Calculating relative intensities for CH stretching polyads of CHI$_3$ with ab initio dipole moment surface

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Abstract

Relative intensities of the Fermi resonance polyads involving CH stretching and bending vibrations for the CHI$_3$ molecule are calculated with one- and two-dimensional dipole moment surfaces. These are obtained by the ab initio density functional method. The two-dimensional dipole moment surface reproduces the relative intra-polyad intensities quite well, indicating the importance of the bending vibrations in dipole moment surface and intensities calculations. The relative inter-polyad intensities are also predicted. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Earlier work has established the importance of Fermi resonances in the appearance of spectra arising from the bending and stretching modes of the CH chromophore in CHX$_3$ molecules [1–18]. Iodoform, CHI$_3$, is one of these species and shows the same spectroscopic and dynamic features. Actually, it has been found that the energy pattern of the CH stretching polyads can be well understood by applying reduced three-dimensional effective vibrational Hamiltonian models, which contain strong Fermi resonance interactions between the CH stretching and CH bending vibrations [18]. However, the calculations of the intensities are less successful, especially in the relative lower energy region. The intra-polyad relative intensities calculations, which were based on the ‘bond dipole model’, agree poorly with the observation in the first Fermi resonance polyad. In the bond dipole model, it is assumed that the C–H stretching carries all strength of the transition and that the stretching–bending combination transitions will borrow some intensity from the pure stretching overtones through resonances. The intra-polyad relative intensities are largely determined by the pure stretching character of the true eigenfunction of each band. This is correct in the region of high excitation energy, but in low energy region, this is not necessarily true. Clearly, we should go beyond the bond dipole model. In two earlier studies, dipole moment surfaces from ab initio calculations have yielded very good results for CHD$_3$ and CHF$_3$ by Quack et al. [13,15]. More recently, the intensities for CHCl$_3$ and CHBr$_3$ species were successfully reproduced by our group.
by using ab initio dipole moment surfaces \[19–21\]. Therefore, it is desirable to investigate the intensities for CHI\(_3\) by using ab initio dipole moment surface.

In the present work, we report on the ab initio dipole moment surface of the isolated C–H chromophore in CHI\(_3\) calculated by the density functional theory (DFT) method. The relative intra-polyad intensities are then calculated and compared with experimental data. The relative inter-polyad intensities are also predicted.

2. Dipole moment surface

The dipole moment surface was obtained in a similar way as that in the study of CHCl\(_3\) \[19\] and CHBr\(_3\) \[21\]. The ab initio calculations which were based on the DFT involved two steps: (1) geometry optimization and (2) single point calculations which give the data points on the dipole moment surface. In both steps, the Becke’s Three Parameter Hybrid Method with Perdew and Wang’s gradient-corrected correlation functional (B3PW91) \[22,23\] method. For the C and H atoms, the 6-311++G(3df,2pd) basis set \[24\] was used, while the LanL2DZ basis set \[25\] was used for the I atom. The calculations were done using the GAUSSIAN94 package \[26\].

The optimized geometry results are:

\[
\begin{align*}
R_{\text{CH}} & = 1.0800 \, \text{Å}, & R_{\text{Cl}} & = 2.1556 \, \text{Å}, & \phi_{\text{IIC}} & = 112.8808 \, \text{deg}, \\
\phi_{\text{IICBR}} & = 105.7926 \, \text{deg}. 
\end{align*}
\]

Comparison of our results with the experimental data: \(R_{\text{CH}} = 1.09 \) Å, \(R_{\text{Cl}} = 2.12 \) Å, \(\phi_{\text{IIC}} = 113.01 \) deg \[27\], shows a reasonable agreement. When evaluating the dipole moment, only the CH bond was stretched or bent while the remaining Cl frame was kept to its equilibrium configuration. Both the one-dimensional and two-dimensional dipole moment surfaces were calculated. In the former, the CH bending is neglected while it has been taken into consideration in the latter.

For the one-dimensional dipole moment surface calculation, 23 data points were obtained by scanning the CH bond length displacement \(r = R - R_0\) in a small step (0.05 Å) ranging from \(-0.50\) to 0.60 Å, where \(R\) denotes the instantaneous bond length and \(R_0\) denotes the equilibrium bond length. We found that the dipole moment surface possesses a strong nonlinearity similar to that in CHCl\(_3\) and CHBr\(_3\). We found that the Mecke type function \[28–30\] cannot fit the data points well. On the other hand, it has been demonstrated that the asymptotic behavior for \(R \rightarrow \infty\) is not important for our intensity calculation \[19,20,31\]. Therefore, a polynomial function up to the fifth order was employed:

\[
M(r) = \sum_{i=0}^{5} \mu_i r^i. \tag{1}
\]

A very good fit has been achieved for these data points (see Fig. 1). The fitted parameters are listed in Table 1.

When calculating the two-dimensional dipole moment surface, the grids were arranged by scanning the bond length displacement \(r\) in steps of 0.10 Å ranging from \(-0.40\) to 0.40 Å, and two H–C–I angle displacements \(\Delta\phi_i = \phi_i - \phi_{i0}\) taking the \(-16, -8, -4, -2, 0, 2, 4, 8, \) and 16 deg, where \(\phi_i\) and \(\phi_{i0}\) \((i = 1 \text{ and } 2)\) denote the instantaneous and equilibrium \(i\)th H–C–I angle. The third H–C–I angle \(\phi_3\) was calculated from \(\phi_1\) and \(\phi_2\) by geometrical considerations, i.e., the orientation of the CH bond is uniquely determined by the \(\phi_1\) and \(\phi_2\) angles. Such an arrangement puts more emphasis

Fig. 1. The one-dimensional dipole moment surface of CHI\(_3\). The surface has a strong nonlinearity in the vicinity of the equilibrium configurations. The polynomial function used in the fitting displays an excellent agreement with the ab initio data points near the equilibrium configurations.
on the configuration near the equilibrium geometry. We should point out that our scanning steps are larger than those typically applied in a force field calculation. However, we found that the steps of scanning used in present study are sufficient to produce good results. In total 405 data points were calculated. Then, the data were transformed into internal coordinate grids by

\[ h_1^\text{1D} = \frac{1}{\sqrt{6}}, \]

\[ h_2^\text{1D} = \frac{1}{\sqrt{2}}. \]

The dipole moment vector \( \mathbf{M} \) has three components \( M_x, M_y, \) and \( M_z \), the \( z \) axis being parallel to the \( C_3 \) axis of the CI_3 frame. The Eckart reference frame is not taken into account [32]. However, due to the very heavy CI_3 frame, the introduced error is believed to be negligible. In the present study, we shall focus on the analysis of the parallel bands. Thus, only \( M_z \) is taken into consideration.

The following function was employed to fit the two-dimensional dipole moment surface \( M_z = M_z(r, \theta_1, \theta_2) = M_z(r, \theta) \), where \( \theta = \sqrt{\theta_1^2 + \theta_2^2} \):

\[
M_z = \mu_{00} + \mu_{10}r + \mu_{02} \theta^2 + \mu_{20}r^2 + \mu_{12}r \theta^2 + \mu_{30}r^3 + \mu_{22}r^2 \theta^2 + \mu_{04} \theta^4.
\]

The fitting results are also listed in Table 1 (see also Fig. 2). It is found that eight terms are sufficient to yield a good fit, and higher order terms such as the \( r^4 \) term cannot be fitted well.

### Table 1

Dipole moment surface by fitting to the ab initio data points

<table>
<thead>
<tr>
<th></th>
<th>One-dimensional</th>
<th>Two-dimensional</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{00} ) (D)</td>
<td>0.577330 (78)</td>
<td>0.57511 (93)</td>
</tr>
<tr>
<td>( \mu_{10} ) (DA)</td>
<td>0.45680 (52)</td>
<td>0.4593 (46)</td>
</tr>
<tr>
<td>( \mu_{02} ) (D( \theta^2 ))</td>
<td>0.0</td>
<td>-0.1351 (89)</td>
</tr>
<tr>
<td>( \mu_{20} ) (DA( \theta^2 ))</td>
<td>-0.9997 (17)</td>
<td>-1.0076 (95)</td>
</tr>
<tr>
<td>( \mu_{12} ) (DA( \theta^2 ))</td>
<td>0.0</td>
<td>-0.236 (13)</td>
</tr>
<tr>
<td>( \mu_{04} ) (DA( \theta^2 ))</td>
<td>0.0</td>
<td>-0.343 (14)</td>
</tr>
<tr>
<td>( \mu_{22} ) (DA( \theta^2 ))</td>
<td>-0.9875 (63)</td>
<td>-0.799 (35)</td>
</tr>
<tr>
<td>( \mu_{40} ) (DA( \theta^2 ))</td>
<td>0.0796 (67)</td>
<td>0.0</td>
</tr>
<tr>
<td>( \mu_{50} ) (DA( \theta^2 ))</td>
<td>0.570 (18)</td>
<td>0.0</td>
</tr>
<tr>
<td>rms (D)</td>
<td>1.9 \times 10^{-4}</td>
<td>7.8 \times 10^{-5}</td>
</tr>
</tbody>
</table>

*The uncertainties given in the parentheses are one S.E. in the least significant digit. See text for details.*
As detailed in [19], the intensities can be obtained with different models:

- **Single Morse (SM) model.** A simple Morse function is used to model the CH stretching vibration motion, the bending mode being neglected. Both the ground and excited states are assumed to be pure stretching states and only the one-dimensional dipole moment is used in this model.

  - **1D model.** A Morse function is used to model the CH stretching vibration motion. The harmonic oscillator basis functions are chosen to be consistent with the harmonic force constant for the bending modes. The ground state is the state \( |v_s = 0, v_b = 0 \rangle \) and the excited state is the state \( |v_s = n_s, v_b = n_b \rangle \) with \( n_s + n_b/2 = N \). The one-dimensional dipole moment surface is used in this model.

  - **2D model.** This is analogous to the ‘1D’ model, but the two-dimensional dipole moment surface is used.

In both the 1D and 2D models, a reduced curvilinear internal coordinate Hamiltonian proposed in [16] was applied in our calculations. Any further details can be found in the quoted literature, and here we just give a brief description.

The Hamiltonian takes the form:

\[
H = T + V, \tag{5}
\]

\[
T = \frac{1}{2}(g_{rr}p_r^2 + g_{\theta\theta}p_\theta^2) + \frac{1}{2}a^{-1}g_{rr}p_r^2 + \frac{1}{2}a^{-1}g_{\theta\theta}p_\theta^2 + \frac{1}{2}g_{r\theta}(\theta_1 p_{\theta 1} + \theta_2 p_{\theta 2}) + (p_{\theta 1} \theta_1 + p_{\theta 2} \theta_2)
+ \frac{1}{24}(g_4 + 2g_3)(p_r \theta_r p_r + p_\theta^2 p_\theta - p_r \theta_r p_r)
+ \frac{1}{2}(a^{-2}g_3 + a^{-1}g_1)y^2 p_\delta^2,
\]

\[
V = D_{y^2} + \frac{1}{2}f_{\theta \theta}y^2 + \frac{1}{2}f_{\theta \theta}y^2 + \frac{1}{2}a^{-1}f_{\theta \theta}y^2 + \frac{1}{2}(a^{-2}f_{\theta \theta} + a^{-1}f_{\theta \theta})y^2. \tag{6}
\]

Here, \( y = 1 - \exp(-ar) \) is the Morse variable, where \( a \) is the Morse parameter. The curvilinear internal CH stretching displacement coordinate is denoted \( r \), as mentioned above, and \( \theta_1 \) and \( \theta_2 \) are the symmetrized CH bending coordinates defined in Eq. (2). The momentum conjugate to \( r \) is denoted \( p_r \), while \( p_{\theta 1} \) and \( p_{\theta 2} \) are momenta conjugate to \( \theta_1 \) and \( \theta_2 \), and \( \theta^2 = \theta_1^2 + \theta_2^2 \), \( p_r^2 = p_{\theta 1}^2 + p_{\theta 2}^2 \), \( \theta_{\pm} = \theta_1 \pm \theta_2 \), \( p_{\delta} = p_{\theta 1} \pm p_{\theta 2} \). The kinetic energy coefficients are \( g_{rr}, g_{\theta \theta} \), and \( g_i \) \((i = 1, 2, \ldots, 7)\), and the potential energy parameters are \( D_y, f_{\theta \theta}, f_{\theta \theta}, f_{\theta \theta} \) and \( f_{\theta \theta} \). Definitions of these kinetic coefficients and potential energy parameters have been given explicitly in [16] and will not be repeated here. Other higher order terms have been neglected due to their small contributions. The matrix elements for the two-dimensional harmonic oscillator and the Morse oscillator can be found in [16] and references therein. For the intensity calculation, we also need the matrix elements for the operator \( r^n \) \((n = 1, 2, \ldots, 5)\). The matrix element in the Morse oscillator basis for \( r \) is calculated using the analytical expressions given in [29]. The analytical expressions of matrix ele-
ments for \( r^n (n \geq 2) \) are however more complicated and we found that by using the completeness relation the matrix elements for \( r^n (n \geq 2) \) can be calculated accurately from the matrix elements of \( r \) calculated analytically. This method is adopted since it is simple, accurate and inexpensive as the number of bound states is limited (only 25 for CHI3). One can also use Gauss–Laguerre quadrature to calculate \( r^n \) matrix element with good accuracy [11].

Briefly, the eigenvalues of the Hamiltonian are calculated variationally with a Morse oscillator basis set for the stretch, and two-dimensional harmonic oscillator basis set for the bend. The Morse functions are chosen to be consistent with the Morse parameters \( a \) and \( D_e \), and the harmonic oscillator basis functions are chosen to be consistent with the force constant \( f_{hh} \). The matrix elements are calculated analytically except for \( r^n (n \geq 2) \). The basis set sizes used in our calculations are such that \( n_s = 12 \) and \( n_b = 24 \). Three kinds of kinetic and potential parameters are used in our calculations. They are all listed in Table 2 for convenience. The first set of parameters denoted as \( (A) \) are taken directly from [18]. The potential parameters of the second \( (B) \) and third \( (C) \) sets are optimized in this work by fitting to the observed band origins from [18]. In the former, the kinetic \( g_4, g_5, g_6, \) and \( g_7 \) terms and the potential \( f_{0000} \) term are not included. But they are taken into account in the latter. Therefore, force field \( (C) \) is the most complete and also best among the three since it incorporates all the kinetic terms up to quartic for the 3D CH motion and the quartic bending potential term. Total 12 band origins equally weighted are used as input. The optimized parameters are listed in Table 2. The root mean square deviation (RMSD) values are 1.15 and 0.23 cm\(^{-1}\) for the second and third sets, respectively. Then the optimized potential parameters are used for intensity calculations. Because only the parallel bands are concerned, the transitions with \( l = 0 \) were exclusively calculated. Here, \( l \) is the vibrational angular momentum quantum number with \( l = -n_b, -n_b + 2, \ldots, n_b \). Both intra-polyad and inter-polyad intensities have been evaluated. The intra-polyad intensities calculated by the 1D and 2D models are given in Table 3. The inter-polyad intensities calculated by the ‘Single Morse’, 1D and ‘2D’ models are listed in Table 4.

4. Discussion

The calculations are compared with the observations. Unfortunately, there are no experimental observations concerning inter-polyad intensities. Only the experimental data for intra-polyad relative intensities are available in the literature [18]. Therefore, only a comparison of the intra-polyad relative intensities is possible. It should be pointed out that the definition of integrated ‘strength’ \( (G) \) rather than that of ‘intensity’ \( (I) \) was used in the experimental reports:

### Table 3

<table>
<thead>
<tr>
<th>( N )</th>
<th>( j )</th>
<th>Obs. (cm(^{-1}))</th>
<th>( G_{\text{obs}} )</th>
<th>( I_{\text{obs}} )</th>
<th>( I_{1D} ) (A)</th>
<th>( I_{2D} ) (A)</th>
<th>( I_{1D} ) (B)</th>
<th>( I_{2D} ) (B)</th>
<th>( I_{1D} ) (C)</th>
<th>( I_{2D} ) (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2117.18</td>
<td>0.21</td>
<td>0.156</td>
<td>0.016</td>
<td>0.126</td>
<td>0.022</td>
<td>0.140</td>
<td>0.004</td>
<td>0.087</td>
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<tr>
<td>2</td>
<td>1</td>
<td>3031.76</td>
<td>0.79</td>
<td>0.844</td>
<td>0.964</td>
<td>0.874</td>
<td>0.978</td>
<td>0.860</td>
<td>0.996</td>
<td>0.913</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
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<td>0.035</td>
<td>0.035</td>
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<td>3</td>
<td>3</td>
<td>5937.25</td>
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<td>0.965</td>
<td>0.964</td>
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<td>0.956</td>
<td>0.987</td>
<td>0.982</td>
</tr>
<tr>
<td>3</td>
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<td>0.02</td>
<td>0.018</td>
<td>0.046</td>
<td>0.002</td>
<td>0.049</td>
<td>0.003</td>
<td>0.030</td>
<td>0.001</td>
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<tr>
<td>4</td>
<td>4</td>
<td>8718.5</td>
<td>0.98</td>
<td>0.982</td>
<td>0.952</td>
<td>0.996</td>
<td>0.950</td>
<td>0.997</td>
<td>0.969</td>
<td>0.993</td>
</tr>
</tbody>
</table>

\(^{a}\) Experimental data taken from [18]. The definitions of \( G \) and \( I \) are given in Eqs. (8) and (9), respectively. See text for details.

\(^{b}\) 1D and 2D denote the 1D and 2D models, respectively. \( A, B \) and \( C \) refers to different sets of force field parameters from Table 2 used. \( E - n \) denotes \( 10^{-n} \).
In order to make a comparison, the relative intra-polyad intensities are calculated by taking advantage of Eq. (9). They are also listed in Table 3.

The intra-polyad intensities calculated by the 1D model agrees only poorly with the observation in the first polyad. The calculations yield the ratios \( I(1)/I(2) = 0.984/0.016, 0.978/0.022, 0.996/0.004 \) by using force field parameters of \( (A), (B) \) and \( (C) \) sets, respectively, while the observation is \( I(1)/I(2) = 0.844/0.156 \). These discrepancies are due to the intensity contribution from the bending modes [6,19], which is not considered in the 1D model. Owing to a growing tendency of wavefunction mixture as the \( N \) increases, the 1D model shows a monotonous decrease of the intensities of the band at the highest wavenumber within each polyad. The value decreases monotonously from 0.984 to 0.952, from 0.978 to 0.950, from 0.996 to 0.969 for force field \( (A), (B) \) and \( (C) \), respectively. The 2D model yields however much better agreement. Especially the calculated ratios of \( I(1)/I(2) = 0.874/0.126, 0.860/0.140 \) and \( 0.913/0.087 \) for force fields \( (A), (B) \) and \( (C) \), respectively, are all much closer to the observed \( N = 1 \) value now. This confirms the importance of the transition dipole moments of the bending motions in reproducing the intensities in the low energy region [19]. Moreover, in contrast to the monotonous decrease of the 1D model, the 2D model would predict that the intensities of the highest band within each polyad increase from \( N = 1 \) to 3. The value increases from 0.874 to 0.996, from 0.860 to 0.997, and 0.913 to 0.993 for force field \( (A), (B) \) and \( (C) \), respectively. Such a calculation agrees very well with the observations, where the value increases from 0.844 to 0.982. This agreement confirms the validity of the reduced three-dimensional Fermi resonance effective vibrational Hamiltonian models for this molecule [18].

It should be pointed out that the result of force field \( (C) \) seems to be worse than that of force field \( (A) \) and \( (B) \), although it includes more kinetic and potential terms. The reason may be due to the uncertain values of the geometry, whose effect on the energy levels is exaggerated through high order kinetic terms.

The inter-polyad intensities calculated by using different models and force field are close to each other, especially in the low energy region. Only the prediction for \( N = 6 \) from the 1D model with force field \( (C) \) is noticeably smaller than that from others calculations. The reason is still unknown.

In addition, we also calculated the dipole moment surfaces by using the LanL2DZ basis sets for all the C, H and I atoms. The result is however far from satisfactory and therefore not given. This implies a critical importance of using large basis sets for the CH chromophore. The CX3 frame is however less crucial. The conclusion can be useful for further study of chromophore in larger molecules and more complex systems.

In summary, we have investigated the relative intensities of the Fermi resonance polyads invol-

### Table 4

<table>
<thead>
<tr>
<th>( N )</th>
<th>( I_{SM} )</th>
<th>( I_{1D} (A) )</th>
<th>( I_{2D} (A) )</th>
<th>( I_{1D} (B) )</th>
<th>( I_{2D} (B) )</th>
<th>( I_{1D} (C) )</th>
<th>( I_{2D} (C) )</th>
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<td>1.00</td>
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<tr>
<td>2</td>
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<td>0.34</td>
<td>0.31</td>
<td>0.34</td>
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<td>0.32</td>
</tr>
<tr>
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<td>0.011</td>
<td>0.011</td>
<td>0.010</td>
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</tr>
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<td>0.31E-4</td>
<td>0.12E-04</td>
<td>0.31E-4</td>
<td>0.88E-5</td>
<td>0.30E-4</td>
</tr>
<tr>
<td>6</td>
<td>0.11E-5</td>
<td>0.10E-5</td>
<td>0.24E-5</td>
<td>0.98E-06</td>
<td>0.24E-5</td>
<td>0.30E-6</td>
<td>0.22E-5</td>
</tr>
</tbody>
</table>

\( ^a \)SM, 1D and 2D denote the Single Morse, 1D and 2D models, respectively. \( A, B \) and \( C \) refer to different sets of force field parameters from Table 2 used. \( E - n \) denotes \( 10^{-n} \).
ing CH stretching and bending vibrations for the CH$_3$ molecule by using one- and two-dimensional ab initio dipole moment surfaces. The two-dimensional dipole moment surface reproduces the relative intra-polyad intensities quite well, indicating the importance of the bending vibrations in dipole moment surface and intensities calculations.

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