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## Potential scans and potential energy distributions of normal vibrational modes of trichloroacetyl isocyanate

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**Abstract** The conformational stability and vibrational infrared and Raman spectra of trichloroacetyl isocyanate ( $\text{CCl}_3\text{CONCO}$ ) were investigated by ab initio MP2 and density functional B3LYP calculations using the 6-311++G\*\* basis set. From the potential energy scans of the internal rotations in both the halomethyl and the isocyanate rotors, the molecule was predicted to exist predominantly in the *cis-cis* conformation. The steric hindrance between the halomethyl group and the nitrogen lone-pair was found to favor the staggered configuration for the chlorine atom, while conjugation effects favor the planar configuration for the C=O and the NCO groups. Vibrational wavenumbers were computed for the molecule at the DFT-B3LYP/6-311++G\*\* level. Normal coordinate calculations were carried out to obtain the potential energy distributions (PED) among the symmetry coordinates of the normal modes for the molecule. The theoretical vibrational assignments were compared with experimental ones and ratios of observed to calculated wavenumbers of about 0.97–1.04 were obtained.

**Keywords** Conformational stability · Internal rotation · Normal coordinate · Vibrational assignments

### Introduction

The conformational behavior of halocarbonyl, halomethyl and haloacetyl isocyanates has been investigated by both theoretical and experimental methods. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] The conformational behavior in these molecules is always dependent on

the nature of the substituents. The stability of these molecules is expected to be controlled by a combination of steric hindrance, dipolar interactions and conjugation effects. In halocarbonyl isocyanates CXO–NCO, conjugation effects tend to stabilize the planar *cis* and *trans* and not the non-planar *gauche* conformers. The conformational stability of these molecules was found to be changed on going from gaseous to condensed phases. For example, in fluorocarbonyl isocyanate the *cis* conformer was determined to be slightly more stable than the *trans* conformer in the fluid states, but the *trans* conformer turned out to be more stable in the solid state. [7] On the other hand, chlorocarbonyl and bromocarbonyl isocyanates were both determined to exist predominantly in the *trans* conformation (isocyanate group *trans* to the carbonyl bond) in the fluid phases. [4, 13]

In halomethyl isocyanates  $\text{CX}_3\text{-NCO}$ ,  $\text{CHX}_2\text{-NCO}$ , and  $\text{CH}_2\text{X-NCO}$ , both the repulsive interaction between the halogen atoms and the lone-pair on the nitrogen and the steric hindrance play a major role in determining the direction of the conformational equilibrium of the molecules. For example, in chloromethyl isocyanate  $\text{CH}_2\text{Cl-NCO}$ , the potential scans governing the internal rotation about the C–N bond were calculated to be consistent with a single minimum corresponding to a structure having the chlorine atom near-*cis* to the NCO moiety with the chlorine atom and the lone-pair in opposite directions with minimum repulsive interaction between them. [1, 3] Similarly, difluoromethyl isocyanate  $\text{CHF}_2\text{-NCO}$  was predicted to exist only in the *trans* (the hydrogen and not a fluorine atom of the difluoromethyl group eclipses the electron lone-pair) conformation again with minimum interaction between the fluorine atoms and the electron lone-pair.

The investigation of the structure and conformations of some haloacetyl isocyanates has been reported. [6, 9, 15, 16, 17] For these two molecular rotor systems, both the halomethyl and the isocyanate groups may adopt more than one configuration around the C–C and C–N bonds. [6, 15] From infrared variable temperature measurements, chloroacetyl isocyanate  $\text{CH}_2\text{Cl-CO-NCO}$

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was suggested to exist as *cis* and *trans* conformers in the liquid phase. [15] Similarly, Balfour et al. have reported the vibrational infrared spectra of the gas and Raman spectra of the liquid of chloro-, dichloro- and trichloroacetyl isocyanates. [9] They reported that the observations indicate that the *cisoid* conformation is the preferred one in the gas phase while substantial amounts of both *cisoid* and *transoid* conformers are present in the liquid. [9]

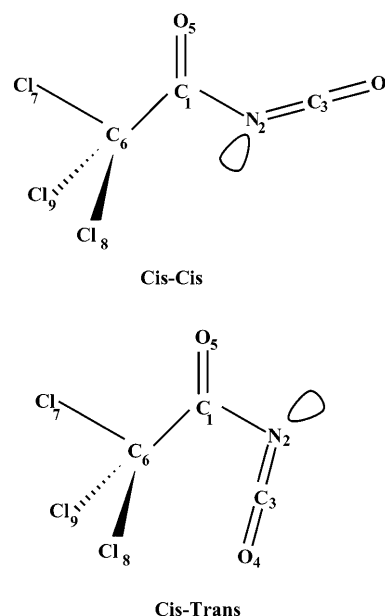
We were interested in this molecule in order to complete our series of studies concerned with the mono- and dichloro- derivatives of this interesting molecular system which is of great importance in synthetic organic chemistry. Furthermore, also to complement experimental investigations, it seems to be important to establish also theoretically the conformational equilibrium, again in comparison to the other derivatives. Since it is very important in vibrational spectroscopy to obtain an unambiguous quantitative assignment of the spectral features of a molecule such as this to atomic motions, which is rather difficult to obtain for all of the spectral lines solely on experimental grounds, it appears to be necessary to perform potential energy distribution (PED) calculations on this important molecular system.

In the present study we calculated the potential scans to describe the internal rotation of the  $\text{CCl}_3$  and NCO rotors in trichloroacetyl isocyanate. Energy optimizations were carried out at both DFT-B3LYP/6-311++G\*\* and second order Moller-Plesset MP2/6-311++G\*\* levels; no effective core potentials (ECP) were used in our calculations. Also, we calculated the vibrational wavenumbers and computed the potential energy distributions for all the normal modes of the molecule from normal coordinate calculations. The results of the work are presented herein.

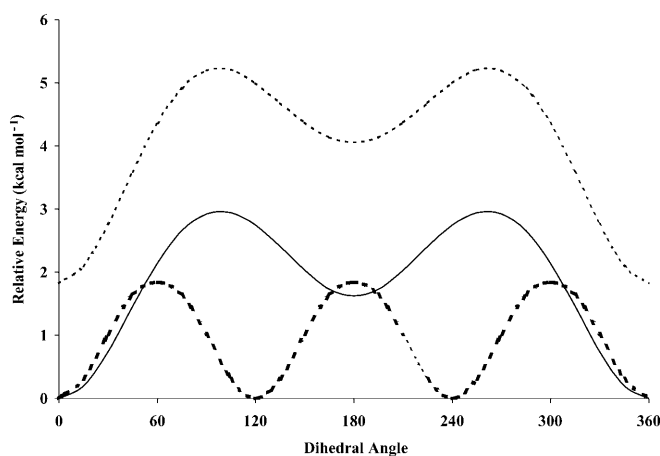
## Ab initio calculations

The GAUSSIAN 98 program [18] running on an IBM RS/6000 43P model 260 workstation was used to optimize the energies, and calculate the vibrational wavenumbers for trichloroacetyl isocyanate. The 6-311++G\*\* basis set was employed to carry out the DFT-B3LYP and MP2 calculations. The conformational stability of the molecule was determined by investigating the potential scans for the internal rotations of each of the  $\text{CCl}_3$  and NCO groups about C–C and C–N bonds respectively (see Fig. 1). This was done in two steps. First we calculated the potential scan for the rotation of the halomethyl group at the fixed position of the *cis* isocyanate group (isocyanate group eclipses the C=O group). Second we calculate the potential scan of the NCO group at the fixed minima in the first halomethyl scan.

We calculated the  $\text{CCl}_3$  scan by varying the CICO dihedral angle  $\theta$  around the C–C bonds at the fixed OCNC dihedral angle  $\phi=0^\circ$ . The calculation was consistent with one energy minimum at  $\theta=0^\circ$ , with a  $\text{CCl}_3$  barrier of about  $1.7 \text{ kcal mol}^{-1}$  as shown in Fig. 2. We then



**Fig. 1** Atom numbering and internal coordinate definitions for trichloroacetyl isocyanate in the *cis-cis* (upper) and *cis-trans* (lower) conformations



**Fig. 2** Potential energy scans for the symmetric  $\text{CCl}_3$  torsion (dotted line) and NCO torsions at *trans*- $\text{CCl}_3$ , where CICO dihedral angle is  $180^\circ$  (dashed line) and *cis*- $\text{CCl}_3$ , where CICO dihedral angle is  $0^\circ$  (bold line) for trichloroacetyl isocyanate

carried out the potential scans of the NCO group about the C–N single bond by varying the OCNC dihedral angle ( $\phi$ ) by  $15^\circ$  from  $0^\circ$  to  $180^\circ$  at each of the fixed CICO dihedral angles of  $\theta=0^\circ$  and  $\theta=180^\circ$ . The results of the scans are shown in Fig. 2. From the potential energy scans, the *trans*  $\text{CCl}_3$  configurations ( $\theta=180^\circ$ ) are calculated to be of higher relative energies than the corresponding *cis* forms ( $\theta=0^\circ$ ) and to turn out to be maxima on full optimization. It was clear from the calculations that trichloroacetyl isocyanate exists in one predominant conformation namely *cis-cis* form with  $\theta=\phi=0^\circ$  (isocyanate group and chlorine atom eclipse the carbonyl C=O bond). Full optimization was then carried out for the sta-

**Table 1** Calculated total energies (hartree) and relative energies (kcal mol<sup>-1</sup>) for possible forms of trichloroacetyl isocyanate

Conformation	B3LYP/6-311++G**			MP2/6-311++G**		
	( $\theta$ , $\phi$ ) <sup>a</sup>	Total energy	Relative energy	( $\theta$ , $\phi$ ) <sup>a</sup>	Total energy	Relative energy
<i>cis-cis</i>	(0, 0)	-1700.262577	0.000	(0, 0)	-1697.743671	0.000
<i>cis-trans</i>	(0, 180)	-1700.259984	1.627	(0, 180)	-1697.741876	1.127
<i>trans-cis</i>	(180, 0)	-1700.259660	1.831	(180, 0)	-1697.739920	2.354

<sup>a</sup>  $\theta$  and  $\phi$  are CICC and OCNC dihedral angles respectively

**Table 2** Calculated structural parameters (Å and degrees), total dipole moment (Debye), and rotational constants (MHz) at B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels for the possible conformers of trichloroacetyl isocyanate

Parameter	B3LYP		MP2		Exp <sup>a</sup> <i>cis</i>
	<i>cis-cis</i>	<i>cis-trans</i>	<i>cis-cis</i>	<i>cis-trans</i>	
Bond length					
$r(\text{C}_1-\text{N}_2)$	1.398	1.387	1.402	1.395	1.388
$r(\text{N}_2=\text{C}_3)$	1.219	1.215	1.233	1.230	
$r(\text{C}_3=\text{O}_4)$	1.156	1.158	1.165	1.168	1.192
$r(\text{C}_1=\text{O}_5)$	1.195	1.192	1.203	1.200	1.215
$r(\text{C}_6-\text{C}_1)$	1.559	1.574	1.550	1.564	1.541
$r(\text{Cl}_7-\text{C}_6)$	1.774	1.769	1.755	1.751	
$r(\text{Cl}_8-\text{C}_6)$	1.798	1.803	1.774	1.778	
$r(\text{Cl}_9-\text{C}_6)$	1.798	1.803	1.774	1.778	
Bond angle					
( $\text{C}_1\text{N}_2\text{C}_3$ )	131.0	138.8	126.6	133.0	125.9
( $\text{N}_2\text{C}_3\text{O}_4$ )	173.7	172.7	179.8	171.5	
( $\text{O}_5\text{C}_1\text{N}_2$ )	125.6	122.8	126.0	122.2	128.7
( $\text{C}_6\text{C}_1\text{N}_2$ )	111.3	115.6	110.2	115.3	
( $\text{Cl}_7\text{C}_6\text{C}_1$ )	110.2	110.3	109.8	110.0	
( $\text{Cl}_8\text{C}_6\text{C}_1$ )	108.2	108.4	107.7	107.9	
( $\text{Cl}_9\text{C}_6\text{C}_1$ )	108.2	108.4	107.7	107.9	
( $\text{O}_5\text{C}_1\text{N}_2\text{C}_3$ )	0.0	180.0	0.0	180.0	0.0
( $\text{Cl}_7\text{C}_6\text{C}_1\text{O}_5$ )	0.0	0.0	0.0	0.0	0.0
( $\text{Cl}_8\text{C}_6\text{C}_1\text{Cl}_7$ )	120.4	120.6	120.4	120.6	
( $\text{Cl}_9\text{C}_6\text{C}_1\text{Cl}_7$ )	-120.4	-120.6	-120.4	-120.6	
Dipole moment ( $\mu$ )	1.053	1.269	1.210	1.709	
Rotational constants					
A	1485	1426	1512	1450	
B	654	796	664	830	
C	624	737	633	764	

<sup>a</sup> Data are obtained for fluoro-carbonyl isocyanate from electron diffraction study in [8]

ble *cis-cis* conformer at both DFT-B3LYP and MP2, levels as shown in Table 1. The calculated structural parameters, total energies, rotational constants and dipole moments of the *cis-cis* conformer of the molecule are listed in Table 2.

## Normal coordinate calculations and vibrational spectra

The vibrational frequencies for trichloroacetyl isocyanate in the *cis-cis* conformation were computed at the DFT-B3LYP/6-311++G\*\* level. The molecule in the planar *cis-cis* form has C<sub>s</sub> symmetry. The 21 vibrational modes span the irreducible representation 14A' and 7A". The A' modes should be polarized while the A" modes

be depolarized in the Raman spectrum of the liquid. Normal coordinate analyses were then carried out for all the stable conformers to provide assignments of the fundamental frequencies for all the conformers of each molecule as described previously. [19, 20] A complete set of internal coordinates (Table 3) was used to form symmetry coordinates (Table 4). The PED for each normal mode among the symmetry coordinates was calculated and is given in Table 5. Finally, the assignments were made based on the calculated PED, infrared band intensities, Raman line activities, depolarization ratios, and comparison with observed values from the experimental spectra of the molecule [9].

The vibrational infrared and Raman wavenumbers ( $\nu_j$ 's) were taken from the Gaussian 98 outputs to perform the plots in the same way as we described previous-

**Table 3** Internal coordinate definition for trichloroacetyl isocyanate

No.	Coordinate <sup>a</sup>	Definition	
1	C <sub>1</sub> -N <sub>2</sub>	Stretch	Q
2	N <sub>2</sub> =C <sub>3</sub>	Stretch	T
3	C <sub>3</sub> =O <sub>4</sub>	Stretch	P
4	C <sub>1</sub> =O <sub>5</sub>	Stretch	R
5	C <sub>6</sub> -C <sub>1</sub>	Stretch	D
6	Cl <sub>7</sub> -C <sub>6</sub>	Stretch	A <sub>1</sub>
7	Cl <sub>8</sub> -C <sub>6</sub>	Stretch	A <sub>2</sub>
8	Cl <sub>9</sub> -C <sub>6</sub>	Stretch	A <sub>3</sub>
9	C <sub>1</sub> N <sub>2</sub> C <sub>3</sub>	Bend	χ
10	N <sub>2</sub> C <sub>3</sub> O <sub>4</sub>	Bend	μ
11	O <sub>5</sub> C <sub>1</sub> N <sub>2</sub>	Bend	ε
12	O <sub>5</sub> C <sub>1</sub> C <sub>6</sub>	Bend	γ
13	Cl <sub>7</sub> C <sub>6</sub> C <sub>1</sub>	Bend	α <sub>1</sub>
14	Cl <sub>8</sub> C <sub>6</sub> C <sub>1</sub>	Bend	α <sub>2</sub>
15	Cl <sub>9</sub> C <sub>6</sub> C <sub>1</sub>	Bend	α <sub>3</sub>
16	Cl <sub>7</sub> C <sub>6</sub> Cl <sub>8</sub>	Bend	σ <sub>1</sub>
17	Cl <sub>7</sub> C <sub>6</sub> Cl <sub>9</sub>	Bend	σ <sub>2</sub>
18	Cl <sub>8</sub> C <sub>6</sub> Cl <sub>9</sub>	Bend	σ <sub>3</sub>
19	C <sub>6</sub> C <sub>1</sub> O <sub>5</sub> N <sub>2</sub>	Wag	η
20	C <sub>1</sub> N <sub>2</sub> C <sub>3</sub> O <sub>4</sub>	Wag	λ
21	Cl <sub>7</sub> C <sub>6</sub> C <sub>1</sub> O <sub>5</sub>	Torsion	τ <sub>1</sub>
	Cl <sub>8</sub> C <sub>6</sub> C <sub>1</sub> O <sub>5</sub>		
	Cl <sub>9</sub> C <sub>6</sub> C <sub>1</sub> O <sub>5</sub>		
22	C <sub>3</sub> N <sub>2</sub> C <sub>1</sub> O <sub>4</sub>	Torsion	τ <sub>2</sub>

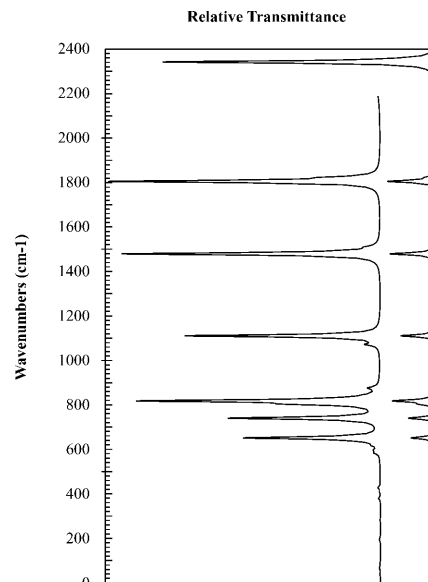
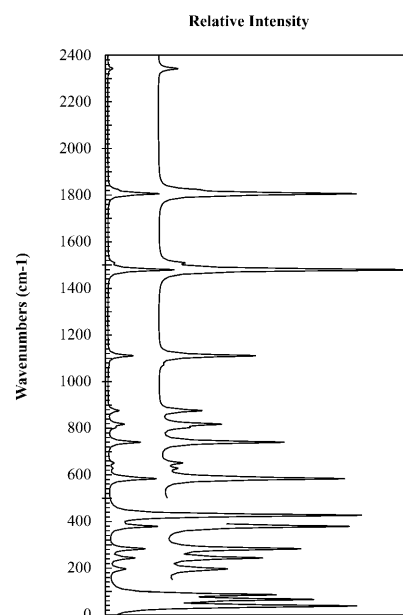
<sup>a</sup> For atom denotation see Fig. 1

**Table 4** Symmetry coordinate definition for trichloroacetyl isocyanate

Species	Description	Symmetry coordinate <sup>a</sup>	
A'	C-C stretch	S <sub>1</sub> =D	
	C=O stretch	S <sub>2</sub> =R	
	C-N stretch	S <sub>3</sub> =Q	
	NCO symmetric stretch	S <sub>4</sub> =P+T	
	NCO antisymmetric stretch	S <sub>5</sub> =P-T	
	CCl <sub>3</sub> antisymmetric stretch	S <sub>6</sub> =2A <sub>1</sub> -A <sub>2</sub> -A <sub>3</sub>	
	CCl <sub>3</sub> symmetric stretch	S <sub>7</sub> =A <sub>1</sub> +A <sub>2</sub> +A <sub>3</sub>	
	CCl <sub>3</sub> symmetric deformation	S <sub>8</sub> =σ <sub>1</sub> +σ <sub>2</sub> +σ <sub>3</sub> -α <sub>1</sub> -α <sub>2</sub> -α <sub>3</sub>	
	CCl <sub>3</sub> antisymmetric deformation	S <sub>9</sub> =2σ <sub>1</sub> -σ <sub>2</sub> -σ <sub>3</sub>	
	NCO in-plane bend	S <sub>10</sub> =μ	
	CCON in-plane bend	S <sub>11</sub> =γ-ε	
	CNC in-plane bend	S <sub>12</sub> =χ	
	CCN deformation	S <sub>13</sub> =2δ-ε-γ	
	CCl <sub>3</sub> rock	S <sub>14</sub> =2α <sub>1</sub> -α <sub>2</sub> -α <sub>3</sub>	
	A''	CCl <sub>3</sub> antisymmetric stretch	S <sub>15</sub> =A <sub>2</sub> -A <sub>3</sub>
		CCON out-of-plane bend	S <sub>16</sub> =η
		NCO out-of-plane bend	S <sub>17</sub> =λ
		CCl <sub>3</sub> antisymmetric deformation	S <sub>18</sub> =σ <sub>2</sub> -σ <sub>3</sub>
		CCl <sub>3</sub> wag	S <sub>19</sub> =α <sub>2</sub> -α <sub>3</sub>
CCl <sub>3</sub> torsion		S <sub>20</sub> =τ <sub>1</sub>	
NCO torsion		S <sub>21</sub> =τ <sub>2</sub>	

<sup>a</sup> Not normalized

ly. [20, 21] To calculate the Raman spectra we used the frequencies  $\nu_j$ , the scattering activities  $S_j$  and the depolarization ratios  $\rho_j$ , as calculated at the DFT-B3LYP level. The calculated vibrational infrared and Raman spectra of trichloroacetyl isocyanate are shown in Figs. 3 and 4.

**Fig. 3** Calculated vibrational infrared spectrum of trichloroacetyl isocyanate at DFT-B3LYP/6-311++G\*\* level**Fig. 4** Calculated vibrational Raman spectrum of trichloroacetyl isocyanate at DFT-B3LYP/6-311++G\*\* level

## Discussion

The reactivity of organic compounds containing the isocyanate group  $-N=C=O$  in synthetic heterocyclic chemistry has attracted the attention to investigate their conformations, structure and vibrational spectra. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 22] Haloacetyl isocyanates are among the reactive reagents of these compounds and the experimental vibrational and Raman spectra of several of these molecules have been reported.

**Table 5** Calculated vibrational frequencies (cm<sup>-1</sup>) at B3LYP/6-311++G\*\* level for the *cis-cis* conformer of trichloroacetyl isocyanate

Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act.	Dep. ratio	Obs. <sup>b</sup>	( $v_{\text{obs}}/v_{\text{calc}}$ )	PED
A	$\nu_1$	2342	1506.6	8.4	0.5	2258	0.985	95% NCO asym. str. (S <sub>5</sub> )
	$\nu_2$	1806	262.9	23.9	0.1	1777	0.904	95% CO. str. (S <sub>2</sub> )
	$\nu_3$	1479	253.0	28.2	0.2	1422	0.961	70% NCO sym. str. (S <sub>4</sub> ), 26% CN str. (S <sub>3</sub> )
	$\nu_4$	1110	191.3	6.0	0.1	1110	1.000	40% CC str. (S <sub>1</sub> ), 18% CN Str. (S <sub>3</sub> ), 18% CC(O)N bend (S <sub>11</sub> ), 15% NCO sym. str.(S <sub>4</sub> )
	$\nu_5$	875	9.5	5.8	0.6	851	0.973	27% CN str. (S <sub>3</sub> ), 23% CC str. (S <sub>1</sub> ), 13% CCl <sub>3</sub> sym. def. (S <sub>8</sub> )
	$\nu_6$	816	226.1	5.1	0.5	814	0.998	60% CCl <sub>3</sub> asym. str. (S <sub>6</sub> ), 10% CCl <sub>3</sub> rock (S <sub>14</sub> )
	$\nu_7$	740	146.6	4.0	0.1	742	1.003	37% CC(O)N bend (S <sub>11</sub> ), 25% NCO bend (S <sub>10</sub> )
	$\nu_8$	583	4.1	1.1	0.1	669	1.147	61% NCO in-plane bend (S <sub>10</sub> ), 15% CC(O)N bend (S <sub>11</sub> )
	$\nu_9$	427	2.4	13.9	0.1	440	1.030	67% CCl <sub>3</sub> asym. str (S <sub>7</sub> ), 13% CC str (S <sub>1</sub> ), 12% CC(O)N bend (S <sub>11</sub> )
	$\nu_{10}$	379	1.9	4.9	0.4			29% CCl <sub>3</sub> asym. str. (S <sub>6</sub> ), 25% CCN def. (S <sub>13</sub> ), 13% CCl <sub>3</sub> sym. def. (S <sub>8</sub> )
	$\nu_{11}$	285	0.2	2.5	0.7			32% CCl <sub>3</sub> sym. def. (S <sub>8</sub> ), 18% CCl <sub>3</sub> asym. def (S <sub>9</sub> ), 13% CCl <sub>3</sub> rock (S <sub>14</sub> )
	$\nu_{12}$	244	0.1	2.3	0.6	251	1.029	35% CCl <sub>3</sub> asym. def. (S <sub>9</sub> ), 22% CCl <sub>3</sub> sym. def. (S <sub>8</sub> ), 15% CCN def. (S <sub>13</sub> ), 12% CCl <sub>3</sub> asym. def. (S <sub>9</sub> )
	$\nu_{13}$	197	0.9	1.4	0.7	202	1.025	49% CCl <sub>3</sub> rock (S <sub>14</sub> ), 16% CNC bend (S <sub>12</sub> ), 12% CCl <sub>3</sub> asym. def. (S <sub>9</sub> )
	$\nu_{14}$	86	0.5	3.5	0.7			68% CNC bend (S <sub>12</sub> ), 15% CCN def. (S <sub>13</sub> ), 12% CCl <sub>3</sub> rock (S <sub>14</sub> )
A''	$\nu_{15}$	803	61.1	4.5	0.8			56% CC(O)N bend (S <sub>16</sub> ), 21% CCl <sub>3</sub> asym. Str. (S <sub>15</sub> ), 20% CCl <sub>3</sub> rock (S <sub>15</sub> )
	$\nu_{16}$	652	132.0	3.4	0.8			57% CCl <sub>3</sub> asym. str. (S <sub>15</sub> ), 27% CC(O) N bend (S <sub>16</sub> )
	$\nu_{17}$	617	3.5	0.2	0.8	600	0.972	91% NCO in-plane bend (S <sub>17</sub> )
	$\nu_{18}$	283	0.0	4.3	0.8	286	1.011	54% CCl <sub>3</sub> asym. def. (S <sub>18</sub> ), 18% CCl <sub>3</sub> asym. str (S <sub>15</sub> )
	$\nu_{19}$	188	0.3	0.2	0.8			65% CCl <sub>3</sub> rock (S <sub>19</sub> ), 10% CCl <sub>3</sub> asym. def (S <sub>18</sub> )
	$\nu_{20}$	66	1.1	3.0	0.8			63% NCO torsion, (S <sub>20</sub> ), 17% CCl <sub>3</sub> rock (S <sub>19</sub> ), 10% CC(O) N bend (S <sub>16</sub> )
	$\nu_{21}$	38	0.7	1.3	0.8			76% CCl <sub>3</sub> torsion (S <sub>21</sub> ), 24% NCO torsion (S <sub>20</sub> )

<sup>a</sup> IR intensities and Raman activities are calculated in km mol<sup>-1</sup> and Å<sup>4</sup> amu<sup>-1</sup> respectively

<sup>b</sup> Observed IR frequencies for trichloroacetyl isocyanate [9]

[6, 9, 15, 16, 17] The vibrational spectra of trichloroacetyl isocyanate (CCl<sub>3</sub>CONCO) have been investigated experimentally and no spectra of the solid phase have been reported. [9] As mentioned earlier, the results indicated that the *cisoid* conformation is the preferred one in the gas phase while substantial amounts of both *cisoid* and *transoid* conformers are present in the liquid. [9]

From energy optimizations and potential scans in the present study, trichloroacetyl isocyanate was predicted to exist predominantly in the *cis-cis* conformation with a small percentage of the *cis-trans* form (Table 2). It was interesting to notice that in the low energy *cis-cis* conformer, the isocyanate group was predicted to eclipse the carbonyl C=O bond with the lone-pair on the nitrogen being away from the carbonyl group. The results of our normal coordinate calculations for the potential energy distributions agree fairly well with the vibrational assignments made based on experimental results. [9] This is evident from the ratio of calculated and experimental wavenumbers that are close to one in most cases as shown in Table 5. The vibrational assignments of many of the fundamental vibrations were straightforward based on the calculated PED for the molecule. However, some of the calculated modes were predicted to mix consider-

ably with other modes. We will try to make tentative assignments for the intense spectral features in the vibrational spectra of the molecule.

The calculated band at 2342 cm<sup>-1</sup> (95% PED) with the strongest infrared intensity is assigned to the NCO antisymmetric stretch in excellent agreement with the observed band at 2258 cm<sup>-1</sup> in the spectrum of trichloroacetyl isocyanate. [9] The corresponding symmetric mode was predicted at 1479 cm<sup>-1</sup> (70% PED) and observed at 1422 cm<sup>-1</sup>. [9] The assignment of the CO stretching mode was straightforward to the intense observed band at 1777 cm<sup>-1</sup> in the infrared spectrum of the molecule, in good agreement with the calculated wavenumber at 1806 cm<sup>-1</sup> with a negligible degree of mixing. The C-C and C-N stretching modes were predicted to have a high degree of mixing; however, their assignments were reasonably consistent with the observed ones as shown in Table 5. The two A'' CCl<sub>3</sub> stretching modes were calculated at 816 cm<sup>-1</sup> (60% PED) and 427 cm<sup>-1</sup> (67% PED). These two modes were observed at 851 and 440 cm<sup>-1</sup> respectively. [9] The corresponding A' mode was observed at 742 cm<sup>-1</sup> but predicted at 652 cm<sup>-1</sup>. However, this mode was predicted to have a PED value of 57% (Table 5). On comparison, the two bending

modes associated with the NCO group agree fairly well with those observed in the infrared spectra of the molecule. [9] For example, the in- and out-of-plane NCO bending modes were calculated at  $583\text{ cm}^{-1}$  (61% PED) and  $617\text{ cm}^{-1}$  (91% PED), while they are observed at  $669$  and  $600\text{ cm}^{-1}$  respectively. [9]

The  $\text{CCl}_3$  rocking modes ( $S_{14}$  and  $S_{19}$  with a PED of 49% and 65%) can be assigned to the calculated wavenumbers of  $197\text{ cm}^{-1}$  and  $188\text{ cm}^{-1}$  respectively, where the A mode ( $S_{14}$ ) was observed at  $202\text{ cm}^{-1}$ . [9] The  $\text{CCl}_3$  and NCO torsions were calculated at  $38$  and  $66\text{ cm}^{-1}$  respectively with weak absorption as shown in Table 5.

In conclusion, our wavenumbers as shown in Table 5 are in reasonable agreement with experiment, as one would expect, given the choice of functional and basis set. It appears to us that the functional dependence of the results should not be of too much significance when going from B3-LYP to BP86, although the latter is said to be better for vibrational spectra. However, we do not expect that the improvements would be very pronounced, because we know from our previous experience that DFT(B3-LYP) gives results of roughly MP2 quality. Also studies of functional dependences of results have been performed previously. Thus another one would not add substantial new information to the literature. Furthermore, as discussed below, the largest discrepancies between our results and experiment can be attributed to anharmonicities in the CH and CO vibrations. This is discussed in more detail in our study on cyclohexanecarboxaldehyde. [23] The vibrations that show the largest disagreements between theory and experiment (see Table 5) all have large contributions from CH stretches and/or NCO motions. Both these vibrations deviate mostly from harmonic behavior [23] and thus deviations of our wavenumbers from experiment in these cases are well accounted for by anharmonicity effects that cannot be tackled in our harmonic treatment. Since the potential for these motions differs from the harmonic one assumed here, both wavenumbers and wavefunctions used for intensity calculations suffer from this effect. We note that this shortcoming cannot be accounted for by another choice of functional, and improvements due to the functional at this level of sophistication are expected to be smaller than errors introduced by the harmonic approximation used. In the case of intensities, the agreement of our spectra with experimental ones is only moderate, because exactly the features dominating the spectra are those that are plagued mostly by anharmonicity effects, which lead to an overestimation of NCO and CH intensities. The Raman activities and depolarization ratios also given in Table 5 are necessary for the calculation of Raman intensities and thus for the construction of our theoretical spectra. Also in case of Raman spectra the agreement of theoretical intensities with experimental ones is, as for IR spectra, only moderate due to the same effects

as discussed above. Finally, this study completes our series of papers on the haloacetyl isocyanates, which complements previously published experimental work on the same molecules. Complete vibrational assignment of all spectral features to atomic motions could be given for trichloroacetyl isocyanate, which is the necessary completion of the body of experimental and theoretical work published in the literature.

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## References

1. Badawi HM, Förner W (1999) *Asian J Spectrosc* 3:161
2. Badawi HM, Förner W (1999) *Asian J Spectrosc* 3:169
3. Durig JR, Little TS, Gounef TK, Gardner JK, Sullivan JF (1996) *J Mol Struct* 375:83
4. Durig JR, Guirgis GA, Krutles KA (1995) *J Mol Struct* 354:1
5. Durig JR, Guirgis GA, Eltayeb S (1994) *J Mol Struct* 324:93
6. Durig JR, Guirgis GA, Krutles, KA (1994) *J Mol Struct* 328:55
7. Durig JR, Guirgis GA, Krutles KA, Phan H, Stidham HD (1994) *J Raman Spectrosc* 25:221
8. Gobbato K, Della Vedova CO, Mack HG (1995) *Spectrochim Acta, Part A* 51:555
9. Balfour WJ, Fougrere SG, Klapstein DT, Nau WM (1993) *J Mol Struct* 299:21
10. Klapstein DT, Nau WM (1993) *J Mol Struct* 299:29
11. Mack HG, Della Vedova CO, Wellner H (1993) *J Mol Struct* 291:197
12. Durig JR, Guirgis GA, Krutles KA, Sullivan JF (1993) *J Raman Spectrosc* 24:259
13. Sullivan JF, Nandy SK, Lee MJ, Durig JR (1992) *J Raman Spectrosc* 23:51
14. Sullivan JF, Nandy SK, Lee MJ, Durig JR (1992) *J Mol Struct* 266:271
15. Yakova EG, Zobova NN, Sagitova RN (1986) *Zh Strukt Khim* 27:800
16. Aminova RM, Zobova NN, Sagitova RN (1993) *Dokl Akad Nauk USSR* 273:391
17. Landsberg BM, Iqbal K (1980) *J Chem Soc Faraday Trans* 76:1208
18. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Frakas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck, AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz, JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DT, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BJ, Chen W, Wong W, Andres JL, Head-Gordon M, Replogle ES, Pople JA (1998) *Gaussian 98*. Gaussian, Pittsburgh, Pa.
19. Wilson EB, Decius JC, Cross PC (1995) *Molecular vibrations*. McGraw-Hill, New York
20. Badawi HM, Förner W, Oloriegbe YS (2001) *J Mol Struct (Theochem)* 548:219
21. Chantry GW (1997) In: Anderson A (ed) *The Raman effect*, vol 1, chapter 2. Merceel Dekker, New York
22. Kamal A (1990) *Heterocycles* 31:1377
23. Förner W, Badawi HM (2001) *J Mol Model* 7:288