Vibron band structure in chlorinated benzene crystals: Lattice dynamics calculations and Raman spectra of 1,2,4,5-tetrachlorobenzene

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From a combined theoretical and experimental study of 1,2,4,5-tetrachlorobenzene (TCB) we conclude that this crystal shows many interesting effects. In agreement with earlier optical measurements, which probe the complete vibron band structure of TCB, we calculate that several of the vibron modes have the dispersion of a one-dimensional crystal with stacks of molecules along the \( \mathbf{k} = 0 \) axis. The inclusion of fractional atomic charges in the atom-atom potential used in the calculations is absolutely necessary to obtain the correct vibron bandwidths. Also the sign of the vibrational coupling matrix elements, which is given correctly by the calculations, is determined by these charges. For other properties, such as the crystal stability, the phonon frequencies, the site splitting in the vibron bands, and also the dispersion of the lower frequency vibrations, the interactions between the “one-dimensional” stacks are essential, however. The calculations predict further, in qualitative agreement with the Raman spectra, that the splitting between the pairs of inequivalent vibron bands in \( \alpha \)-TCB (the site splitting) is significantly larger than the factor group splitting in \( \beta \)-TCB. Finally we have found that, for those vibrations where the conditions are shown by the calculations to be favorable, the \( ^{35}\text{Cl}/^{37}\text{Cl} \) isotope effects are clearly visible in the Raman spectra.

I. INTRODUCTION

In a recent paper\(^1\) an optical technique has been described to measure the frequencies of vibrational excitons in the molecular crystal of 1,2,4,5-tetrachlorobenzene (TCB). In contrast with the usual infrared and Raman spectroscopy, this technique yields not only the frequencies of vibrions with wave vector \( \mathbf{k} = 0 \), but it gives information on the complete vibron band structure. In the experiment the crystal is optically excited to the lowest electronic triplet exciton state and the phosphorescence spectrum to the vibrationally excited states at the top of the band\(^2\), information about the vibron band structure can be directly obtained.

The interesting result obtained from these measurements is that the vibron bands can be interpreted by a simple one-dimensional band model, analogous to that for the electronic triplet excitation. In other words, it could be concluded that the couplings between the vibrational excitations are significant only within the stacks of TCB molecules that lie along the crystallographic \( \alpha \) axis. This conclusion applies to the three different (gerade) vibrational modes that have been studied in detail, but it is striking that the actual size of the coupling parameters that determine the bandwidths is very different for the various modes and also that their signs are different.

In the present paper we describe lattice dynamics calculations on TCB which have been undertaken in order to understand the origin of the observed phenomena. In particular, it is interesting to investigate the one-dimensional character of the vibron bands and the relationship between their dispersion and the intermolecular interactions. Further, since TCB crystallizes in two different phases, it might be possible to reveal the effect of the crystal structure on the vibronic dispersion. These phases are the triclinic \( \alpha \) phase, with two molecules in the unit cell that are not related by any space group operation,\(^3,4\) and the monoclinic \( \beta \) phase with two molecules in the unit cell that are related by a glide plane.\(^5\) The \( \alpha \) phase is stable below 188 K, the \( \beta \) phase above this temperature.

Lattice dynamics calculations on chlorinated benzene crystals have been reported earlier.\(^6-10\) Especially Bonadeo
et al. have investigated the structure and stability of the \( \alpha \) and \( \beta \) phases of TCB and the lattice modes (phonons). The internal vibrations were not considered because it was expected that the vibron band structure in chlorinated benzenes would be completely obscured by the broadening effects due to the occurrence of various \( ^{35}\text{Cl} \) and \( ^{37}\text{Cl} \) isotope combinations. In the present paper we have explicitly calculated the chlorine isotope effects and we find that, rather than obscuring the vibron band structure, they yield interesting phenomena for some of the vibrational modes in TCB.

In addition, we have measured Raman spectra for both phases of TCB. By comparing the phonon frequencies for these phases with those previously reported,\(^7\) the Raman spectra ascertained that the experiments described in Ref. 1 were indeed performed on \( \alpha \)-TCB. The Raman measurements on the internal vibrations, yielding vibron frequencies for \( k = 0 \), can be compared with the results of the lattice dynamics calculations on \( \alpha \)- and \( \beta \)-TCB.

II. LATTICE DYNAMICS METHOD

A. Theory

The lattice dynamics calculations which yield the vibron and phonon frequencies have been made by the standard harmonic method, as extended by Taddei and Califano et al.,\(^1^1,1^2\) in order to include vibrons and their coupling with the phonons. This extended method can be written very compactly as follows. The harmonic crystal Hamiltonian

\[
H = \frac{1}{2} \sum_p P_p^2 + \frac{1}{2} \sum_{pp'} Q_{pp'}^2,
\]

with the generalized inertia tensor \( G_p \) and force constant matrix \( F_{pp'} \) (defined below) is expanded in the normal coordinates \( Q_p = \{Q_{\lambda p}\}_{\lambda = 1}^{3N} \) of the free molecules and their conjugate momenta \( F_p \). The column vectors \( Q_p \) are defined as

\[
Q_p = \begin{pmatrix} u_{\lambda p}^p & \text{for } \lambda = 1,2,3 & \theta_{\lambda p}^p & \text{for } \lambda = 4,5,6 & \phi_{\lambda p}^p & \text{for } \lambda = 7,\ldots,3N \end{pmatrix},
\]

where \( N \) is the number of atoms in each molecule \( P \). The “external” molecular coordinates \( u_{\lambda p}^p \) and \( \theta_{\lambda p}^p \) describe the center of mass translations and the rigid body rotations of the molecules, respectively, relative to the lattice-fixed frame. The “internal” molecular coordinates \( \phi_{\lambda p}^p \) are the normal coordinates of the free molecule vibrations. The latter can be calculated by means of Wilson’s FG-matrix method\(^1^3\) if the intramolecular force field is known. Thus they are obtained with respect to a molecule-fixed frame of reference, but they can be easily rotated to the lattice frame.

Each of the (orthogonal) normal coordinates \( \{Q_{\lambda p}\}_{\lambda = 1}^{3N} \) is a function of the Cartesian displacements \( x_p = \{x_{\lambda p}\}_{\lambda = 1}^{3N} \) of the individual atoms. Conversely, the atomic displacements can be expressed in terms of the molecular normal coordinates as follows:

\[
x_p = A_p Q_p + \frac{1}{2} B_p [Q_p \otimes Q_p] + \ldots
\]

The blocks of the linear transformation matrices \( A_p \), associated with the molecular translations \( u_{\lambda p}^p \) and rigid body rotations \( \theta_{\lambda p}^p \), follow directly from the Eckart conditions.\(^1^3\) The blocks associated with the vibrational normal coordinates \( \phi_{\lambda p}^p \) are the (rotated) FG-matrix eigenvectors of the free molecules. The nonlinear terms in Eq. (3), which are required in order to ensure the correct invariance conditions (see below), with the cross product denoting the dyadic product of the two column vectors \( Q_p \), arise from the use of curvilinear rotational coordinates \( q_{\lambda p}^p \). The coefficients \( B_p \) of the rotational–rotational blocks have been given by Neto et al.,\(^1^4\) Further nonzero coefficients \( B_p \) occur for the mixed rotational–vibrational blocks; these can be derived similarly.

The general force constant matrix \( F_{pp'} \) is given by

\[
F_{pp'} = A_p^T \Phi_p^{(2)} A_p + \delta_{pp'} \Phi_p^{(1)} B_p + \delta_{pp'} \omega_p^2,
\]

where \( \Phi_p^{(1)} \) and \( \Phi_p^{(2)} \) are matrices comprising the first and second derivatives of the intermolecular crystal potential with respect to the Cartesian atomic displacements in the molecules \( P \) and \( P' \), and \( \omega_p^2 \) is a diagonal matrix containing the squares of the vibrational frequencies of the free molecules, i.e., the FG-matrix eigenvalues. If the intermolecular potential is approximated by a sum of analytical atom–atom potentials, of exp-6-1 type for instance, then the derivatives \( \Phi_p^{(1)} \) and \( \Phi_p^{(2)} \) can be easily found, using the formulas given in Ref. 11.

In the original paper by Taddei et al.,\(^1^1\) the rotational coordinates \( q_{\lambda p}^p \) have been linearized or, in other words, the matrices \( B_p \) occurring in Eq. (3) and in the self term \( F_{pp'} \) of Eq. (4) have been set to zero. In that case, the crystal Hamiltonian is not invariant under overall rotations of the crystal, however. Later it has been shown\(^1^5\) that the inclusion of the second term of Eq. (4) in the self term \( F_{pp'} \) leads to the correct rotational invariance conditions\(^1^2\) (if one starts from a crystal with the molecules adopting their equilibrium positions and orientations). The translational invariance conditions are satisfied in any case.

The generalized inertia tensor \( G_p^{-1} \) can be written as

\[
G_p^{-1} = A_p^T g_p^{-1} A_p
\]

with the mass tensor \( g_p^{-1} \) associated with the Cartesian atomic coordinates \( x_p \), containing the atomic masses on the diagonal. Fourier transformation of the crystal Hamiltonian (1) and diagonalization of each block corresponding with a given wave vector \( k \) yields the lattice vibrations which, in general, can be (mixed) translational phonons, librational phonons, and vibrons.

B. Test calculations on benzene

The computer program in which we have implemented this method has been tested via calculations on solid benzene, using the same intra- and intermolecular potential as Taddei et al.\(^1^1\) and Neto et al.\(^1^4\). Both ways of writing the self term \( F_{pp'} \) in Eq. (4) have been investigated. The linearized transformation between the atomic and the molecular displacements, i.e., setting \( B_p = 0 \), gave results which are practically identical to those of Taddei et al.\(^1^1\) Inclusion of the full self term from Eq. (4), which we have derived by using the rotational invariance conditions,\(^1^2\) gave results identical to those of Neto et al.\(^1^4\). The translational phonon modes do not depend on the way of writing the rotational and rotational–vibrational self terms; the effect on the vibron fre-
III. INTRA- AND INTERMOLECULAR POTENTIAL AND THE MOLECULAR VIBRATIONS OF TCB: ISOTOPE EFFECTS

The intramolecular potential which we have used to calculate the vibrations of the free TCB molecule is Scherer’s force field for chlorinated benzenes.\(^1\)\(^6\)\(^7\) This harmonic force field contains the force constants with respect to the internal coordinates: stretch, bending, torsion, and out-of-plane wagging, and it includes also mixed terms. Using the well-known formulas\(^13\) for the transformation from such internal coordinates to the Cartesian atomic displacements, we have written the FG-matrix problem in terms of the latter coordinates. Solution of this problem yields 6 zero eigenvalues which correspond with the 3 center-of-mass translations \(u^a\) and the 3 rotations \(\theta^a\), and 30 eigenvalues and eigenvectors which represent the vibrational normal modes \(q^a\) of the free TCB molecule, cf. Eq. (2). The vibrational eigenvectors have been directly used as input for the lattice dynamics calculations, cf. Sec. II; instead of the eigenvalues we have substituted the squares of the experimental frequencies\(^16\)\(^7\) into Eq. (4), however. The experimental frequencies are close to the values calculated from Scherer’s force field but, according to the reasoning of Taddei et al.,\(^11\) they probably yield slightly better results.

We have explicitly studied the effect of isotopic substitution on our calculated vibrational frequencies by considering the seven possible distributions of \(^35\)Cl and \(^37\)Cl isotopes over the TCB molecule. For each of the seven different molecular species, with different atomic mass distributions, we have calculated the vibrational frequencies using Scherer’s force field. If we weight each species with a factor that can be derived from the natural isotope abundance, \(^35\)Cl/\(^37\)Cl = 0.7553/0.2447, we obtain the root mean square amplitude of the vibrational frequency distribution, relative to the (isotopically weighted) average frequency. The size of the isotope effect so defined, for each particular mode in TCB, is indicated in Table I. The average frequency for a given mode is almost the same as the frequency calculated for that mode with all chlorine atoms given their average nuclear mass, 35.453 amu. If we use the nuclear mass of \(^35\)Cl for all chlorine atoms in TCB our calculated vibrational frequencies are practically the same as Scherer’s.\(^1\)\(^6\)\(^7\) How these isotope splittings of the vibrational frequencies can manifest themselves in the solid will be discussed in Sec. IV.

Intermolecular potentials for chlorinated benzenes are available from Bonadeo et al.\(^6\) and from Reynolds et al.\(^10\) Both these potentials are based on the empirical atom-atom exp-6 interaction model. Reynolds et al. have supplemented their potential by Coulomb interactions, by introducing polarized C–Cl bonds with negative charges of \(-0.25e\) on the Cl atoms. In our lattice dynamics studies of TCB we have used both these intermolecular potentials; the relevant parameters are given in Table II. The use of polarized bonds appeared to be essential (see Sec. IV); we have also introduced polarized C–H bonds with a positive charge of +0.10e or 0.15e on the H atoms.

IV. LATTICE DYNAMICS CALCULATIONS ON \(\alpha\) AND \(\beta\)-TCB

A. Crystal structure and phonons

From x-ray diffraction\(^1\) it is known that the crystal structure of \(\alpha\)-TCB is triclinic with two molecules in the unit
The crystal structure of \( \beta \)-TCB is completely known from x-ray diffraction and nuclear quadrupole resonance (although the matrix of direction cosines given in Ref. 5 contains a mistake). This phase is monoclinic, space group \( P2_1/c \), with two molecules in the unit cell. These molecules are located at inversion centers and their orientations are related by reflection with respect to the \( ac \) plane. In our calculations on \( \beta \)-TCB we have always used the experimental angles to better than a few degrees because of the differences in the molecular geometries. We have also tried to relax the unit cell parameters in our structure optimization. Using the experimental triclinic unit cell as a starting point, we have solved this problem by using spectroscopic evidence, in combination with packing and lattice dynamics calculations based on the available empirical atom–atom potentials. We have started our calculations by repeating the structure optimization of Bonadeo et al., using the same empirical atom–atom potentials. However, we have chosen a more regular molecular geometry than these authors, who used the strongly distorted nonplanar geometry derived from the x-ray data on \( \alpha \)-TCB. Our choice is justified by the observation that the older x-ray measurements on dichlorobenzene seem to imply a strongly distorted geometry as well, whereas the more recent x-ray data lead to a much more regular geometry. The structure and cohesion energy that we calculate agree fairly well with the results in Ref. 4, but we could not compare the molecular orientation angles to better than a few degrees because of the differences in the molecular geometries. We have also tried to relax the unit cell parameters in our structure optimization. Using the experimental triclinic unit cell as a starting point, we obtained a monoclinic lattice, however, with the two molecules in the unit cell being symmetry related as in \( \beta \)-TCB. So we conclude that the empirical atom–atom potentials are not sufficiently accurate to reproduce the experimental structure of \( \alpha \)-TCB in a full structure optimization. In our further calculations on \( \alpha \)-TCB we have fixed the unit cell parameters at the experimental values determined at \( T = 150 \) K (see Table III) and we have optimized the orientations of both molecules in the unit cell independently (see Table IV), for each potential used, before we started the lattice dynamics calculations.

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TABLE IV. Calculated fractional atomic coordinates given by Bonadeo et al. (Ref. 4) for the optimum crystal structure of \( \alpha \)-TCB and x-ray data for \( \beta \)-TCB (Ref. 5), compared with our results using Bonadeo's atom-atom potential parameter set. In our calculations we used as bond lengths \( \text{C-H} = 1.08 \, \text{Å}, \text{C-C} = 1.39 \, \text{Å}, \text{C-Cl} = 1.74 \, \text{Å} \); bond angles \( \angle \text{C-C-C} = \angle \text{C-C-H} = \angle \text{C-C-Cl} = 120^\circ \), and masses \( m_\text{H} = 1.008 \, \text{amu}, m_\text{C} = 12.011 \, \text{amu}, \) and \( m_\text{Cl} = 35.453 \, \text{amu} \).

Calculations using Reynolds' parameter set with or without fractional atomic charges yield about the same crystal structure.

\[
\begin{array}{cccc|cccc}
\text{\( \alpha \)-TCB} & \text{Bonadeo et al. (Ref. 4)} & \text{This work} \\
\hline
\text{Molecule 1} & x & y & z & x & y & z \\
C(1) & 0.0201 & 0.1267 & 0.0425 & 0.0255 & 0.1272 & 0.0469 \\
C(2) & 0.1761 & 0.0322 & 0.1407 & 0.1548 & 0.0379 & 0.1423 \\
C(3) & 0.1710 & -0.0906 & 0.0882 & 0.1293 & -0.0893 & 0.0954 \\
Cl(1) & 0.0011 & 0.2848 & 0.0993 & 0.0575 & 0.2864 & 0.1055 \\
Cl(2) & 0.4070 & 0.0763 & 0.3187 & 0.3485 & 0.0854 & 0.3203 \\
H(3) & 0.2976 & -0.1571 & 0.1606 & 0.2997 & -0.1587 & 0.1695 \\
\text{Molecule 2} & & & & & & \\
C(1) & 0.0450 & 0.6240 & 0.4593 & 0.0385 & 0.6246 & 0.4606 \\
C(2) & -0.1824 & 0.5242 & 0.3661 & -0.1651 & 0.5249 & 0.3612 \\
C(3) & -0.1497 & 0.4042 & 0.4175 & -0.1566 & 0.4003 & 0.4006 \\
Cl(1) & -0.0637 & 0.7792 & 0.4030 & -0.0191 & 0.7807 & 0.4112 \\
Cl(2) & -0.4212 & 0.5580 & 0.1972 & -0.3718 & 0.5562 & 0.1874 \\
H(3) & -0.2614 & 0.3336 & 0.3492 & -0.2783 & 0.3228 & 0.3234 \\
\end{array}
\]

\[
\begin{array}{cccc|cccc}
\text{\( \beta \)-TCB} & \text{Experiment (Ref. 5)} & \text{This work} \\
\hline
\text{Molecule 1} & x & y & z & x & y & z \\
C(1) & 0.0193 & 0.1252 & 0.0425 & 0.0315 & 0.1254 & 0.0417 \\
C(2) & 0.1817 & 0.0322 & 0.1362 & 0.1714 & 0.0312 & 0.1378 \\
C(3) & 0.1623 & -0.0929 & 0.0937 & 0.1399 & -0.0941 & 0.0961 \\
Cl(1) & 0.0434 & 0.2818 & 0.0957 & 0.0708 & 0.2823 & 0.0939 \\
Cl(2) & 0.4090 & 0.0727 & 0.3067 & 0.3859 & 0.0703 & 0.3104 \\
H(3) & 0.2885 & -0.1650 & 0.1666 & 0.2486 & -0.1672 & 0.1709 \\
\end{array}
\]

Structure at \( T = 300 \, \text{K} \) (given in Table III) as a starting point, but we have optimized the molecular orientations (see Table IV), while maintaining the reflection symmetry.

Phonon frequencies of \( \alpha \)-TCB calculated with the atom-atom potentials of Bonadeo et al.\(^6\) and Reynolds et al.,\(^10\) with and without addition of fractional atomic charges (see Table II), are listed in Table V. In the lattice sums for each of the two primitive molecules we have included all molecules lying within a center-of-mass distance of 12 Å, which is amply sufficient to converge the results. The results deviate substantially from those of Bonadeo et al.\(^4,\,8\) even though we used the same atom-atom potential, because of the differences in the molecular geometries used. We have checked that changes in the molecular orientation angles of

TABLE V. Observed and calculated frequencies in cm\(^{-1}\) of the lattice vibrations in \( \alpha \)-TCB. Our values are obtained from complete calculations including the vibrons; values from rigid body calculations are given in parentheses. The cohesion energy for the optimum crystal packing is also given.

<table>
<thead>
<tr>
<th>Experiment (Ref. 7)</th>
<th>Bonadeo et al. (Ref. 4)</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bonadeo pot.</td>
<td>Reynolds pot.</td>
</tr>
<tr>
<td>(( w ) \ldots)</td>
<td>47</td>
<td>46 (48)</td>
</tr>
<tr>
<td>(( w ) \ldots)</td>
<td>63</td>
<td>76 (89)</td>
</tr>
<tr>
<td>(( w ) \ldots)</td>
<td>90</td>
<td>90 (99)</td>
</tr>
<tr>
<td>(( g ) 33)</td>
<td>33</td>
<td>21 (23)</td>
</tr>
<tr>
<td>(( g ) 43)</td>
<td>38</td>
<td>44 (45)</td>
</tr>
<tr>
<td>(( g ) 48)</td>
<td>46</td>
<td>50 (52)</td>
</tr>
<tr>
<td>(( g ) 55)</td>
<td>62</td>
<td>66 (68)</td>
</tr>
<tr>
<td>(( g ) 68)</td>
<td>68</td>
<td>70 (72)</td>
</tr>
<tr>
<td>(( g ) \ldots)</td>
<td>88</td>
<td>95 (102)</td>
</tr>
</tbody>
</table>

Cohesion energy in kcal mol\(^{-1}\)

\(-18.82\) \(-17.67\) \(-22.05\) \(-19.81\)
the size that corresponds with the differences in the molecular geometries alter the phonon frequencies by substantial amounts. The differences between the results obtained from the different atom–atom potentials are not very large; the addition of the Coulomb interactions by putting fractional charges on the atoms does not have a very significant effect on the phonon frequencies. Moreover, part of these differences are caused by the changes in the equilibrium orientations of the molecules that result from the optimization procedures with the different potentials. The agreement with experimental data is reasonably good. We have not tried to minimize the remaining deviations, as it is sometimes done, by adjusting the parameters in the atom–atom potentials.

In order to verify whether \( \alpha \)-TCB is really an effective one-dimensional crystal as the experimental data\(^1\) suggest, we have also made lattice dynamics calculations on a single stack of TCB molecules lying along the crystallographic \( \mathbf{a} \) axis. If we use the molecular orientations found in the optimization of the three-dimensional crystal structure, some phonon frequencies become imaginary, however, which indicates the instability of this one-dimensional crystal. On the other hand, if we relax the molecular orientations in the one-dimensional stack, the optimized structure becomes very different from the actual structure of the stacks in \( \alpha \)- and \( \beta \)-TCB. Moreover, we have found that the phonon frequencies show considerable dispersion in the directions orthogonal to the stacks. So we conclude that both for the crystal packing and for the lattice modes (and, as we shall see below, also for the dispersion of the lower frequency vibrons and for the splitting of all \( k = 0 \) vibrons) the interactions between the stacks in TCB are essential.

### B. Vibron frequencies for \( k = 0 \)

Before we discuss the complete dispersion in the vibron bands, we consider the splitting in the \( k = 0 \) vibron frequencies, since this splitting can be directly obtained from the Raman spectra given in Sec. V and it also plays a role in the interpretation of the experimental data of paper 1. The splittings obtained from the lattice dynamics calculations are listed in Table VI and they can be understood as follows. Both in \( \alpha \)- and \( \beta \)-TCB there are two molecules in the unit cell and the molecular centers of inversion coincide with the inversion centers of the whole crystal. So we can expect\(^4\) that all (gerade) Raman active vibrational modes of the free TCB molecule will remain Raman active in the crystal, and that all (ungerade) infrared active modes of the molecule will also be infrared active in the solid. For \( k = 0 \) each of these

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**TABLE VI.** Calculated splittings for \( k = 0 \) vibron frequencies and vibron bandwidths in the \( \mathbf{a}^* \) directions for \( \alpha \)- and \( \beta \)-TCB in cm\(^{-1} \).

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( \alpha )-TCB</th>
<th>( \beta )-TCB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reynolds pot.</td>
<td>Reynolds pot. with charges</td>
</tr>
<tr>
<td></td>
<td>Splitting</td>
<td>Dispersion(^a)</td>
</tr>
<tr>
<td>( 190 \ (A_2)^b )</td>
<td>6.5</td>
<td>-2.3/</td>
</tr>
<tr>
<td>( 209 \ (B_3)^b )</td>
<td>4.7</td>
<td>-12.8/</td>
</tr>
<tr>
<td>( 218 \ (B_2)^b )</td>
<td>6.7</td>
<td>7.4/</td>
</tr>
<tr>
<td>( 225 \ (B_3)^b )</td>
<td>12.1</td>
<td>-3.5/</td>
</tr>
<tr>
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<tr>
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<td>-9.1/</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>( 3094 \ (B_3)^b )</td>
<td>10.0</td>
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</tr>
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</table>

\(^a\)The two columns refer to the widths of the two bands.

\(^b\)Bandwidths in the \( \mathbf{b}^* \) and \( \mathbf{e}^* \) directions of the Brillouin zone are smaller than 0.5 cm\(^{-1} \), except for these modes.
modes will split into two peaks with frequencies that are different (in principle). In β-TCB the two molecules in the unit cell are equivalent and the splitting of the k = 0 vibron frequencies is caused only by off-diagonal terms F_{pp} in the dynamic matrix of Eq. (4). In the α-TCB the two primitive molecules are not related by symmetry, however, so that also the single-molecule or crystal-field terms F_{pp} may be different. So in α-TCB the splitting of the k = 0 vibrons is caused both by the off-diagonal terms F_{pp} and by the differences in the crystal-field terms F_{pp} for the two inequivalent molecules. In Table VI we observe that, indeed, the frequency splittings between most of the k = 0 vibrons in α-TCB are considerably larger than the splittings in β-TCB. The differences in the crystal-field terms appear to be dominant in determining the splitting. Since these differences in the single-molecule terms F_{pp} are larger than the off-diagonal terms F_{pp}, we find that most of the vibrons are localized on either one of the two sublattices in α-TCB.

In our calculations we have further analyzed the origin of the crystal-field splittings in α-TCB and their dependence on the intermolecular potential. We have found that they are not so much caused by the interactions between molecules within the stacks along the a axis, but mainly by the interactions between molecules lying in adjacent stacks. So, as far as these splittings are concerned, α-TCB is not an effective one-dimensional crystal. It is the repulsive exponential terms in the atom–atom potential that account for most of the splittings. Their effect is partly compensated by an opposite but smaller effect from the attractive r^{-6} interactions. The Coulomb interactions between fractionally charged atoms have practically no effect on the crystal-field splittings. We have also found that these splittings depend very sensitively on the molecular orientations. Changing the atom–atom potential changes the splittings too, but mainly through the change in the equilibrium orientations of the molecules. The strong dependence of the vibron splittings on the molecular orientations might indicate a rather important vibration–rotation coupling. Although this coupling is indeed visible, for instance in the differences between the nonrigid and rigid molecule (gerade) lattice mode frequencies in Table V, it does not lead to substantial vibron–phonon mixing. Even the lowest vibron frequencies shift by less than 2 cm^{-1} through mixing with the phonons (see the end of Sec. II). We return to the splittings of the k = 0 vibron frequencies in α- and β-TCB after the presentation of the Raman spectra in Sec. V.

C. Vibron band structure

The dispersion calculated for some typical vibrons, along various directions in the Brillouin zone, is illustrated in Fig. 1 and the bandwidths for most of the vibrons in α- and β-TCB are tabulated in Table VI. These results have been obtained with the atom–atom potential of Reynolds with and without fractional atomic charges. As can be seen in Table VI the vibron bandwidths in the two phases of TCB are about the same. Since the crystal structure of α-TCB is so similar to that of β-TCB and since we found from our calculations that the bandwidth of the vibrons is hardly affected by small changes in the molecular orientations, this behavior can be understood. It is in marked contrast with the variation of the lattice mode frequencies and with the splittings of the k = 0 vibron frequencies, however, which depend sensitively on the molecular orientations and are significantly different in the two phases of solid TCB. The lattice dynamics calculations show further that in most cases there is almost no interaction between vibrons that correspond with different molecular vibrations, and that also the vibron–phonon mixing is practically negligible. So we could have obtained the vibron band structure from separate calculations in which only a specific molecular vibration is excited and we can discuss the results for each vibration separately. An exception with interesting consequences (discussed below) is the Fermi resonance between the 352 cm^{-1} (A_{g}) vibration and the 348 cm^{-1} (B_{2g}) mode. The mixing of these modes by the intermolecular interactions is symmetry al-

![FIG. 1. Calculated dispersion along the a*, b*, and c* directions in the Brillouin zone of four different internal vibrational modes of α-TCB in cm^{-1}, using the potential set of Reynolds with (−−) and without (−) fractional atomic charges.](image-url)
It appears from Fig. 1 that several vibrons show dispersion, mainly in the \( a^* \) direction of the Brillouin zone, and that the frequencies display a cosine dependence on the wave vector \( k \) in this direction. So the intermolecular interactions responsible for most of the dispersion in the vibrons occur within the stacks of molecules along the \( a \) axis, mainly between nearest neighbors. Therefore, the conclusion of a one-dimensional vibron band structure in paper 1 seems justified. Exceptions are the low frequency internal vibrations [80 \((A_g)\), 190 \((A_g)\), 209 \((B_{2g})\), 218 \((B_{1u})\), and 225 cm\(^{-1}\) \((B_{2g})\)], which show significant dispersion in all directions of the Brillouin zone, indicating important interactions between molecules in different stacks.

An interesting observation is that without the fractional charges on the atoms the vibrational bands in the higher frequency region (above 600 cm\(^{-1}\)) are practically flat. So in order to obtain the correct experimentally observed dispersion of these bands (see below), it is absolutely necessary to add electrostatic interactions to the exp-6 atom–atom potential. For the lower frequency vibrons it appears that, in addition to the fractional atomic charges, also the repulsive exponential terms contribute to the dispersion. Since the amount of charge on the atoms is the dominating factor in determining the widths of the vibron bands, it is not surprising that calculations either with the potential sets of Reynolds et al. or with the sets of Bonadeo et al. yield practically the same vibron band structure if the same charges are used.

The sign of the dispersion, which determines whether the \( k = 0 \) states lie at the top of the vibron band or at the bottom, appears to be related to the charges on the atoms. If the Cl atoms, which carry a negative charge, are involved in the vibration, the sign is positive in most cases. The dispersion is negative if the H atoms, with a positive charge, are involved. One exception is the 348 cm\(^{-1}\) \((B_{1g})\) vibration, a pure C–Cl out-of-plane vibration, with a negative dispersion. As we discuss next, the calculated signs of the dispersion agree with the experimental results reported in Ref. 1.

The results of the calculations will now be compared in detail with the experimentally reported vibron bandwidths in Ref. 1. A nice example of a one-dimensional vibron band with significant dispersion is the 860 cm\(^{-1}\) \((B_{2g})\) C–H out-of-plane vibration (see Fig. 1). This mode is reported in Ref. 1 as the 864 cm\(^{-1}\) \((B_{2g})\) vibration, and the theoretical dispersion agrees with the experimental results reported in Ref. 1.

An interesting case is the 352 cm\(^{-1}\) \((A_g)\) vibration (see Fig. 1). This mode is reported as 355 cm\(^{-1}\) \((A_g)\) with the largest experimental dispersion of about — 15 cm\(^{-1}\). In our calculations we observe a very small bandwidth for this vibration, even with the charges on the atoms. In paper 1 it is already suggested that the \((A_g)\) vibration is in resonance with the nearby lying 348 cm\(^{-1}\) \((B_{1g})\). In the calculations we observe that this \((B_{1g})\) C–Cl out-of-plane vibration has a large negative dispersion of — 15 cm\(^{-1}\) (— 10 cm\(^{-1}\) without charges on the Cl atoms), but this vibration should be very weak in the phosphorescence spectrum. However, as we can read from Table I, the frequency of the strong 352 cm\(^{-1}\) \((A_g)\) vibration is very sensitive to the mass of the Cl atoms and in the crystal this vibration will not lead to a single sharp peak, but to several peaks or to a broad structure of several cm\(^{-1}\) (see the remarks on isotope effects below). Further, we calculate that the \((A_g)\) and \((B_{1g})\) modes mix for those wave vectors \( k \) for which their frequencies nearly coincide. Hence the 348 cm\(^{-1}\) \((B_{1g})\) vibration can steal intensity from the \((A_g)\) mode over a wide frequency range, and the large dispersion of the \((B_{1g})\) mode can become visible in the spectrum. It can now be understood why it was impossible to fit the observed line shape to a simple model.

For the 1165 cm\(^{-1}\) \((A_g)\) breathing vibration, which is reported in paper 1 as 1159 cm\(^{-1}\) \((A_g)\), the experimental dispersion of + 7.4 cm\(^{-1}\) cannot be reproduced quantitatively. The addition of the charges on the Cl atoms gives a dispersion of only + 1.0 cm\(^{-1}\) in the \( a^* \) direction. Increase of these charges from — 0.25 to — 0.40 e increases the dispersion to + 2 cm\(^{-1}\), but with these large charges the optimization yields a crystal structure which is no longer stable. So, the correct size of the dispersion in this vibration cannot be obtained from the atom–atom potential; the sign is given correctly by the calculations.

Finally for the 225 cm\(^{-1}\) \((B_{2g})\) C–Cl out-of-plane vibration, which has been reported as 233 cm\(^{-1}\) \((B_{2g})\) with a dispersion of less than 2 cm\(^{-1}\), we calculate a dispersion of 3 cm\(^{-1}\) in all three directions of the Brillouin zone, caused mainly by the short range exponential terms in the atom–atom potential (see Fig. 1). The charges on the atoms change the absolute frequency, but the splitting at \( k = 0 \) and the dispersion are hardly affected. We conclude that this vibration is not a simple one-dimensional vibrational excitation.

### D. Isotope effects

The differences in the vibrational frequencies of TCB due to the occurrence of different \(^{35}\)Cl and \(^{37}\)Cl mass distributions can manifest themselves in different ways in the crystal. It should be realized that the seven different molecular isotopic species, for which we have calculated the vibrational spectra in Sec. III, occur randomly in the crystal. So TCB is a solid with random (isotopic) disorder, for which interesting effects can occur. The nature of the spectrum is determined by the size of the isotope shifts in the intramolecular vibrational frequencies relative to the size of the intermolecular coupling elements in the dynamical matrix. The latter coupling elements also determine the size of the dispersion in the vibron bands given in Table VI.
One extreme situation occurs when the intramolecular shifts are much smaller than the intermolecular couplings. In that case, the vibrational exciton may become localized in clusters of isotopically identical molecules. Such clusters occur with random sizes in the crystal. The spectrum of the solid will then show the vibrational peaks of each of the seven molecular species, broadened by the intermolecular interactions within these clusters. A clear example of this case is the 312 cm\(^{-1}\) \(B_\text{xy}\) vibration which has an intramolecular rms isotope shift of 1.62 cm\(^{-1}\) (see Table I) and intermolecular coupling matrix elements smaller than 0.15 cm\(^{-1}\) [i.e., a vibron dispersion less than 0.5 cm\(^{-1}\) (see Table VI)]. In Fig. 2 we have constructed a theoretical spectrum for the 312 cm\(^{-1}\) \(B_\text{xy}\) mode in the solid by taking the frequencies and weights of the stick spectrum for the seven molecular isotopic species, and simulating the cluster broadening, as well as temperature broadening and experimental resolution, by adding Gaussian line broadening to the stick spectrum of the molecular vibrations. We will see in Sec. V that this theoretical spectrum agrees very well with the experimentally observed Raman spectrum of this mode.

The other extreme occurs when the intramolecular isotope shifts are much smaller than the intermolecular couplings. In that case, the vibrational excitation will move very fast between the different isotopic species and the crystal spectrum will resemble the spectrum calculated for a homogeneous solid with the various isotopic masses replaced by the average mass (the so-called virtual crystal model). In the intermediate case, when the intramolecular shifts are comparable with the intermolecular couplings, the spectrum of the solid becomes very complex.\(^{21,22}\)

Another important effect due to the occurrence of the random isotope distributions concerns the selection rules. In general, random disorder lowers the symmetry and, thereby, weakens the selection rules. In the particular case of TCB, the most frequently occurring (42\%) isotopic species contains three atoms of \(^{35}\)Cl and one atom of \(^{37}\)Cl. This species has no inversion symmetry, and neither have several other of the seven possible species. Therefore, vibrational modes which are only Raman active in the homogeneous crystal will be infrared active as well, in the “natural” crystal. And, similarly, the infrared active modes will become Raman active too. This breaking of the selection rules will be most visible for those vibrational modes which involve particularly the chlorine atoms.

V. RAMAN EXPERIMENTS

A. Experimental

Raman spectra were obtained by exciting the crystal with 1 W of the 488.0 nm line of a Spectra-Physics Ar-ion laser (model 171). The scattered light was inspected with a Spex model 1402 double monochromator with two 1200 l/mm ruled gratings blazed at 1000 nm, which was operated at a resolution of about 1 cm\(^{-1}\). The output was collected by a cooled photomultiplier (EMI 9658B) and processed by a photon counting system (EG&G 1182 amplifier/discriminator and Ortec 449 log/rate meter). The positions of the lines were measured relative to the laser line and were reproducible to 1 cm\(^{-1}\). For the spectra at 210 K, just above the phase transition, and at 90 K, the sample was cooled in a stream of nitrogen vapor. The temperature of the sample was monitored via a resistor. Due to differences in location and heating of the sample the estimated accuracy of the temperature during the recording of these spectra is 5 to 10 K. For the spectra between 4.2 and 1.2 K the sample was immersed in liquid \(^4\)He.

1,2,4,5-Tetrachlorobenzene was obtained from Aldrich Chemical Company and zone refined for 140 passes. Crystals were grown from the melt by the Bridgeman technique and annealed for three days at 2 °C below the melting point to reduce structural imperfections. Analysis by gas chromatography and mass spectroscopy established the presence of 20 ppm 1-bromo,2,4,5-trichlorobenzene and less than 1 ppm 1,2,3,5-TCB in the final product. The sample, a single crystal with a thickness of less than 0.5 mm, was selected using a polarization microscope.

B. Results and discussion

The Raman experiments have been performed for several purposes. First, the experiments yield the phonon frequencies, which makes it possible to distinguish between the \(\alpha\)-phase and the \(\beta\)-phase crystal structure. In this way we were able to ascertain that the earlier experiments\(^1\) were indeed performed on TCB crystals in the low temperature \(\alpha\) phase since the observed frequencies are in agreement with those previously reported.\(^7\) At 300 and at 210 K the \(\beta\)-phase lattice mode frequencies were observed. Upon cooling the crystal structure changed, giving the frequencies of the \(\alpha\) phase. Either by quick or slow cooling it proved impossible to maintain \(\beta\)-phase crystals at liquid helium temperatures.

Further, we wanted to see whether the site splittings calculated for \(k = 0\) in \(\alpha\)-TCB and the \(^{35}\)Cl/\(^{37}\)Cl isotope effects could be observed in the Raman spectrum. In Fig. 3 the Raman signals of six internal vibrations at different temperatures are shown. These vibrations have been selected because there are no nearby lying gerade vibrations, which facilitates...
Although the calculated $k = 0$ vibron splittings, small in $\beta$-TCB and substantially larger in $\alpha$-TCB, are qualitatively confirmed by the Raman measurements, the quantitative agreement between calculations and experiments is poor. The calculated splittings (see Table VI) are much larger than the observed values. Since the calculations show that the splittings depend very sensitively on the molecular orientations and since it is unlikely that the empirical atom–atom potentials reproduce the experimental crystal packing really accurately, the discrepancy might be explained by the inaccuracy in the calculated orientations of the molecules in the crystal.

The effect of the different CI isotope masses on the vibrational frequencies is relatively large in modes with in-plane CI vibrations such as the $190 (A_g)$, $312 (B_{3g})$, $352 (A_g)$, $209 (B_{2g})$, $218 (B_{1u})$, $510 (B_{1u})$, and the $645 \text{ cm}^{-1} (B_{2u})$, see Table I. Let us first discuss the gerade modes, which are Raman active in the homogeneous crystal. Especially in the $312 \text{ cm}^{-1} (B_{3g})$ mode, where the ratio between the intramolecular isotope splitting and the vibron dispersion (see Tables I and VI) is very favorable, the isotope splitting should be visible (see Sec. IV). The Raman spectrum of this mode given in Fig. 3 shows that this is indeed the case. The $\beta$-phase spectrum taken at 300 K is strikingly similar to the theoretical simulated spectrum in Fig. 2 with a linewidth of 1.75 cm$^{-1}$ and the $\alpha$-phase spectrum at 90 K perfectly resembles the theoretical spectrum with a linewidth of 1.0 cm$^{-1}$. The $\alpha$-phase spectrum at 1.2 K is slightly different, which is probably caused by a more marked site splitting at this temperature. A similar isotope splitting has been observed for the $328 \text{ cm}^{-1} (A_g)$ mode in the Raman spectrum of $p$-dichlorobenzene by Bellows et al.\textsuperscript{23} These authors have not performed any lattice dynamics calculations, but they conclude on the basis of the experiments that the vibron bandwidth for this $328 \text{ cm}^{-1}$ mode should be less than 4 cm$^{-1}$.

For the other gerade vibrations that are candidates for displaying visible isotope effects, the situation is more complicated. The $190 \text{ cm}^{-1} (A_g)$ mode has a considerably larger dispersion (see Table VI), i.e., larger intermolecular coupling matrix elements. The experimental Raman spectrum only shows a single peak which remains broader than the experimental resolution even at the lowest temperature, but which displays no clear structure. The dispersion of the $352 \text{ cm}^{-1} (A_g)$ mode is smaller but this mode is engaged in a Fermi resonance with the much more dispersed $348 \text{ cm}^{-1} (B_{1g})$ mode. We have observed three peaks in this region in the higher temperature spectra and five peaks at the lower temperatures, but the precise assignments of these peaks is difficult because of the various effects occurring (isotope splitting, site splitting, Fermi resonance). We expect that at least part of the structure in this region is due to isotope effects, however.

The ungerade modes are infrared active in the homogeneous solid, but in the isotopically disordered crystal these modes may become Raman active as well. Especially those isotopically mixed molecular species which lack an inversion center will contribute to the Raman scattering. In the region around $230 \text{ cm}^{-1}$ we observe three peaks which sharpen at lower temperatures. We attribute the peak at $235 \text{ cm}^{-1}$ to
the 225 cm\(^{-1}\) \((B_{3g})\) vibration, in agreement with the phosphorescence spectrum\(^1\) where this vibration is observed at 233 cm\(^{-1}\). In view of the small isotope splitting calculated for this vibration (see Table I) it is very unlikely that the other two peaks at 228 and 221 cm\(^{-1}\) are caused by different isotopic species of this \((B_{3g})\) vibration. We assign the peak at 228 cm\(^{-1}\) to the 218 cm\(^{-1}\) \((B_{1u})\) and the peak at 221 cm\(^{-1}\) to the 209 cm\(^{-1}\) \((B_{2g})\) vibration. Both these vibrations have a rather strong intermolecular coupling so it could be expected that no simple isotope splitting of these peaks is visible. So, both these peaks demonstrate the breaking of the selection rules due to the isotopic disorder. Another peak, which splits into two components in the \(\alpha\) phase, is visible around 510 cm\(^{-1}\) but it is not clear whether, besides the 511 cm\(^{-1}\) \((B_{2g})\) mode, the 510 cm\(^{-1}\) \((B_{1u})\) contributes anything to the Raman scattering.

It is remarkable that no isotope or site splittings are observed in the low temperature \(T_\alpha\rightarrow T_\beta\) phosphorescence spectrum of \(\alpha\)-TCB in paper 1. This can now be understood, however, since the overall resolution in Ref. 1 was about 2 cm\(^{-1}\) and all splittings observed in the Raman spectra are smaller than a few cm\(^{-1}\).

All Raman lines show a temperature dependent linewidth. The narrowest lines are obtained at 1.2 K, where the width of the 1165 cm\(^{-1}\) \((A_g)\) vibration is almost equal to the resolution limit of the monochromator, whereas, for instance, the 1560 cm\(^{-1}\) \((B_{2g})\) vibration shows a width of 2.7 cm\(^{-1}\) which is constant below 90 K. It is known that the observed linewidth of Raman transitions can be affected by inhomogeneities (like impurities and crystal defects) or by relaxation. Keeping in mind that a lifetime in the order of a few ps can account for a linewidth of a few cm\(^{-1}\) the narrowing observed in our spectra upon cooling might be explained by an increase of the vibron lifetime. This narrowing even continues for some vibrations \(190 \text{ cm}^{-1}\) \((A_g)\) and 1165 cm\(^{-1}\) \((A_g)\) between 90 and 1.2 K, in contrast with the benzene crystal\(^2\) where no decrease in the Raman linewidth is observed between liquid N\(_2\) and liquid He temperatures. It has been pointed out that inhomogeneities have a negligible effect on the line broadening at low temperatures,\(^5,26\) so the observed narrowing in the low temperature region indicates an increase of the relaxation time.

VI. CONCLUSIONS

From the lattice dynamics calculations and the Raman spectra of the low temperature \(\alpha\) phase and the high temperature \(\beta\) phase of TCB presented in this paper, and from the optical spectra of \(\alpha\)-TCB given in Ref. 1, we can draw the following conclusions.

The calculations, based on empirical atom–atom potentials, show that the structure of the vibrational exciton bands, especially those above 600 cm\(^{-1}\), is one-dimensional, in agreement with the interpretation of the phosphorescence spectra in Ref. 1. Significant dispersion occurs only in the \(a^*\) direction of the Brillouin zone, due to the importance of the (nearest-neighbor) interactions between the molecules lying in the stacks along the \(a\) axis. The signs of the nearest-neighbor vibrational coupling elements in the dynamical matrix, which determine whether the \(k = 0\) states lie at the top of the band or at the bottom, are correctly reproduced by the lattice dynamics calculations. It is striking that the electrostatic interactions between the molecules, which are modeled in the atom–atom potential by the inclusion of fractional atomic charges, are absolutely essential to obtain the correct vibron bandwidths. An exception is the 1165 cm\(^{-1}\) \((A_g)\) vibrational band which remains considerably too narrow in the calculations, even when the atomic charges are included. This vibration involves mainly the breathing motion of the Cl atoms, so we conclude, in agreement with previous experience,\(^27-29\) that for the interactions between Cl atoms the use of an isotropic atom–atom potential is insufficient. From the calculations it follows further that the widths of the vibron bands are not extremely sensitive to the crystal structure. So the vibrational band structure in \(\beta\)-TCB will not be very different from that observed\(^1\) in \(\alpha\)-TCB. The Raman spectra have confirmed that the optical experiments in Ref. 1, which were carried out at temperatures below 4.2 K, refer to the \(\alpha\) phase of TCB.

The calculations also predict, in agreement with the Raman spectra for several vibrations, that the splitting of the \(k = 0\) vibron frequencies is significantly larger in \(\alpha\)-TCB than in \(\beta\)-TCB. This appears to be caused by the crystal-field terms, i.e., the self terms in the dynamical matrix, of the solid. In \(\alpha\)-TCB the two molecules in the unit cell are not equivalent and they experience a different crystal field, whereas in \(\beta\)-TCB these molecules are equivalent. However, the splittings observed in the Raman spectra are considerably overestimated by the calculations. Since these \(k = 0\) site splittings appear to depend very sensitively on the molecular orientations, this discrepancy is probably due to the approximate nature of the atom–atom potential model, which leads to inaccuracies in the orientations of the molecules in \(\alpha\)-TCB (remember that these have not yet been determined experimentally).

The conclusion that the band structure, especially for the vibrations at higher frequencies, is one-dimensional does not imply that the interactions between the stacks of TCB molecules are negligible. It becomes clearly evident from the calculations that for the overall crystal stability, for the dispersion of the phonon bands and also the lower frequency vibron bands, and for the site splitting of the \(k = 0\) vibron frequencies in \(\alpha\)-TCB, the interstack interactions are essential.

Another interesting phenomenon, which emerges from the Raman spectra of both \(\alpha\) and \(\beta\)-TCB, is the observation of isotope splittings. The statistical occurrence of \(^3\)Cl and \(^\text{\textsuperscript{37}}\)Cl atoms in the ratio 3:1 leads to seven different TCB species, which are randomly distributed over the crystal. The calculations show that particularly for the 312 cm\(^{-1}\) \((B_{2g})\) mode, which has large molecular isotope shifts and small intermolecular coupling matrix elements, the isotope splitting should be visible. The perfect resemblance between the theoretically simulated spectrum for this mode and the observed Raman spectrum confirms this conclusion. This mode demonstrates one of the effects that can occur in crystals with random disorder: the (vibrational) excitations may lose their Bloch wave character and become localized in clusters of (isotopically) similar species. Also for other vi-
ibrations we have observed effects of random disorder, such as peak broadening and the detection of transitions that would be forbidden in homogeneous crystals (i.e., the breaking of selection rules). Summarizing, we conclude that the vibron band structure in TCB is not masked by chlorine isotope effects. For most of the vibron bands the dispersion appears to be significantly larger than the isotope shifts. For one vibration where the isotope shifts are larger, the peaks from the seven different molecular species are clearly separated, and for the vibrations where the two quantities are comparable, the spectra show interesting structures.

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