectrum. Pioneering studies in this region were carried out with a grating spectrometer by Durig and Lord[2] and then in more detail by FTIR (Fourier transform infrared) interferometry

by Borgers and Strauss.[3] These latter authors were able to observe a sequence progression in the puckering mode up to 9 quanta of vibrational excitation. Of direct interest to the present study was their observation that the ($v=8$) \rightarrow ($v=7$) and ($v=9$) \rightarrow ($v=8$) sequence transitions resulted in infrared bands that were split into doublets. By an analyses of the hot band satellites in the microwave spectrum, Sharpen and Laurie[4] showed that this doublet splitting was the result of a localized perturbation. This study demonstrated that while the A, B, and C rotational constants showed a smooth increase with increasing puckering quantum number, for $v=8$ all three constants were displaced from their expected positions. This shift confirmed that the perturbation was restricted to a single $v=8$ level, at 560.45 cm^{-1} .

The other experimental data about the out-of-plane displacements comes from the hot band structure in the $S_1 \rightarrow S_0$ absorption that lies in the near ultraviolet region of the spectrum.[5-6] The intensities of the bands in an electronic system depend on Franck-Condon overlap factors that, in turn, depend on the structural differences between the states connected by the electronic transition. The major differences between the S_0 and S_1 states is an out-of-plane distortion of the C=O group in the upper S_1 electronic state. As a result, the spectrum displays long progressions in the wagging normal mode Q_{19} . At room temperature, the intervals between the hot bands at the red end of the spectrum establish the vibrational intervals in the wagging mode.

The present studies were undertaken as a prelude to an analyses of the electronic $S_1 \rightarrow S_0$ band spectrum of CB. A simulation of the vibronic fine structure in the jet-cooled ultraviolet system requires a knowledge of the puckering-wagging hypersurfaces of both the ground and excited electronic states as well as the molecular structures. This paper represents the first of a two part spectroscopic study of cyclobutanone and an extension to a recent calculation on the S_0 and S_1 states [7].

2. METHODS

The general procedure that is followed here is to use standard *ab initio* molecular orbital calculations to establish a set of potential and kinetic energy functions from which to determine an initial set of puckering - wagging vibrational energy levels. These energy levels are then fitted to the observed levels by adjusting the coefficients in the expansion that forms the potential function. This is the so-called morphing procedure whereby the *ab initio* potential surface is stretched and bent until the observed spectral features are reproduced in the calculations.

Both the ring puckering and the carbonyl wagging motions are needed for the description the low frequency modes of cyclobutanone. Energy points on a grid defined by selected values of the internal coordinates were obtained from fully optimized Hartree-Fock calculations with Møller Plesset corrections for electron correlation. These data points were fitted to the power series expansion

$$V = \sum_k^{N_V} V_k^0 \prod_j^2 f_{kj} \quad (1)$$

while the V are the coefficients in the expansion for the potential energy and are obtained from the fitting procedure while the f_{kj} represent the puckering and wagging internal coordinates. N_V is the number of terms on the series expansion. The kinetic energy contributions were generated in a somewhat similar way from the fully optimized geometry as elements of the rovibrational G matrix. The kinetic energy parameters were obtained by the inversion of the inertial matrix

$$\begin{pmatrix} I & X \\ X^t & I \end{pmatrix} \quad (2)$$

where I is the inertial tensor corresponding to the overall rotation, Y is the vibration submatrix and X is the interaction term between the external and internal motions.

$$X_i = \sum_a m_a \left(\vec{r}_a \times \frac{\partial \vec{r}_a}{\partial \alpha_i} \right)_i \quad (3)$$

$$Y_{ij} = \sum_a m_a \left(\frac{\partial \vec{r}_a}{\partial \alpha_i} \times \frac{\partial \vec{r}_a}{\partial \alpha_j} \right)_i \quad (4)$$

The mass of atom a is given by m_a and its displacement vector by \vec{r}_a . The general Hamiltonian \hat{H} was used for the treatment of the multivibrational problem,

$$\hat{H} = \sum_i^n \sum_j^n \left(-B_{ij} \frac{\partial^2}{\partial q_i \partial q_j} - \frac{\partial B_{ij}}{\partial q_i} \frac{\partial}{\partial q_j} \right) + \hat{V} \quad (5)$$

where the number of vibrations, n , is two.

The two-dimensional Hamiltonian was solved variationally for the eigenvalues and eigenvectors using harmonic oscillator basis functions for the puckering and wagging coordinates. Nonrigid group theory was used for the labelling of the energy levels, factorization of the Hamiltonian matrix and the generation of the selection rules. The existence of the single plane of symmetry allows the wavefunctions to be classified according to the switch operator, \hat{S} ,

$$\hat{S}f(z, \theta) = f(-z, -\theta) \quad (6)$$

where z and θ are the two coordinates.

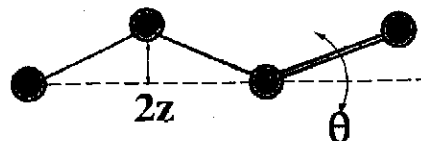


Figure 1. The ring puckering, z , and oxygen wagging, θ , coordinates in cyclobutanone.

3. CALCULATIONS

The model for the two low frequency modes, Q_{19} (wagging) and Q_{20} (puckering) was constructed from the two displacements that are illustrated in figure 1. The wagging internal coordinate is defined by the angle 2 between the C=O bond and the projection of the bisector of the carbonyl CCC angle. The ring puckering coordinate, z , is represented as the separation between the two imaginary diagonal lines that connect the opposite corners of the square ring in the out-of-plane direction. For a ring consisting of four identical atoms, this definition of z leads to a potential function that is governed by a single quartic term. The potential and kinetic energies for the joint puckering-wagging motions were evaluated as points on a grid defined by increments in the z and 2 coordinates. The data points for z ranged from $\pm 0.32\text{\AA}$ on either side of the plane, in steps of 0.08\AA , whereas the angle 2 was incremented from -10 to $+10^\circ$ in steps of 5° .

Standard *ab initio* molecular orbital calculations were performed at a number of different levels of theory using the GAUSSIAN code.[8] Beyond the molecular orbital approximation of HF (Hartree-Fock) theory, the effect of electron correlation on the barrier to molecular inversion was investigated using Møller-Plesset many body perturbation theory, (MP2, MP3, MP4). The total energy evaluated at the grid points was transformed into the analytical form of equation (1) by a least squares fitting to a power series in the two coordinates. As the potential function for ring puckering contains a central barrier at $2=0^\circ$, it was necessary to employ a flexible function that consisted of quadratic, quartic and hexic terms, z^2 , z^4 and z^6 . At the other end of CB, the CCC=O group is planar and the potential for the C=O wagging is nearly quadratic in form. It is represented by the harmonic term 2^2 with a small anharmonic correction, 2^4 . The coupling between these two internal coordinates that leads to the Q_{19} and Q_{20} normal coordinates was taken into account by the cross terms, $z2$, z^22 and $z2^3$. The expansion coefficients associated with these terms for two separate calculations, MP2/6-31G(d,p) and MP4/6-31G(2d,p) are collected together in Table 1. A plot of the two dimensional potential $V(z,2)$ is given in fig. 2. The kinetic energy contributions were found to be relatively insensitive to displacements along the puckering and wagging coordinates. Reduced masses were determined for the optimized equilibrium geometry as elements of the inverse G matrix,[9], eqn. (2). The B_{zz} and B_{22} constants for the puckering and wagging internal coordinates and the B_{z2} interaction term are also given in Table 1. The Schrödinger equation corresponding to the Hamiltonian operator, eqn. (5), was solved variationally.[10] The symmetry properties imposed by the $\sqrt{\quad}$ operator were

taken into account by combining the harmonic oscillator basis functions into even and odd products.[11] It was found that 30 functions for both puckering and wagging were sufficient to reproduce the energy levels below 800 cm^{-1} . The results for the two *ab initio* calculations are given in Table 2.

4. RESULTS AND DISCUSSION

Table 1. The Calculated and Fitted Potential Energy Expansion Coefficients for the Ring-Puckering and Oxygen-Wagging Coordinates in Cyclobutanone, (z in Angstroms, 2 in radians and energy in cm^{-1}).

term	two-dimensions morphed	two-dimensions MP4/6-31G(2d,p)	two-dimensions MP2/6-31G(d,p)	puckering-only MP2/6-31G(d,p)
z^2	-640.459	-3019.23	-4752.02	-4394.605
z^4	58337.5	82231.5	88698.8	77562.78
z^6	-77033	-77033.6	-86115.8	
2^2	9923.69	10385.6	11534	
2^4	5181.97	-895.38	181.418	
$z2$	6354.81	-5593.06	-7492.83	
z^32	-32244.9	-16154.2	-11816.1	
$z2^3$	2354.81	-183.16	-2512.86	
cons.	0.1602	0.1602	1.3141	-1.232
B_{zz}	1.03	0.776	0.776	0.429
B_{z2}	1.354	1.278	1.278	
B_{22}	2.897	4.707	4.707	

The results of the two calculations are different and before any comparisons can be made, it is necessary to make a correlation with the experimental data. The most useful level data is found in the gas phase infrared spectra. In the $30-100\text{ cm}^{-1}$ far infrared region of CB, the series of bands observed by Borgers and Strauss displayed a regular vibrational anharmonicity.[3] From the low frequencies it is clear that these bands can be attributed to the c-type central Q branches of a sequence series in the ring puckering mode. In terms of the ring puckering quantum number, v_z , the transitions to the hot bands have the designations: $(v_z)7(v_z-1)$. The sum of

the energies, cm^{-1} , of the band centres gives the ring puckering energy levels. These energy levels are given in Table 2. At the positions expected for the transitions terminating at $v_z=8$ and 9, the overall contours of the bands change abruptly and the bands split into doublets. Moreover, a microwave study by Scharpen and Laurie[4] of the hot satellite rotational lines shows a clear anomaly in the variation of the A, B and C rotational parameters at this level of vibrational excitation. Both Borgers and Strauss and Scharpen and Laurie suggest that a vibrational perturbation is operative at this energy. In their view, the pure puckering level $v_z=8$ interacts with the combination level $(v_z=3) + (v_2=1)$. In terms of the joint two dimensional description for the two quantum numbers (v_z, v_2) , the perturbation for the first band would be described by $(8,0) : (3,1)$ interaction.

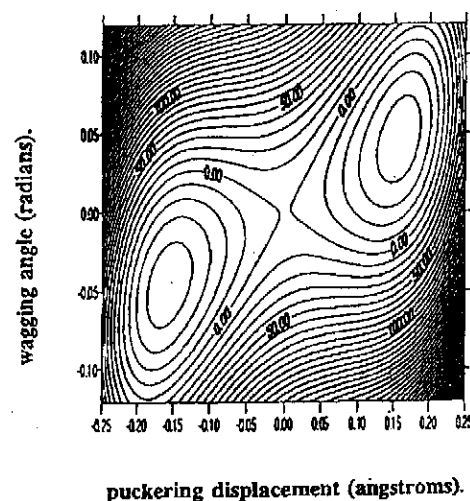


Figure 2. A plot of the two dimensional potential surface $V(z,2)$ for the ring puckering, z , and oxygen wagging, 2 , coordinates. Contour lines spaced at 10 cm^{-1} intervals.

Table 2. The Observed and Calculated Puckering + Wagging Vibrational Energy Levels in Cyclobutanone. Parameters from Table 1. (in cm^{-1})

v_z	v_2	sym.	obs.	fitted morphed	2 - D MP4	2 - D MP2	1 - D MP2
0	0	aN	0	0	0	0	0
1	0	aO	35.85	36.09	31.37	13.36	20.76
2	0	aN	92.25	92.39	107.92	97.94	93.06
3	0	aO	156.85	156.85	191.88	168.23	168.06
4	0	aN	228.65	228.26	288.47	259.33	258.25
5	0	aO	305.65	305.13	393.62	359.18	358.25
6	0	aN	386.75	386.59	443.66	468.41	467.63
0	1	aO	394.2	394.12	409.01	428.81	
1	1	aN		435.94	507.63	444.59	
7	0	aO	471.55	472.07	521.56	583.32	584.5
2	1	aO		495.13	627.24	527.75	
8	0	aN	560.45	561.03	608.82	705.53	708.33
3	1	aN	561.65	562.73	753.36	603.11	
9	0	aO	653.75	653.78	708.82	833.73	838.51
4	1	aO		636.33	853.41	697.28	
0	2	aN	791.4	791.3	813.27	800.92	

The other necessary piece of information, the energy for the $v_z=1$ first quantum of Q_{19} wagging, comes from the hot band intervals in the UV spectrum. The $n \rightarrow \pi^*$ electronic excitation in CB that leads to the first excited electronic state is accompanied by a planar to pyramidal structural distortion. Thus, on Franck-Condon grounds those modes that are most closely associated with the structural changes between the S_0 and S_1 electronic states will be those most active in the spectrum. In this case, it is the Q_{19} out-of-plane wagging mode that is expected to form the dominant progressions in the spectrum. The progression that originates from the first excited wagging level in the S_0 state has been measured to be 394.2 cm^{-1} . This information is collected together in Table 2 and is illustrated in fig. 3.

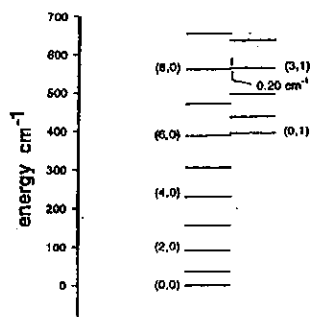


Figure 3. The ring puckering and oxygen wagging energy levels in the S_0 state of cyclobutanone.

The starting point for the fitting procedure was the potential surface derived from the MP4/6-31G(2d,p) energy points and the kinetic energy constants of Table 1. In the initial morphing of potential surface, only the levels up to the onset of the wagging fundamental at 394.2 cm^{-1} were considered. A fit of the first six levels in the puckering mode, (0,0) to (5,0), created a set of expansion parameters that were used as a starting point for an extrapolation to the higher (6,0) and (7,0) levels. At this point the wagging level (0,1) was introduced to complete the morphing of the uncoupled levels. For the final fitting, the levels directly involved in the perturbation, (8,0) : (3,1) were then added. The results of the fitting are given in Table 2 where excellent agreement is achieved. The conclusion that may be drawn from the nine parameter model potential is that the existing literature assignments are essentially correct and that the anomalies in the band positions at high quanta of ring puckering mode are indeed the result of a wagging - puckering vibrational perturbation.

A comparison between the MP4/6-31G(2d,p) and MP2/6-31(d,p) calculations (columns 6 and 7 of Table 2) that were used as a starting point for the refinement of the level positions reveals a number of trends. As the puckering

motion in CB is directed out of the molecular plane, it may be regarded as an inversion-interconversion of two equivalent nonplanar equilibrium conformations. The first two levels, $v_z(\text{aN})=0$ and $v_z(\text{aO})=1$ then form the 0+ and 0- components of the inversion manifold, (in the notation of the high barrier approximation). The first quantum of puckering, $v_z = 1$, observed at 35.85 cm^{-1} correlates to the inversion doubling splitting. The MP4 calculations place this value at 31.37 cm^{-1} in good agreement with the observed splitting, whereas the calculated separation for the MP2 calculation at 13.36 cm^{-1} is unreasonably small. As the inversion splitting is dependent on the curvature at the bottom of the potential well, it follows that the barrier heights for the MP2 case are simply too high. At higher energies the positions of the puckering levels are determined by the widths and the steepness of the potential well. In all cases, the calculated levels are greater than the observed levels and consequently the potential wells obtained from the *ab initio* procedure are too steep and too narrow. Along the wagging direction, the calculated value for the MP4 case at 409.01 cm^{-1} is in excellent agreement with the observed 394.2 cm^{-1} value.

Table 3. The One-Dimensional Ring Puckering Function for Cyclobutanone. Quartic and Quadratic Coefficients, Barrier Heights and Equilibrium Displacements, in cm^{-1} and \AA .

no.	level of calculation	A	B	V_{max}	Z_{min}
I	MP2/6-31G(d,p)	69752.2	4889.26	83.02	0.186
II	MP2/6-311++G(3df,2dp)	69516.1	5787.85	130.22	0.204
III	QCISD(T)/6-31G(d,p)	64269.4	2850.86	31.59	0.148
IV	QCISD(T)/6-311++G(3df,2dp) ^a	64033.3	3749.45	54.88	0.171
V	adiabatic correction	892.3	178.11	0.00	0.000
VI	effective vibrationally adiabatic	64292.6	2857.09	31.73	0.149
VII	experimental	24095.4	538.64	3.01	0.105

a) interpolated

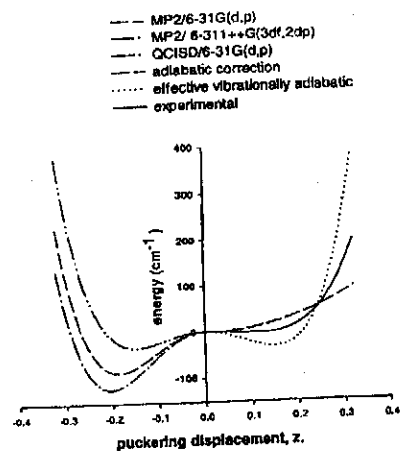


Figure 4. Calculated one-dimensional ring puckering potential functions with varying orbital basis sets and corrections for electron correlation. Only one half of each curve is illustrated.

5. IMPROVEMENTS TO THE POTENTIAL ENERGY

As the final part of this study we looked at the effects of improvements in the *ab initio* calculations on the ability of the one-dimensional ring puckering function to reproduce the observed far-infrared spectrum. Our intention here is not to make a systematic investigation of the effects of the corrections for electron correlation or the improvements that can be gained at the Hartree-Fock level by expanding the number of basis functions. Rather we will follow a procedure that has been successfully applied by Schaefer and coworkers to calculate the shapes of the potential functions for a group of nonrigid molecules.[12] In essence, these workers showed that the improvements in the *ab initio* methods on the heights of the barriers associated with inversion, torsion and puckering were additive. That is, they demonstrated that a calculation performed with a modest basis set and high levels of correction for electron correlation could be combined with a similar calculation with a highly extended basis set and low levels of electron correlation to yield a

potential function that contained both sets of improvements. Following their procedure, we generated a reference potential from optimized structures at the level MP2/6-31(d,p) and then converted the energy points into the two-parameter puckering potential function, $V(z) = Az^4 - Bz^2$. This function was found to have a central barrier of 83.02 cm^{-1} with minima at $z_{\text{min}} = \pm 0.186 \text{ \AA}$. A plot of this function is shown in fig. 4. The first correction, (electron correlation) was made at QCISD(T) and the 6-31G(d,p) reference, and reduced the barrier to 31.59 cm^{-1} . A plot of this QCISD(T)/6-31G(d,p) function is also shown in fig. 4. The final calculation at MP2/6-311++G(3df,2dp) had the reverse effect on the barrier and increased the height to 130.22 cm^{-1} . These three sets of calculations were combined to form an extrapolated QCISD(T)/6-311G(3df,2dp) potential. With a barrier of 54.88 cm^{-1} and out-of-plane displacement of $z_{\text{min}} = \pm 0.171 \text{ \AA}$ this "best" function is in disappointing agreement as the observed barrier is 3.01 cm^{-1} . It should be recognized that the potential is determined not only by electron and nuclear repulsion energies but by the zero-point vibration energies, (ZPVE), of the remaining other 3N-7 vibrational modes. Their inclusion gives rise to an effective potential for the puckering mode with its own minima, z_{eff} and barrier height, V_{eff} . The corrections for ZPVE given in Table 3 and illustrated in fig. 4 are lacking a central barrier and consequently have the effect of depressing the barrier relative to the sides of the potential well. When all of the corrections are combined together the calculated effective, vibrationally adiabatic, potential has a barrier height of 31.73 cm^{-1} . Our final calculation may be regarded as disappointing as the barrier is still an order of magnitude greater than the 3.01 cm^{-1} observed value. From this somewhat limited analysis it is clear that even greater computational power will be required to produce a potential function that begins to approach the accuracy of the far-infrared data. Undoubtedly, the most successful improvements would be expected to come from the incorporation of quadratic and quintic zeta extensions to the basis functions.

6. CONCLUSIONS

The dynamics of the ring puckering mode result from a balance between the ring strain forces that generate the quartic potential and strive to maintain the ring atoms in a planar conformation. Opposing the influences of the ring strain are the torsional repulsions between the bonds of the CH groups. When sighted along the carbon-carbon bonds, the CH groups totally eclipse each other and the torsional repulsion is maximized when the ring adopts the planar conformation. To reduce these repulsions it is necessary to stagger the dihedral angles between the CH groups by

bending the two halves of the ring through an out-of-plane distortion. If the torsional forces prevail over the ring strain forces, the equilibrium structure will be nonplanar and the corresponding potential function will contain a central maximum. The height of this barrier can then be related to the influence of the torsional repulsion forces. In the case of CB, the barrier height, at 3.01 cm^{-1} , is well below the vibrational zero point level and the ring structure is said to be pseudoplanar. The difficulty in modelling the bottom part of the puckering potential is thus a result of the near balance between the ring strain and the torsional repulsion forces.

It seems that the Møller - Plesset corrections for the effects of electron correlation are able to account for the through space influences of the CH repulsions and thereby increase the height of the barrier to puckering. Increases in the number of basis functions are able to account for the changes in hybridization that result from the creation of the four membered ring and thus influence the ring strain energy. Thus, when both the electron correlation and the basis length corrections are improved to the same degree, the two influences tend to balance each other and only subtle differences occur in the shape of the potential function.

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