

The Conformational Equilibria and Vibrational Spectra, Including Infrared Matrix Isolation Spectra, of Chloroacetyl Chloride and Chloroacetyl Bromide

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Infrared spectra of the title compounds as liquids and as unannealed and annealed solids at 85 K were recorded in the 4000–50 cm⁻¹ range. Matrix isolation spectra in argon and in nitrogen matrices were obtained at 14 K in a 1:500 ratio, with gas mixtures heated to various temperatures between 313 and 900 K. With CsI windows in the helium cryostat the matrix isolation spectra were restricted to the region above 200 cm⁻¹. After annealing to 30–34 K the spectra changed considerably, and the high-energy conformer (*gauche*) vanished, indicating barriers lower than 8 kJ mol⁻¹. Raman spectra of the compounds were recorded as liquids at various temperatures and as amorphous and crystalline solids.

From the variable-temperature measurements the enthalpy differences between the conformers were found to be: 8.4 ± 0.4 (liquid, Raman), 3.2 ± 0.5 ('vapour', Ar matrix, IR) and 4.3 ± 0.5 kJ mol⁻¹ ('vapour', N₂ matrix, IR) for chloroacetyl chloride and 8.5 ± 0.4 (liquid, Raman), 5.1 ± 0.5 ('vapour', Ar matrix, IR) and 4.7 ± 0.5 kJ mol⁻¹ ('vapour', N₂ matrix, IR) for bromoacetyl chloride, the *anti* conformer invariably being the more stable.

The conformations of the haloacetyl halides XH₂C–COY (X, Y = halogens) have been studied by several authors during the last 40 years. Chloroacetyl chloride and some of the other haloacetyl halides have for a long time been commercially available as important reagents in organic synthesis. Most of the earlier investigations were concerned with the infrared and Raman spectra^{1–8} of the two title compounds: chloroacetyl chloride (hereafter abbreviated CAC) and chloroacetyl bromide (CAB). Additional studies regarding CAC were concerned with the dipole moments,⁹ microwave spectra¹⁰ and gaseous electron diffraction.¹¹ It has been well established that the *anti* conformer (relative to the C–X and C–Y bonds) is the more stable in all the haloacetyl halides and is the conformer which is present in the crystalline solids. The high-energy conformer in the haloacetyl halides appears to be *gauche*, with a dihedral angle ca. 120° from *anti*. An exception is provided by fluoroacetyl fluoride,^{12,13} which definitely has *syn* as the second conformer. In fluoroacetyl chloride the *ab initio* and torsional potential functions reveal *syn*,¹⁴ whereas results from gaseous electron diffraction¹⁵ might indicate *gauche* as the high-energy conformer.

When the present work was initiated some years ago, most of the spectroscopic work on the haloacetyl halides

was fairly old, and the reported results contained several inconsistencies. We therefore intended to make complete IR and Raman studies in the vapour, liquid and crystalline states, and furthermore to study the matrix-isolated spectra. By combining the experimental results with normal coordinate analyses we hoped to make reliable assignments for both conformers and to determine the enthalpy difference between the conformers with a higher precision than obtained previously.

While this work was in progress we learned that the vibrational spectra of these molecules were being studied in the laboratory of J. R. Durig at the University of South Carolina, and that his results were close to being published.¹⁶ We therefore restricted our research to certain aspects of the spectra which were not covered by Durig. In particular, we recorded IR spectra of the matrix-isolated molecules. Because the bands are generally much sharper in the matrix-isolated species at 14 K than in the vapour and liquid, bands of different conformers overlapping in the condensed states can frequently be detected, particularly when more than one matrix gas is employed.

With the aid of the hot nozzle technique, first employed by Günthard¹⁷ and by Squillacote *et al.*,¹⁸ in which the matrix gas mixture can be heated to 900 K or even higher before being quenched on the cold window, a very large temperature range can be employed for measuring ΔH° .

Some of our preliminary results for the haloacetyl halides have already been reported,^{19,20} while the complete data for CAC and CAB will be discussed in the present paper.

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Experimental

Chemicals. Chloroacetyl chloride (CAC) was a commercial product from Merck which contained considerable amounts of impurities. The compound was distilled *in vacuo* through a column of 10 plates, which improved the purity considerably. Chloroacetyl bromide (CAB) was prepared by the reaction of phosphorus tribromide with monochloroacetic acid.²¹ The raw product was distilled *in vacuo*. The final purification of both compounds was carried out by preparative gas chromatography on a column of UUAUU-DMCS, 2.5 m long and with 8 mm i.d. using a column temperature of 373 K. The purity was checked by analytical GC and seemed to be better than 99%. In particular, the removal of unreacted PBr₃ was important, since quite small amounts of this reagent give rise to Raman bands of considerable intensities. However, a certain amount of CAC could be detected in the spectra of CAB. The compounds were stored *in vacuo* in a deep freezer.

Instrumental. The IR spectra were recorded with a Perkin-Elmer model 225 spectrometer (4000–200 cm⁻¹) and an evacuable FTIR instrument (model 114c from Bruker) (4000–50 cm⁻¹). A spectrometer from Dilor (model RT 35) with a triple monochromator was employed for the Raman spectra. The instrument was interfaced to the Aspect 2000 computer of the Bruker FTIR. An argon ion laser from Spectra-Physics (model 2000) was used for exciting the spectra.

The IR and Raman cryostats, cooled with liquid nitrogen, and the Miller-Harney cell used for cooling a glass capillary with cold, gaseous nitrogen have all been described in a recent paper.²²

A closed-cycle helium-cooled Displex unit from Air Products with inner and outer windows of CsI was employed for the matrix experiments. The compounds were mixed with the inert gases argon and nitrogen in ratios from 1:500 to 1:1000, and the gas mixtures were deposited on the cold window at ca. 14 K for several hours. The cryostat had a nozzle which could be heated electrically to temperatures between ambient and 900 K. No decomposition products formed during the deposition were detected. Various spectra were recorded after shorter and longer deposition periods to obtain strong as well as weak bands with optimal absorbance. After the unannealed samples had been recorded, the samples were annealed to 32 K (nitrogen) or to 34 K (argon) for 0.5–1 h and recooled to 14 K, before the spectra of the annealed samples were recorded.

Results and discussion

The IR and Raman spectra of CAC and CAB in various phases have recently been reported^{23,24} and will not be given here. Instead one band pair for CAC (717 and 564 cm⁻¹) and one for CAB (525 and 457 cm⁻¹) employed for the ΔH° calculations are reproduced in Figs. 1 and 2, respectively. They represent an *anti* and a *gauche* band of

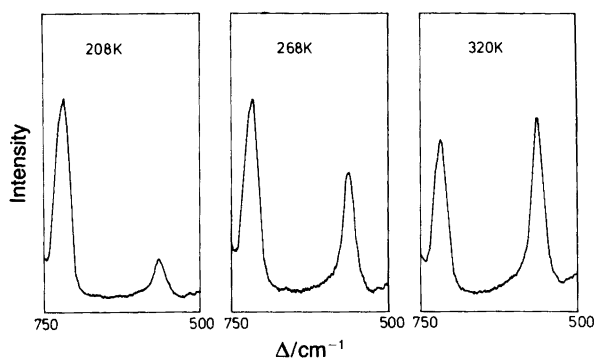


Fig. 1. The Raman bands at 717 cm⁻¹ (*anti*) and 564 cm⁻¹ (*gauche*) of chloroacetyl chloride (CAC) as a liquid, recorded at three temperatures.

the liquid in each of the compounds and were carefully recorded at different temperatures.

IR spectra (2000–300 cm⁻¹) of CAC in an unannealed argon matrix (1:500) are shown in Fig. 3 and recorded at nozzle temperatures of 313 K (ambient) and 700 K. Considerable intensity variations with temperature can be seen. The IR spectra in a nitrogen matrix (Fig. 4), presented with higher dispersion, give the curves of the unannealed (solid line) and the annealed (dashed line) sample, demonstrating a conversion to the stable (*anti*) conformer after annealing.

Argon matrix curves of CAB, recorded with a nozzle temperature of 450 K, are shown in Fig. 5, giving the C=O stretch, CH₂ deformation and C–C stretching regions for unannealed and annealed samples. IR spectra of an unannealed and annealed sample of CAB in a nitrogen matrix are given in Fig. 6. The experimental results for CAC and CAB are collected in Tables 1 and 2, together with the spectral assignments.

Variable-temperature Raman spectra. It can easily be seen from Figs. 1 and 2 that the two pairs of Raman bands have

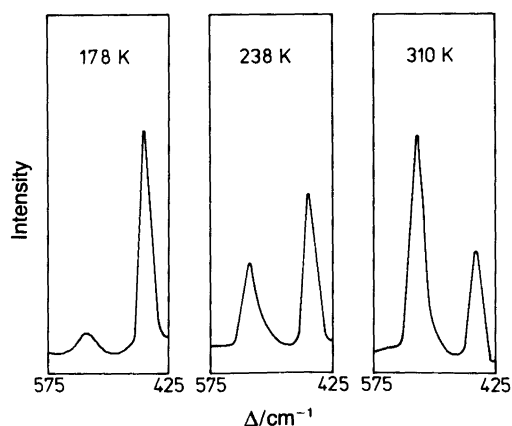


Fig. 2. The Raman bands at 525 cm⁻¹ (*anti*) and 457 cm⁻¹ (*gauche*) of chloroacetyl bromide (CAB) as a liquid, recorded at three temperatures.

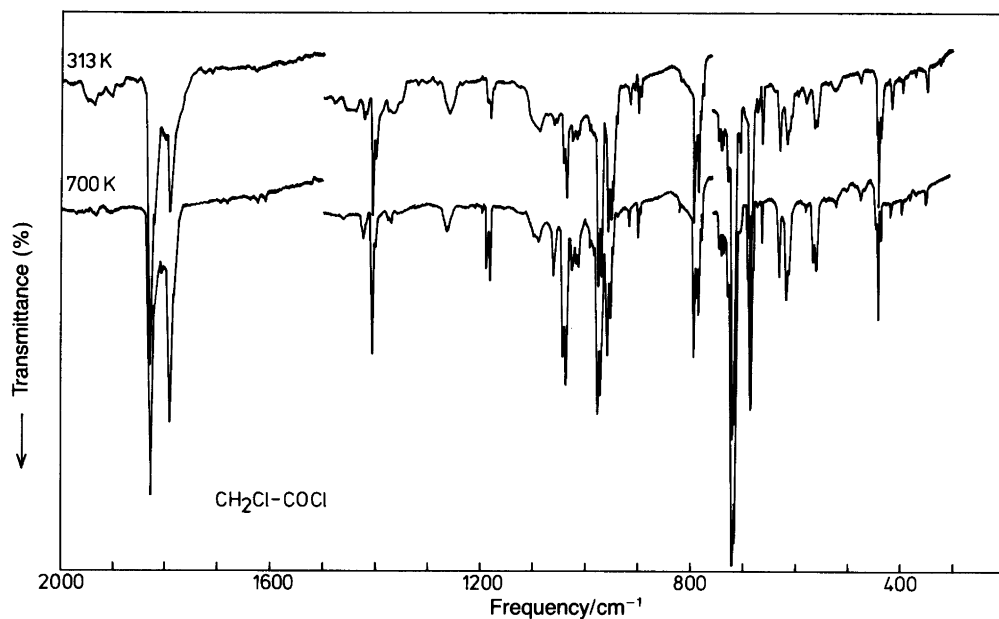


Fig. 3. IR matrix spectrum of unannealed CAC in argon (1 : 500) at 14 K, nozzle temperatures 313 (top) and 700 K (bottom).

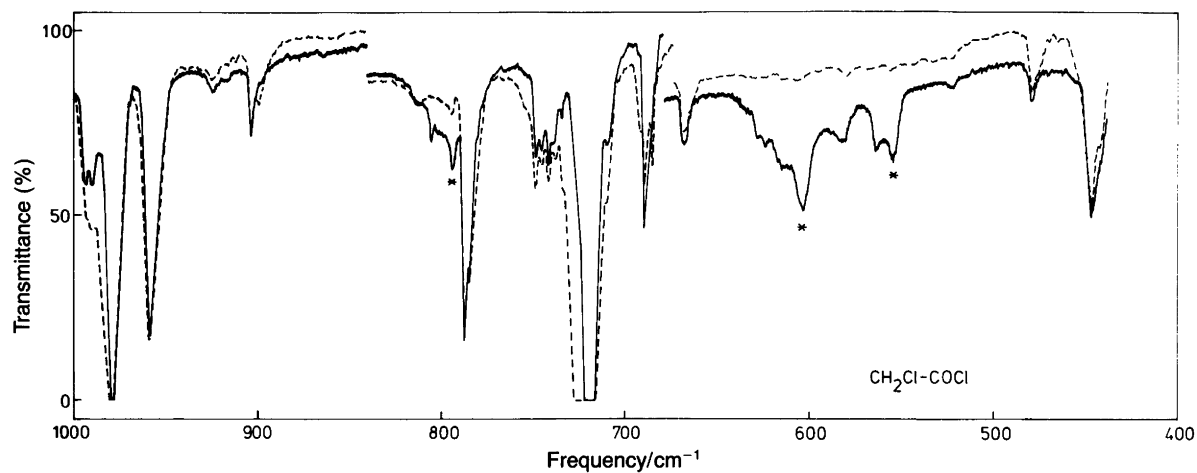


Fig. 4. IR matrix spectrum of CAC in nitrogen (1 : 500) at 14 K, nozzle temperature 450 K (solid line, unannealed; dashed line, annealed for 0.5 h at 32 K).

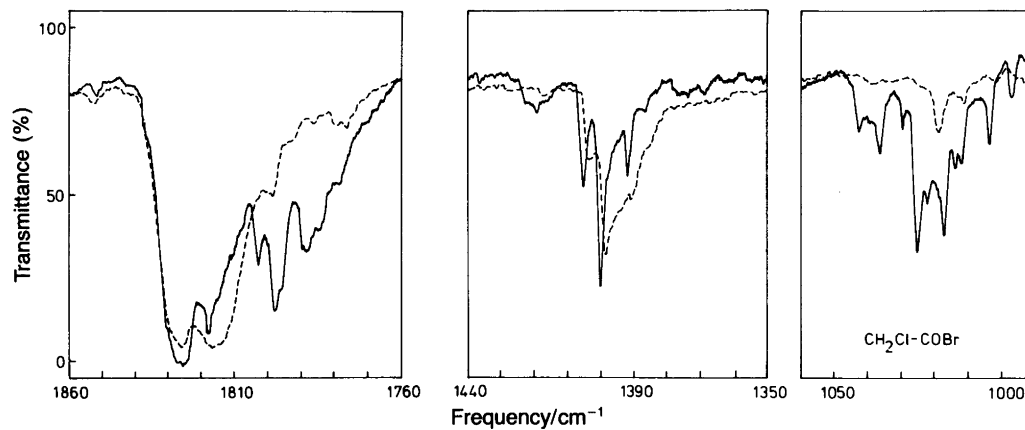


Fig. 5. IR matrix spectra of selected regions of CAB in argon (1 : 500) at 14 K, nozzle temperature 450 K (solid line, unannealed; dashed line, annealed for 0.5 h at 34 K).

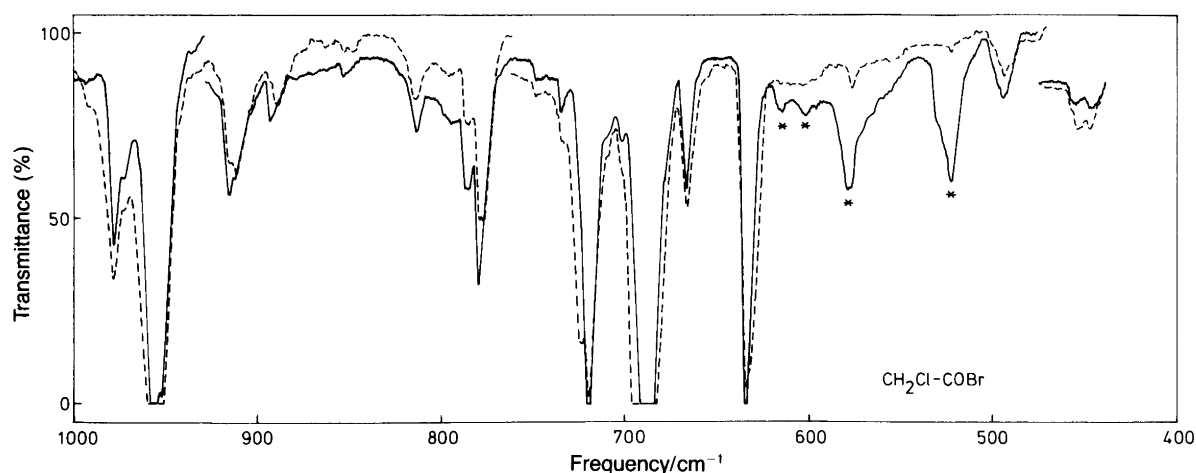


Fig. 6. IR matrix spectrum of CAB in nitrogen (1 : 500) at 14 K, nozzle temperature 450 K (solid line, unannealed; dashed line, annealed at 34 K for 0.5 h).

Table 1. Infrared and Raman spectral data^a for chloroacetyl chloride (CAC).

Infrared				Raman		Assignment	
Liquid	Crystal, 203 K	Ar matrix, 450 K ^f	N ₂ matrix, 450 K ^f	Liquid	Crystal, 233 K	C _s	C ₁
3042 sh ^b	*			3041 vw, br	*		v ₁
3000 s	2980 s			3002 m, D	2993 m	v ₁₁	
2950 s	2940 s			2951 vs, P	2948 vs	v ₁	v ₂
1810 vs ^c	1800 vs	{ 1828 vs 1825 vs 1816 m	{ 1828 vs 1817 m	1808 s, P	{ 1814 w 1800 s	v ₂	
1780 s ^c	*	{ 1790 s,* 1784 m,*	{ 1790 m,* 1783 s,*	1782 sh, P	*		v ₃
1320 sh	1760 w					v ₄ +v ₁₄	
1400 s	*	1422 w,*	1421 w,*	1422 w, P	*		v ₄
1400 s	1390 s	{ 1405 s 1399 w	{ 1406 s 1402 m	1400 s, P	1394 s	v ₃	
1373 m	1367 s	{ 1376 w 1368 w	{ 1379 w 1372 w	1374 w, P	1372 m	v ₅ +v ₈	
1283 w	{ 1285 w 1277 w	1278 w	1285 w	1286 m, P	{ 1291 m 1282 w	v ₄	
1264 w	*	{ 1265 w,* 1263 w,*	1271 w,*	1261 sh, P 1180 m, D	*		v ₅
1177 m	*	{ 1189 m,* 1185 w,* 1182 m,*	{ 1189 m,* 1182 w,*	1175 sh, P	*		v ₆
1065 sh	*	{ 1062 w,* 1059 w,*	1058 m,*				v ₁₀ +v ₁₂
1035 s	*	{ 1043 s,* 1040 m,* 1037 s,*	{ 1041 s,* 1036 m,*				v ₇
988 m ^c	991 m	993 w	992 w	994 sh	995 w	v ₆ +v ₁₀	
974 vs ^c	982 vs	{ 976 vs 971 vs	{ 980 vs 976 m	977 m, D	981 m	v ₁₃	
955 s ^c	958 s	{ 961 m 958 s 952 m	{ 960 s 953 m	959 m, P	959 m	v ₅	
936 sh	934 vw	{ 926 w,* 918 w,*	{ 926 w,* 919 w,*	927 vw, P	*		v ₈
900 m	898 s	{ 901 w 897 vw	{ 906 w 900 vw	897 w, P	899 w	v ₇ +v ₁₀	
800 sh	*	823 w,*	{ 807 w,* 795 w,*	805 sh, P	*		v ₉
780 s	780 s	{ 793 s 789 m 784 m	{ 789 s 786 m	781 vs, P	782 vs	v ₆	cont.

Table 1. Cont.

Infrared				Raman		Assignment	
Liquid	Crystal, 203 K	Ar matrix, 450 K ^f	N ₂ matrix, 450 K ^f	Liquid	Crystal, 233 K	C _s	C ₁
750 sh	{ 758 m 752 m	{ 746 w 739 w	{ 750 w 743 w	767 sh, P	765 w	v ₈ +v ₉	
714 vs	724 vs	{ 728 m 721 vs 719 vs 718 vs	{ 725 m 721 vs 719 vs	717 s, P	{ 731 s 719 w 713 w	v ₇	
687 sh	691 m	{ 689 w 686 m 665 w	{ 694 m 688 w 669 w			v ₁₀ +v ₁₄ CO ₂	
620 w	*	{ 632 m,* 617 m,* 613 m,*	{ 625 w,* 616 m,* 605 m,*	623 vw, P	*		v ₁₀
561 m	*	{ 567 m,* 563 m,*	{ 565 w,* 557 m,*	564 s, P	*		v ₁₁
478 m	{ 479 m 469 vw	{ 479 w 477 w	{ 480 w 478 w	482 w, D	483 w	v ₁₄	
446 s	452 s	{ 443 s 439 m	{ 448 s 443 m	449 vs, P	{ 457 vs 451 sh 435 m	v ₈	v ₁₄
358 w ^d	*	364 w,*	360 w,*	361 vw 339 vw	*		v ₁₃
299 m ^d 269 vw ^d 204 w ^d 183 w ^d	301 m 272 vw 216 w *	303 m	300 m	300 vs, P 208 m, P 186 w, P	339 vw 303 vs 214 m *	v ₉ +v ₁₅ v ₉ v ₁₀ +v ₁₅ v ₁₀	v ₁₄
					165 w 95 s ^e 77 s ^e 57 vw ^e 49 s ^e 43 s ^e 38 s ^e		

^aWeak bands in the regions 4000–3100, 2850–1850 and 1700–1500 cm⁻¹ have been omitted. ^bAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; P, polarized; D, depolarized; asterisks (*) denote bands vanishing (crystal) or highly reduced in intensity (annealed matrices). ^cCS₂ solution. ^dCyclohexane solution. ^eLattice modes. ^fNozzle temperature.

Table 2. Infrared and Raman spectral data^a for chloroacetyl bromide (CAB).

Infrared				Raman		Assignment	
Liquid	Crystal, 208 K	Ar matrix, 450 K ^f	N ₂ matrix, 450 K ^f	Liquid	Crystal, 213 K	C _s	C ₁
2990 s ^b	2984 s	{ 3010 vw 2998 vw		2996 m, D	2986 m	v ₁₁	
2940 s	2941 s	{ 2977 vw,* 2969 w 2962 w 2955 m		2946 vs, P	2939 vs	v ₁	v ₂
1807 vs ^c	1800 vs	{ 1828 vs 1825 vs 1819 s	{ 1830 vs 1827 vs	1814 m, p	{ 1831 sh 1812 m	v ₂	
1775 s ^c	*	{ 1803 m,* 1798 s,* 1789 m,*	{ 1805 m,* 1795 s,* 1784 sh,*	1795 w, sh, P	*		v ₃
1417 sh	1765 w *	1419 w,*	1417 w,*	1778 w, P 1415 w, P	1778 vw *	2v ₁₃	v ₄
1390 s	{ 1383 s 1375 s	{ 1399 m 1391 w	{ 1400 m 1392 m	1394 m, P	{ 1391 s 1384 vw	v ₃	
1335 vw	1335 vw	1340 vvw	1348 vvw	1345 vw, br	1344 vw	v ₁₃ +v ₁₄	
1273 m	1275 m	1268 w	1267 w	1276 m, p	{ 1279 m 1271 vw	v ₄	cont.

Table 2. Cont.

Infrared				Raman		Assignment	
Liquid	Crystal, 208 K	Ar matrix, 450 K ^f	N ₂ matrix, 450 K ^f	Liquid	Crystal, 213 K	C _s	C ₁
1262 w	*	1261 w,*	1262 w,*	1264 sh	*		v ₅
1170 m	*	{ 1183 w,* 1174 w,*	1183 w,*	1174 mw, D	1174 m	v ₁₂	
1145 w	*	{ 1160 w,* 1153 w,*	1160 w,*	1162 sh	*		v ₆
1038 sh	*	{ 1098 w 1043 w,* 1037 w,*	{ 1096 w 1057 w,* 1038 w,*			v ₆ +v ₈	2v ₁₁
1012 s	*	{ 1026 m,* 1023 w,* 1018 m,* 1013 w,* 1004 w,*	{ 1025 m,* 1017 w,* 1009 w,*	1016 w, P	*		v ₇
977 w	{ 978 w 971 vw 968 vw	{ 976 vw 971 vw	{ 979 w 973 vw	974 vw	975 vw	imp. (CAC)	
955 vs	{ 957 vs 950 s	{ 954 m 949 vs 941 m	{ 958 vs 953 s	956 m, P	{ 961 sh 954 m	v ₅	
912 s	{ 913 sh 908 s 901 w 895 w	{ 917 w,* 909 w	{ 916 m,* 912 w	913 w/m, P	911 w/m		v ₈
888 s	886 m	{ 890 w 886 w	{ 895 w 891 vw, D	891 vw, D	890 w	v ₁₃	
771 s	{ 781 m 774 s 771 sh	{ 789 w 785 m 777 m	{ 786 w 781 w	773 s, P	773 vs	v ₆	v ₉
716 vw	719 vw	{ 721 vw 718 vw	{ 724 vw 721 vw	717 vw	721 vw	imp. (CAC)	
681 vs ^c	685 vs	{ 691 vs 689 vs 686 vs 665 w	{ 691 vs 687 vs 685 m 667 w	682 m, P	{ 695 w 686 w 672 s	v ₇	
624 s	{ 632 s 624 sh	{ 633 w 631 m	{ 636 m 633 w			CO ₂	
		{ 619 vw,* 613 vw,*	615 vw,*			v ₁₀ +v ₁₄	v ₈ +v ₉
597 w	*	{ 599 w,* 583 w/m,* 581 w/m,* 574 w,*	{ 605 vw,* 581 w/m,* 579 w/m,*	604 vw, P	*		v ₁₀
522 m	*	{ 533 w/m,* 529 w/m,* 525 w/m,*	{ 531 w,* 527 w,* 524 w/m,*	525 m, P	*		v ₁₁
455 m	455 m	453 w	457 w	457 w	459 w	v ₁₄	
355 m ^d	364 m	{ 353 w/m 351 w	{ 358 w/m 352 w	358 s, P	{ 363 sh 360 vs	v ₈	v ₁₂
320 m ^d	*	{ 330 w,* 324 w,*	{ 327 w,* 323 w,*	323 vw P	*		v ₁₃
297 vw ^d	303 vw			300 vw	301 vw	imp. (CAC)	
245 m ^c	248 m			246 vs, P	{ 251 sh 246 vs	v ₉	
188 m ^d	197 w			192 w, P	194 w 140 w	v ₁₀	v ₁₄
105 w ^d 85 w ^d 64 w ^d	100 vw 83 w				82 s ^e 69 s ^e 60 sh ^e 52 vs ^e 48 sh ^e 40 w ^e 34 s ^e		
46 w	44 vw						

^{a-f}See Table 1.

a large intensity variation with temperature, the CAC band at 564 being enhanced compared to 717 cm^{-1} , whereas the CAB band at 525 increases in intensity compared to 457 cm^{-1} . The effect is clearly due to the large conformational enthalpy difference in the two haloacetyl halides; the former bands are assigned as *gauche* by earlier workers,^{5,7,23,24} while the latter are *anti* (*s-trans*).

In CAC ΔH° (*gauche-anti*) was recently²³ determined to be $7.8 \pm 0.3 \text{ kJ mol}^{-1}$ in the pure liquid, and for CAB a corresponding value of $5.9 \pm 0.3 \text{ kJ mol}^{-1}$ was reported in the neat liquid.²⁴ In spite of the excellent work recently reported for CAC and CAB,^{23,24} we found it worthwhile to repeat the ΔH° measurements, using more than one pair of bands. It is essential for reliable temperature measurements that the *anti* and *gauche* bands are 'pure', meaning that no fundamental or combination band from the other conformer contributes to the observed intensity. For these reasons we feel that, whenever possible, such calculations should be based upon more than one band pair.

For CAC we choose the four *anti* bands, 717, 449, 300 and 208 cm^{-1} , while only the two *gauche* bands at 564 and 186 cm^{-1} were suitable. Integrated band areas were employed rather than peak extinctions, and the band pairs listed in Table 3 were used. From the van't Hoff plots for the five band pairs listed in Table 3 it appears that the slopes of the band pairs at 208/564 and 208/186 cm^{-1} deviate considerably from the others. The arithmetic average of the three remaining pairs gives ΔH° (*gauche-anti*) = $8.4 \pm 0.4 \text{ kJ mol}^{-1}$ for CAC in the liquid (Table 3) and is comparable with values from the literature. Consequently, the present

values for ΔH° (*gauche-anti*) in liquid CAC agree within the limits of uncertainty with those of Durig *et al.*,²³ whereas they are higher than those reported from IR⁴ and Raman⁶ measurements in the older studies.

Similar procedures were carried out for CAB: the *anti* bands at 1394, 773, 682 and 457 cm^{-1} were combined with the *gauche* bands at 913, 525 and 323 cm^{-1} , and four ratios are listed in Table 4. The average value obtained in the liquid (Table 4) was: ΔH° (*gauche-anti*) = $8.5 \pm 0.4 \text{ kJ mol}^{-1}$ for CAB. Durig and Phan²⁴ have reported the value $5.9 \pm 0.3 \text{ kJ mol}^{-1}$ in liquid CAB from Raman measurements of one band pair (525 / 683 cm^{-1}) which was also included in our calculations.

Matrix-isolated IR spectra. It is easily seen from Figs. 3 and 4 for CAC and Figs. 5 and 6 for CAB, as well as from Tables 1 and 2, that the IR bands attributed to the unstable *gauche* conformer are present in the unannealed matrix spectra. Moreover, the matrix spectra of CAC in argon, presented in Fig. 3, reveal that the *gauche* conformer is enhanced at 700 K (lower spectrum) compared to 313 K (upper spectrum). Qualitatively, the same features were observed when CAC or CAB were mixed with argon or with nitrogen, although the fine structure of the guest are quite different in the two matrices.

The spectra demonstrate that when the matrices are heated to 32–34 K (the highest temperatures compatible with the vapour pressures) for 0.5 h, the *gauche* bands vanish or are drastically reduced in intensity as shown in Fig. 4 for CAC and in Figs. 5 and 6 for CAB. The results of

Table 3. Raman intensity data with temperature for chloroacetyl chloride (CAC) and the resulting enthalpies ΔH° (*gauche-anti*).

Band pair (<i>anti/gauche</i>) / cm^{-1}	T/K						ΔH° / kJ mol^{-1} ^a
	208	228	248	268	298	320	
717/564	4.612	2.810	2.000	1.469	0.989	0.832	8.48
449/564	31.000	17.833	13.040	9.447	6.640	5.700	8.33
300/564	37.200	21.888	16.240	11.632	8.040	6.700	8.41
208/564	2.367	1.456	1.043	0.762	0.492	0.467	(10.32) ^b
208/186	23.200	12.643	8.167	5.600	3.708	2.800	(5.41) ^b

^a $\Delta H^\circ/\text{kJ mol}^{-1} = 8.4 \pm 0.4 \text{ kJ mol}^{-1}$ (this work); 5.82 ± 0.4 (Ref. 4, IR); 4.16 (Ref. 6, Raman); 7.82 ± 0.33 (Ref. 23, Raman). ^bValues omitted.

Table 4. Raman intensity data with temperature for chloroacetyl bromide (CAB) and the resulting enthalpies ΔH° (*gauche-anti*).

Band pair (<i>anti/gauche</i>) / cm^{-1}	T/K						ΔH° / kJ mol^{-1} ^a
	178	208	238	268	298	310	
1394/323	47.000	19.563	10.200	6.150	4.040	3.833	8.85
773/525	143.333	60.428	33.666	20.737	13.571	11.818	8.61
682/525	23.500	9.950	5.676	3.426	2.337	2.108	8.39
457/323	19.250	8.625	4.571	2.850	2.040	1.821	8.26

^a $\Delta H^\circ/\text{kJ mol}^{-1} = 8.5 \pm 0.4$ (this work); 5.9 ± 0.3 (Ref. 24, Raman).

the annealing experiments were quite similar whether argon or nitrogen was employed as matrix gas.

The IR matrix spectra can be used to evaluate ΔH° (*gauche* – *anti*) in the same manner as in the liquid state by Raman spectroscopy. Clearly, the large temperature range of typically 400–600 K which we have covered in the matrix experiments should be a distinct advantage for measuring enthalpies. This range can be compared with those generally used in isothermal vapour cells in Raman^{23,24} or IR^{7,8} spectroscopy, for which 100 and 60 K temperature spans, respectively, are common.

The small half-bandwidths of the matrix spectra in comparison with those of the vapour represent another advantage of the matrix spectra. A larger number of *anti* and *gauche* bands with no or with negligible overlap can be employed in the ΔH° calculations. From the spectra of CAC we have selected five *anti* bands and four *gauche* bands in the argon matrix and four *anti* and five *gauche* bands in nitrogen. Correspondingly, for CAB four *anti* and three *gauche* (argon matrix) and four *anti* and three *gauche* (nitrogen) bands were employed. Among these bands in CAC and CAB are the C=O stretches, lying around 1830 to 1780 cm^{-1} in the matrices. It has been noticed by all previous workers that an *anti* band at higher and a *gauche* band at lower wavenumbers for the C=O stretch are observed in the haloacetyl halide spectra. While they overlap too much to be used in the vapour of liquid states, these bands can be employed in the matrix spectra.

Table 5. Infrared intensity data with nozzle temperature for chloroacetyl chloride (CAC) from matrix isolation studies and the resulting enthalpies ΔH° (*gauche*–*anti*).

Band pair (<i>anti/gauche</i>) / cm^{-1}	T/K			ΔH° / kJ mol^{-1} ^a
	313	450	700	
Ar matrix				
1825/1790	4.043	2.362	1.862	3.68
1405/1790	1.153	0.822	0.624	2.89
976/1036	2.552	1.687	1.184	3.61
976/617	5.286	3.767	2.875	2.87
958/1790	0.891	0.607	0.492	2.81
958/1182	3.708	2.440	1.938	3.07
793/617	4.125	2.835	2.158	3.06
				Average 3.1 ± 0.5
N ₂ matrix				
1828/1783	7.908	4.896	3.551	3.78
1406/605	3.406	2.043	1.426	4.11
980/1783	4.246	2.604	2.059	3.43
960/1783	2.000	1.181	0.783	4.41
960/1189	7.434	3.620	2.076	6.01
960/1058	6.912	3.910	2.491	4.81
960/1041	4.690	2.414	1.539	5.26
				Average 4.5 ± 0.5

^a $\Delta H^\circ/\text{kJ mol}^{-1} = 4.06 \pm 0.2$ (Ref. 7, IR); 5.4 ± 0.4 (Ref. 1, gas-phase electron diffraction); 6.0 ± 1.7 (Ref. 23, Raman).

Table 6. Infrared intensity data with nozzle temperature for chloroacetyl bromide (CAB) from matrix isolation studies and the resulting enthalpies ΔH° (*gauche*–*anti*).

Band pair (<i>anti/gauche</i>) / cm^{-1}	T/K			ΔH° / kJ mol^{-1} ^a
	313	450	700	
Ar matrix				
1825/1798	5.123	2.975	2.038	4.35
1825/1026	9.350	5.087	3.107	5.18
1399/1026	2.411	1.347	0.787	5.25
949/1026	4.563	2.574	1.502	5.21
949/529	11.109	6.047	4.129	4.67
686/1026	17.425	9.942	5.770	5.18
				Average 4.9 ± 0.5
N ₂ matrix				
1827/1795	6.236	3.433	2.143	5.02
979/1025	0.833	0.462	0.308	4.69
979/524	2.778	1.452	1.000	4.83
958/1025	5.315	2.950	1.946	4.73
781/1025	1.126	0.696	0.457	4.24
781/524	3.963	2.319	1.485	4.61
				Average 4.7 ± 0.5

^a $\Delta H^\circ/\text{kJ mol}^{-1} = 7.78 \pm 0.27$ (Ref. 7, IR); 4.6 (Ref. 11, gas-phase electron diffraction); 4.3 ± 0.8 (Ref. 24, Raman).

In principle every *anti* band selected can be combined with every *gauche* band, making 20 combinations possible for both the argon and nitrogen spectra of CAC, and 12 combinations for both matrices of CAB. However, since no independent information can be achieved using all these combinations, the calculations were based upon a selection. For CAC seven band pairs from argon and seven from nitrogen (the band pairs were not all the same) were used in the calculations, as is apparent from Table 5. Correspondingly, six band pairs were used both in the argon and nitrogen matrix spectra of CAB, and the data are listed in Table 6.

All the measurements were carried out at three temperatures: (A) with no heating of the nozzle, which turned out to be 313 K, (B) 450 K and (C) 700 K. Some additional measurements were made at 900 K, but they are not included in the tables or the plots. Only one van't Hoff plot for CAB is given as an example in Fig. 7 (nitrogen). The ΔH° values calculated for each band pair are listed in the tables. The deviations in ΔH° as calculated from various band pairs are larger in the matrices compared with the Raman data of the liquids (Tables 3 and 4). Based upon all the data presented in Tables 5 and 6 the ΔH° (*gauche* – *anti*) values in the matrices are as follows (in kJ mol^{-1}): 3.1 (argon) and 4.5 (nitrogen) for CAC, and 4.9 (argon) and 4.7 (nitrogen) for CAB.

Compared with the earlier vapour values it can be seen from Tables 3–6 that the present results differ considerably and that the limits of uncertainty given by various researchers are generally too optimistic. All the ΔH° measurements

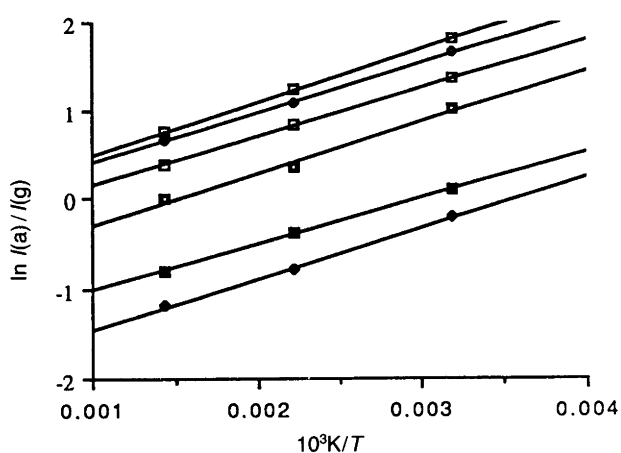


Fig. 7. van't Hoff plots of CAB from IR spectra in nitrogen matrices.

based upon vibrational spectra depend upon the conditions that the bands selected are 'pure' (i.e. have no contribution from the other conformer) and that the Beer-Lambert law is valid for the bands of each conformer at all temperatures. Practical factors, including the partial overlap of bands, a background which varies with temperature and very different intensities of the bands being compared, may severely restrict the number of bands suitable for ΔH° calculations. With modern FTIR and Raman spectrometers coupled with computers, some of these limitations have been partly overcome. However, it is our experience that band convolution procedures, for example, will not improve the precision of these measurements. Therefore, 'pure' bands which are well separated from others with reasonably flat backgrounds are required.

If the ΔH° values calculated from the matrix spectra are to be equal to those obtained in isothermal vapour cells the following conditions must be fulfilled: (a) no chemical reaction must take place during the heating of the matrix gas mixture; (b) the matrix gas mixture should reach the temperature of the nozzle and thermodynamic equilibrium be achieved between the conformers at the nozzle temperature; (c) the conformational equilibrium of the nozzle temperature should be maintained at the cold window during deposition, and no specific interaction between one (or both) conformer(s) and the matrix should take place.

Since no additional bands were detected in the spectra recorded with an elevated nozzle temperature compared to ambient, the first condition is fulfilled. The nozzle is made of quartz, since stainless steel caused pyrolysis of various organic compounds such as 1,5-hexadiyne at 500 K,²⁵ whereas quartz has worked successfully with a number of compounds. The nozzle tube is ca. 10 cm long, of which ca. 7 cm are heated, and it makes a 90° bend. Estimates have shown that this length should be sufficient for the gas to reach the nozzle temperature at the deposition rates employed. Our matrix unit has also given results for ΔH° (*gauche* - *anti*) in 1,2-dichloroethane (a popular com-

pound in conformational analysis) comparable to those reported in the vapour phase.

An important factor in deciding if the conformational equilibrium of the nozzle temperature is maintained at the cold window is the barrier to internal rotation between the unstable and stable conformers and the temperature of the window. Also the molecule/matrix ratio, the thickness and thermal conductivity of the deposit and the speed of deposition play a role. All these factors influence whether or not the molecules are quenched so fast at the window that they are unable to convert the conformer from unstable to stable. A simple plot²⁶ of the barrier to conversion against window temperature demonstrates that a nozzle temperature of 14 K should effectively trap a conformer with a barrier larger than 4-5 kJ mol⁻¹.

Asymmetrical torsional potentials for CAC and CAB have been derived from far-IR spectral data,^{23,24} giving 6.4 and 7.1 kJ mol⁻¹, respectively, for the conversion from *gauche* to *anti*. Therefore, the barriers in CAC and CAB should be sufficient for the *gauche* conformers to be trapped in the matrices at the cold window. However, it is not certain that the barrier obtained in the vapour phase is also valid in the matrices as recently observed for azidoethane.²⁷ When nozzle temperatures of 900 K were employed, the *gauche/anti* ratio for CAC and CAB appeared smaller than expected in the van't Hoff plots (Fig. 7), suggesting that the *gauche* conformer was not completely trapped at this temperature.

Spectral interpretations

Chloroacetyl chloride (CAC). Since the spectral assignments for CAC are fairly similar to those of Durig *et al.*,²³ only the cases for which we disagree with the earlier interpretations will be discussed.

In four instances bands were attributed²³ to overlapping *anti* and *gauche* conformers: 2965, 1186, 792 and 446 cm⁻¹. Separate bands belonging to *anti* and *gauche* were now detected for the three latter. The depolarized Raman band at 1180 cm⁻¹ was attributed to ν_{12} (*anti*), while the IR bands around 1177 cm⁻¹ were assigned as ν_6 (*gauche*). Closely spaced bands at 800 and 780 cm⁻¹ could barely be detected in the liquid, but were easily seen in the matrix spectra and are assigned as ν_9 (*gauche*) and ν_6 (*anti*), respectively. Also, ν_8 (*anti*) and ν_{12} (*gauche*) appeared as separate bands with distances of 6 and 5 cm⁻¹ in the argon and nitrogen matrices, respectively.

Some discrepancies exist between the assignments in the region 1000-900 cm⁻¹. The bands at 988, 974 and 955 cm⁻¹ all belong to the *anti* conformer, while 936 cm⁻¹ is a *gauche* band. The band at 974 cm⁻¹ with a depolarized Raman counterpart is assigned as ν_{13} , but previously²³ was attributed to ν_5 . We have instead considered the band at 955 cm⁻¹ with a polarized Raman counterpart as ν_5 , earlier²³ considered a combination(?). Furthermore, we have assigned the bands at 936 cm⁻¹ (earlier left open)²³ to ν_8 (*gauche*), whereas the bands at 900 cm⁻¹ are assigned as

$\omega_7 + \nu_{10}$ (*anti*) by us, previously²³ reported as ν_{13} . The Raman polarization measurements, the appearance (disappearance) of bands in the crystal and particularly the matrix spectra seem to support the present assignments.

Chloroacetyl bromide (CAB). Very few discrepancies exist between the earlier interpretations of Durig and Phan²⁴ and ours for CAB. However, a few bands listed in their experimental table might belong to PBr_3 , used in the synthesis of CAB from the chloroacetate. Some of these bands were also present in our spectra prior to an additional purification, and in the older spectra of Khan and Jonathan.⁷ It is very difficult to separate CAB and PBr_3 by distillation, and in our case preparative gas chromatography was used; not only once but twice. The four fundamentals of PBr_3 are situated at 392 (E), 378 (A), 163 (A) and 116 (E) cm^{-1} in our Raman spectra and reported at 392, 392, 161 and 116 cm^{-1} in the IR.²⁸ Additional, but weaker, bands were observed (in our non-purified sample of PBr_3) at 1018, 933, 757 and 517 cm^{-1} . We believe that the bands at 934, 756, 499, 384 and 164 and 115 cm^{-1} observed²⁴ in various phases and spectra and assigned as overtones, combinations and as *gauche* and *anti* fundamentals²⁴ are due to PBr_3 , since these bands were not found in our spectra.

All the fundamentals for the *anti* conformer agree with those of Durig and Phan,²⁴ while some discrepancies are found for *gauche*. The *gauche* fundamental ν_4 was considered²⁴ to overlap ν_3 (*anti*) at 1390 cm^{-1} , but we have instead assigned ν_4 to the band at 1417 cm^{-1} . Correspondingly, ν_6 (*gauche*) is attributed to bands around 1160 cm^{-1} rather than overlapping ν_{12} (*anti*).²⁴ Since the IR matrix bands at 917 (argon) and 916 (nitrogen) cm^{-1} vanish after annealing, ν_8 (*gauche*) is assigned to these bands rather than overlapping ν_{13} (*anti*).²⁴ The fact that the IR and Raman bands do not vanish upon crystallization may be due to an overlapping overtone $2\nu_{14}$.

We have not found a band for the C–Cl stretch (*gauche*) among the three peaks in the matrices around 785 cm^{-1} which remain after annealing, and therefore, like earlier workers,²⁴ consider ν_9 as overlapping ν_6 (*anti*). We assign the bands around 597 cm^{-1} vanishing in the crystal to ν_{10} (*gauche*), previously assigned to a combination.²⁴ A Raman shoulder reported at 518 cm^{-1} (and assigned to ν_{11})²⁴ was not observed by us. The two torsional modes for *anti* and *gauche* have been accurately determined in the far IR for CAC and CAB by Durig *et al.*^{23,24} and used for determining the torsional potential functions for both molecules.

Our assignments agreed reasonably well with the results of a force-constant calculation, to be reported elsewhere, which was carried out on the whole series of haloacetyl halides with an overlay technique.

Note added in proof. A paper on chloroacetyl chloride trapped in a xenon matrix appeared after the present work was submitted.²⁹

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References

- Nakagawa, I., Ichishima, I., Kuratani, K., Miyazawa, T., Shimanouchi, T. and Mizushima, S. *J. Chem. Phys.* 20 (1952) 1720.
- Mizushima, S. I., Shimanouchi, T., Nakagawa, I. and Miyake, A. *J. Chem. Phys.* 21 (1953) 215.
- Bellamy, L. J. and Williams, R. L. *J. Chem. Soc.* (1958) 3465.
- Tanabe, K. and Saeki, S. *Spectrochim. Acta, Part A* 28 (1972) 1083.
- Tanabe, K. and Saeki, S. *Bull. Chem. Soc. Jpn.* 47 (1974) 2754.
- Fausto, R. and Teixeira-Dias, J. J. C. *J. Mol. Struct.* 144 (1986) 225.
- Khan, A. Y. and Jonathan, N. *J. Chem. Phys.* 50 (1969) 1801.
- Khan, A. Y. and Jonathan, N. *J. Chem. Phys.* 52 (1970) 147.
- Aroney, M. J., Le Fevre, R. J. W. and Singh, A. N. *J. Chem. Soc.* (1965) 564.
- Van Eijck, B. P., Brandts, P. and Maas, J. P. M. *J. Mol. Struct.* 44 (1978) 1.
- Steinnes, O., Shen, Q. and Hagen, K. *J. Mol. Struct.* 64 (1980) 217; 66 (1980) 181.
- Saegebarth, E. and Wilson, E. B. *J. Chem. Phys.* 46 (1967) 3088.
- Durig, J. R., Phan, H. V., Hardin, J. A., Berry, R. J. and Little, T. S. *J. Mol. Struct.* 198 (1985) 365.
- Durig, J. R., Phan, H. V., Hardin, J. A. and Little, T. S. *J. Chem. Phys.* 90 (1989) 6840.
- Hagen, K. *Personal communication*.
- Durig, J. R. *Personal communication*, April 1988.
- Günthard, H. H. *J. Mol. Struct.* 80 (1982) 87.
- Squillacote, M. E., Sheridan, R. S., Chapman, O. L. and Anet, F. A. L. *J. Am. Chem. Soc.* 97 (1975) 3243; 101 (1979) 3657.
- Klaeboe, P., Gatial, A. and Nielsen, C. J. In: Jordanov, B., Kirov, N. and Simova, P., Eds., *Recent Developments in Molecular Spectroscopy*, World Scientific, Singapore 1989, p. 75.
- El-Bindary, A. A., Klaeboe, P. and Nielsen, C. J. *J. Mol. Struct.* 218 (1990) 73.
- Pattison, F., L. M., Fraser, R. R., O'Neill, G. J. and Wilshire, J. F. K. *J. Org. Chem.* 21 (1956) 887.
- Gatial, A., Horn, A., Klaeboe, P., Nielsen, C. J., Pedersen, B., Hopf, H. and Mlynek, C. *Z. Phys. Chem.* 1991, *In press*.
- Durig, J. R., Zhao, W., Lewis, D. E. and Little, T. S. *J. Chem. Phys.* *In press*.
- Durig, J. R. and Phan, H. V. *Struct. Chem.* 1 (1989) 61.
- Braathén, G. O. *Spectrochim. Acta Part A* 41 (1985) 933.
- Barnes, A. In: Barnes, A., Orville-Thomas, W. J., Müller, A. and Gaurès, R., Eds., *Matrix Isolation Spectroscopy*, Reidel, Dordrecht 1981, p. 531.
- Nielsen, C. J., Kosa, K., Priebe, H. and Sjøgren, C. E. *Spectrochim. Acta, Part A* 44 (1988) 409.
- Davis, P. W. and Oetjen, R. A. *J. Mol. Spectrosc.* 2 (1958) 253.
- Davidovics, G., Allouche, A. and Monnier, M. *J. Mol. Struct.* 243 (1991) 1.

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