The fundamental vibration-rotational band of gaseous DCI in absorption at 297 K and at 12 K

S. KLEE and J. F. OGILVIE*

Physikalisch-Chemisches Institut der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-6300 Giessen, Germany

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Abstract—Infrared spectra of gaseous deuterium chloride have been measured with an interferometric spectrometer in the region of the fundamental vibration—rotational band with resolution 0.23 m⁻¹. For these measurements the conditions were either a static sample of DCl in a conventional cell of length 0.27 m at 297 K or DCl in admixture with CO and argon flowing through a slit nozzle into an evacuated chamber. By means of adiabatic expansion the latter conditions produced a supersonic jet, in which the effective rotational temperature of both DCl and CO at the region of the measurements was (12 ± 1.5) K. The relative precision 0.004 m⁻¹ and absolute accuracy 0.04 m⁻¹ of the measurements of the bands of ²H³⁵Cl and ²H³⁷Cl of the static gas make the lines suitable as secondary standards for calibration of the scale of spectrometers in the range of wavenumber 189,000 < $\bar{\nu}/m^{-1}$ < 224,000.

INTRODUCTION

OF ALL possible volatile diatomic molecular compounds, hydrogen chloride is among the easiest to prepare and to handle in conventional cells for spectral measurements. In a comprehensive survey of data available on the IR spectra of the isotopic variants of HCl in both absorption and emission for the purpose of a collective determination of the potential energy function [1], we discovered that the fundamental band of deuterium chloride, ${}^{2}H^{35}Cl$ and especially ${}^{2}H^{37}Cl$, had been previously measured at a resolution [2] much inferior to that either of overtones of DCl or of several bands of other isotopic variants. For this reason we deemed advisable remeasurement of the fundamental band of a static sample at a resolution such that the instrumental line width was less than the width 0.42 m^{-1} attributed to dopplerian broadening at 297 K. In the event the standard deviation of the fit of the measured lines to the conventional band parameters surpassed that of any previous fits of vibration–rotational data of HCl, or indeed of most other species as well.

We measured the spectrum also under conditions of adiabatic expansion that produced a supersonic jet; by this means the rotational temperature of the molecules became greatly decreased from 300 K. Although the vibration-rotational absorption of several stable diatomic molecules has been measured in this way (for instance, Ref. [3]), apparently no hydride species had been included as a subject of primary interest; there have, however, been recent investigations of complexes between DCl and argon [4] or CO [5] under related experimental conditions, following many earlier measurements of complexes between hydrogen halides and diverse species [6]. In particular we sought to compare the effect of the rotational cooling of hydride and non-hydride species under the same conditions. For this purpose we undertook measurements on a supersonic jet containing both DCl and CO diluted in argon; this combination of absorbing molecules is convenient for concurrent spectral measurements because the fundamental bands lie adjacent in the mid-IR region, close enough to be examined readily within a single pass band but not greatly overlapping. The spectra measured under these diverse conditions and their analyses are the subject of this report.

^{*} Author to whom correspondence should be addressed. Present address: Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 10764, Taiwan.

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EXPERIMENTAL

The wavenumber scale of the interferometric spectrometer (Bruker, IFS 120 HR, Germany) was calibrated with respect to standard lines of CO [7] and SCO [7, 8]; the latter compounds were either added deliberately to the sample mixture or were present fortuitously to a minor extent. By means of a diffusion pump we evacuated the optical path of the interferometer outside the sample cell to a pressure less than 0.8 N m^{-2} , but even under these conditions spectral lines due to residual water vapour were observed because of the length (~10 m) of the optical path. For the spectral measurements of both static gaseous DCl at 297 K and the supersonic jet we used as source a glowing rod of SiC and as detector a photovoltaic device of InSb, with an optical filter having a band pass appropriate to the measured range of wavenumber.

We conducted the measurements of the gaseous samples in two ways. In both cases the DCl gas was prepared from the reaction of benzoyl chloride with D_2O [9]. Static samples of gaseous DCl at (297 ± 0.4) K, either containing only adventitious traces of SCO or with deliberately added CO, were contained at pressures ~ 210 N m⁻² in a cell of length 0.27 m. Samples of gaseous DCl in admixture with CO and argon were made to flow through a nozzle into a chamber evacuated to 10^{-4} N m⁻² (when no sample was flowing) by means of a diffusion pump of speed 6 m³ s⁻¹ in series with a Roots blower and a rotary pump. The orifice of the nozzle had the shape of a slit of length 1.0 mm and height 0.05 mm, determined by diffraction measurements with a He-Ne laser. The molecular jet and the focused beam of the IR radiation intersected perpendicularly 7 mm downstream from the orifice of the nozzle; the volume of intersection was determined experimentally to be within the core of the isentropic expansion. Under the operating conditions (the pressures of the sample gas behind the nozzle and in the expansion chamber), the Mach disk (beyond which region collisions of the molecules in the jet with those in the background lead to reheating of the adiabatically cooled gas) was located more than 10 mm downstream from the orifice of the nozzle. The DCl sample was maintained in a trap at \sim 143 K, cooled by a slush of pentane and liquid N₂; a premixed stream of gaseous argon and CO passed over the DCl to carry it through the nozzle. We adjusted the temperature of the slush bath and the flow conditions of the other gases so as to obtain approximately the following partial pressures/N m⁻²: DCl, 2000; CO, 5000 and Ar, 15,000. When the total pressure behind the nozzle was \sim 20,000 N m⁻², the background pressure in the expansion chamber was at most 0.2 N m^{-2} . The mechanical and optical design according to which the jet apparatus was coupled to the interferometer is described elsewhere [10].

ANALYSIS OF THE SPECTRA OF DCI IN THE STATIC SAMPLE

The vibration-rotational bands of almost pure gaseous DCl in absorption in a static cell, in the range of wavenumber $188,000 < \overline{\nu}/m^{-1} < 224,000$ (Fig. 1) consist of 33 measurable lines of each of ²H³⁵Cl and ²H³⁷Cl; by inspection we assigned directly the quantum numbers. Other lines near 190,000 m⁻¹ are due to water vapour in the incompletely evacuated optical path of the interferometer outside the sample cell. By means of the DECOMP program (version 2.5), we measured separately each isolated absorption line by fitting the interpolated profile to a convolution of lorentzian and dopplerian shapes within a small range of wavenumber about each line centre. On the basis of standard spectra of CO [7] and SCO [7, 8], the calibration factor 1.000000664 \pm 0.00000023 was applied to the fitted wavenumber signifying the centre of each line; this factor effectively adds an increment $\sim (0.13 \pm 0.04)$ m⁻¹ to the wavenumber of each line, and the absolute accuracy of the wavenumbers is consequently limited to ~ 0.04 m⁻¹. The relatively large standard deviation of the calibration factor arose because the intensities of few lines of CO in the spectrum of the static mixture of CO and DCl were suitable to provide usable measurements of the wavenumber, whereas all lines of SCO present adventitiously were so weak as to preclude measurements of the wavenumber of quality comparable with those of DCl. Lists of wavenumbers of the lines of ${}^{2}H^{35}Cl$ and ${}^{2}H^{37}Cl$ appear in Tables 1 and 2, respectively; the reproducibility and relative precision of the wavenumbers of the lines is deduced to be about 0.004 m⁻¹ except for the weakest lines, those having $J \ge 15$ of ²H³⁵Cl and $J \ge 14$ of ²H³⁷Cl, for which the precision degraded ultimately to 0.020 and 0.025 m⁻¹, respectively. From these wavenumbers of the lines of DCl we derived the spectral parameters of the bands according to two procedures. Using



Fig. 1. Spectrum of the fundamental vibration-rotational bands of gaseous ²H³⁵Cl and ²H³⁷Cl at 297 K; the total pressure was approximately 210 N m⁻¹ and the length of absorbing path was 0.27 m; some extraneous lines in the region 188,000-200,000 m⁻¹ are due to atmospheric water vapour outside the sample. The experimental resolution was 0.23 m⁻¹.

a commercial spreadsheet program [11], we fitted the wavenumbers by means of combination differences and sums to determine separately the parameters of each vibrational state from the combination differences and the band origin and a test of the differences of the band parameters from the combination sum; using a standard algorithm for general weighted linear regression [12], we fitted simultaneously all the band parameters. Although the former procedure yielded (on the same computer) almost the same numerical precision and standard deviation of the fit, there was no provision for the use of weights required to take into account the inferior precision of the

	$R(J)/m^{-1}$	$P(J)/m^{-1}$		
Calc.	Obs.	J	Calc.	Obs.
161.7863	210161.7845 21	0		
194.8823	211194.8832 21	1	208027.4737	208027.4711
204.8309	212204.8289 21	2	206926.9257	206926.9244
191.3060	213191.3076 21	3	205804.5674	205804.5727
153.9850	214153.9842 21	4	204660.7406	204660.7409
92.5492	215092.5528 21	5	203495.7892	203495.7911
06.6837	216006.6804 21	6	202310.0599	202310.0583
396.0775	216896.0790 21	7	201103.9015	201103.9025
760.4239	217760.4226 21	8	199877.6648	199877.6607
599.4205	218599.4231 21	9	198631.7026	198631.7079
12.7694	219412.7667 21	10	197366.3691	197366.3641
200.1771	220200.1782 22	11	196082.0201	196082.0202
61.3549	220961.3547 22	12	194779.0125	194779.0093
596.0188	221696.0192 22	13	193457.7042	193457.7105
103.8898	222403.8907 22	14	192118.4542	192118.4546
184.6940	223084.6801 22	15	190761.6217	190761.6067
738.1624	223738.1886 22	16	189387.5666	189387.5758
	218359.4231 21 219412.7667 21 220200.1782 22 220961.3547 22 221696.0192 22 222403.8907 22 223084.6801 22 223738.1886 22	10 11 12 13 14 15 16	197366.3691 196082.0201 194779.0125 193457.7042 192118.4542 190761.6217 189387.5666	197366.3641 196082.0202 194779.0093 193457.7105 192118.4546 190761.6067 189387.5758

Table 1. Observed and calculated wavenumbers of lines in the fundamental vibration-rotational band of ²H³⁵Cl

P(J)	/m ⁻¹		R(J)	/m ⁻¹
Obs.	Caic.	J	Obs.	Calc.
		0	209858.7803	209858.7781
207730.6819	207730.6797	1	210888.9190	210888.9181
206633.3852	206633.3859	2	211896.0127	211896.0141
205514.3795	205514.3770	3	212879.7454	212879.7416
204373.9897	204373.9924	4	213839.7760	213839.7797
203212.5739	203212.5737	5	214775.8116	214775.8113
202030.4611	202030.4654	6	215687.5202	215687.5231
200828.0143	200828.0139	7	216574.6018	216574.6057
199605.5655	199605.5678	8	217436.7524	217436.7541
198363.4827	198363.4777	9	218273.6719	218273.6676
197102.0899	197102.0960	10	219085.0545	219085.0504
195821.7860	195821.7770	11	219870.6150	219870.6112
194522.8782	194522.8765	12	220630.0605	220630.0642
193205.7463	193205.7521	13	221363.1280	221363.1284
191870.7644	191870.7624	14	222069.5075	222069.5289
190518.2565	190518.2677	15	222749.0179	222748.9960
189148.6706	189148.6296	16	223401.2883	223401.2664

 Table 2.
 Observed and calculated wavenumbers of lines in the fundamental vibration-rotational band of ²H³⁷Cl

wavenumbers of the weakest lines; because, particularly for ²H³⁷Cl, a few lines with J'' > 14 had ratios of signal to noise approaching unity, the proper use of all data required weighting and consequently the second procedure. The best sets of spectral parameters to reproduce the measured wavenumbers appear in Table 3, in which each indicated uncertainty denotes one estimated standard error of the associated parameter; the parameters determined by means of the first procedure differ inappreciably from those in Table 3. The standard deviations of the fits were 0.0037 m⁻¹ for ²H³⁵Cl and 0.0049 m⁻¹ for ²H³⁷Cl. Although the values of the parameters H_v for the centrifugal distortion are determined well, the parameters L_v of the succeeding order were found to have only marginal statistical significance; for this reason they were excluded from the final sets of parameters we have calculated the wavenumbers of the lines that appear in Tables 1 and 2. Both the standard deviations of the fits and the agreement between observed and calculated wavenumbers of the lines are consistent with the estimated precision of the measurements.

The apparent widths (full widths at half maximum absorbance) of these lines of DCl were $\sim 0.45 \text{ m}^{-1}$ for lines near the band centres, decreasing slightly towards each extremity of the bands. These values are comparable with what is expected, $\sim 0.42 \text{ m}^{-1}$, on the basis of dopplerian broadening at the temperature (297 ± 0.4) K of the static gaseous sample. The most intense lines of ²H³⁵Cl in both P and R branches were subject to effects of saturation, the complete absorption of light at the centres of the lines.

Table 3. Spectral parameters/m⁻¹ of the fundamental vibrationrotational band of ²H³⁵Cl and ²H³⁷Cl

	² H ³⁵ Cl	² H ³⁷ Cl	
	209105.8725 ± 0.0015	208805.9217±0.0019	
B_0	539.2274193 ± 0.00016	537.648826±0.00021	
D_0	$0.01399821 \pm 0.00000141$	0.01391087 ± 0.0000020	
$H_0/10^{-7}$	2.3437±0.038	2.1950 ± 0.056	
B ₁	527.984644 ± 0.00015	526.455790 ± 0.00020	
$\dot{D_1}$	$0.01386893 \pm 0.00000125$	0.01378649 ± 0.0000018	
$H_{1}/10^{-7}$	2.28619 ± 0.030	2.2691 ± 0.046	



Fig. 2. Spectrum of the fundamental bands of gaseous CO and DCl in a supersonic jet after expansion through a nozzle; a line of ²H³⁷Cl is indicated by an asterisk.

ANALYSIS OF THE SPECTRA OF DCI IN THE SUPERSONIC JET

The absorption spectrum of DCl, CO and argon in a gaseous mixture in the proportions approximately 2:5:15 expanded through the slit nozzle into an evacuated space appears in Fig. 2. The lines P_1 , R_0 , R_1 and R_2 of ²H³⁵Cl, P_1 , R_0 and R_1 of ²H³⁷Cl below 212,300 m⁻¹, and P_1 - P_5 and R_0 - R_5 of ¹²C¹⁶O above 212,300 m⁻¹ were detected; because rapid consumption of the available samples of DCl precluded protracted measurements, the ratio of signal to noise of the lines of DCl in Fig. 2 is inferior to that in Fig. 1. According to the same procedure as for the static sample of DCl, we measured the intensities of each individual line; the relative integrated intensities listed in Table 4 are subject to uncertainty of measurement ± 0.0005 (in the same units as those in the table) or $\pm 5\%$, whichever is greater. Fits of the logarithm of these intensities (divided by the wavenumber of the line and by the value of either J for lines in the P branch or J + 1 for lines in the R branch) to the rotational energy of the lower state yielded separate estimates of the effective rotational temperatures of ²H³⁵Cl, ²H³⁷Cl and CO; the influence of vibration-rotational interaction was neglected in these calculations of the relative populations of the effective rotational temperatures, another method was to compare

Table 4. Relative integrated intensities of lines of DCl and CO from the measurements of the supersonic jet

² H ³⁵ Cl	P	0.0133	2H37Cl	P_1	0.0030
	R_0	0.0351		R_0	0.0115
	R_1	0.0201		R_1	0.0061
	R_2	0.0018		-	
¹² C ¹⁶ O				R ₀	0.116
	P_1	0.0795		$\vec{R_1}$	0.155
	P_2	0.0680		R_2	0.106
	P_3	0.0356		R_3	0.0493
	P_4	0.0137		R.	0.0200
	P ₅	0.0028		R,	0.0038



Fig. 3. Plots of the relative rotational populations of CO and DCl in the molecular jet under various conditions of expansion: (a) free jet of pure CO at a pressure 20,000 N m⁻²; (b) CO at 5000 N m⁻² in argon at a total pressure 15,700 N m⁻²; (c) CO at 5000 N m⁻² with DCl at 2000 N m⁻² and argon at 15,000 N m⁻²; (d) ²H³⁵Cl in the jet of (c); (e) ²H³⁷Cl in the jet of (c). In each case the line represents a linear fit of data at small values of J.

visually the relative statures of the lines with those calculated at a particular temperature. By either means we deduce the effective rotational temperatures of the CO molecules to be (12 ± 1) K and of ²H³⁵Cl and ²H³⁷Cl to be (12 ± 1.5) K. The calculated spectra of CO and ²H³⁵Cl in Figs 4 and 5 may be compared with the experimental spectrum in Fig. 2.



Fig. 4. Calculated spectrum of the fundamental vibration-rotational band of gaseous ${}^{12}C^{16}O$ at 12 K.



Fig. 5. Calculated spectrum of the fundamental vibration-rotational band of gaseous ${}^{2}H^{35}Cl$ at 12 K.

The widths (full widths at half maximum absorbance) of the lines of both CO and DCl in Fig. 3 are -0.32 m^{-1} ; the latter value reflects the effective resolution of the interferometer under the conditions of operation, because the dopplerian widths of lines of CO and DCl at 12 K are estimated to be 0.10 and 0.08 m⁻¹, respectively.

DISCUSSION

The quality of the spectrum of gaseous DCl at 297 K has enabled the definition of the wavenumbers of the lines with a precision ~0.004 m⁻¹, an uncertainty of about 2% that of the values previously recommended [2]; consequently our values of the band parameters are far more precise than those previously determined [13]. This precision is consistent with expectation according to the relation $P \sim 0.6 (\Delta \bar{\nu})/R$ [14], in which $\Delta \bar{\nu}$ is the full width of the line at half maximum absorbance and R is the ratio of net maximum absorbance to twice the mean amplitude of the noise; for $\Delta \bar{\nu} \sim 0.4 \text{ m}^{-1}$ and $R \sim 50$, the reproducibility is estimated to be ~0.006 m⁻¹ for the more intense lines. For this reason we propose that the calculated values of the wavenumbers of the lines are applicable as secondary standards for the calibration of scales of IR spectrometers within the range of wavenumber 189,000 < $\bar{\nu}/m^{-1}$ < 224,000. To serve as such a standard, gaseous DCl proves convenient because a sample is relatively easily and inexpensively prepared in a sufficiently pure form, because the lines are readily assigned, and because they are available at intervals about 500 m⁻¹ throughout almost the entire specified range.

The rotational and centrifugal-distortion parameters of the ground vibrational states of both ${}^{2}\text{H}^{35}\text{Cl}$ and ${}^{2}\text{H}^{37}\text{Cl}$ have been determined [15] from pure rotational spectra in the range $0 \le J'' \le 16$; the values/m⁻¹ are for ${}^{2}\text{H}^{35}\text{Cl}$ $B_{0} = 539.2271966 \pm 0.0000137$, $D_{0} = 0.0139950 \pm 1.25 \times 10^{-7}$ and $H_{0}/10^{-7} = 2.25620 \pm 0.00306$; for ${}^{2}\text{H}^{37}\text{Cl}$ $B_{0} = 537.6490262 \pm 0.0000106$, $D_{0} = 0.01391294 \pm 1.01 \times 10^{-7}$ and $H_{0}/10^{-7} = 2.23239 \pm 0.00244$. For some lines the effects of both the coupling of the quadrupolar nuclei ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$ with the internal electric field and the interaction of the nuclear spin with the rotational angular momenta were observable [15]; the significantly smaller dopplerian broadening in the far-IR and the greater spectral resolution attained there relative to our measurements

enabled the detection of such effects. As a result of these advantages, the parameters of the ground vibrational states were determined about 10 times as precisely as from our measurements. When we constrained the values of the spectral parameters of the ground vibrational state to those determined from the pure rotational spectra [15], we derived the values/m⁻¹ of the parameters of ²H³⁵Cl $\tilde{\nu}_{1-0}$ =209105.8706±0.0021, B_1 = 527.984592±0.000083, D_1 =0.01386809±0.6×10⁻⁷ and $H_1/10^{-7}$ =2.26308±0.0185; of ²H³⁷Cl, $\tilde{\nu}_{1-0}$ =208805.92106±0.00275, B_1 =526.456050±0.000112, D_1 =0.013789447± 1.06×10⁻⁶ and $H_1/10^{-7}$ =2.3354±0.027. The respective differences of our values of B_0 , D_0 and H_0 from those from the pure rotational spectra [15] lie within about two estimated standard errors. The respective differences of the above values of the spectral parameters of the excited vibrational state, determined in the constrained fits, from those of the unconstrained fits of the mid-IR data fall also within about two estimated standard errors; the agreement is considered satisfactory in all cases. To reproduce the wavenumbers of the lines of DCl in the mid-IR, the values of the spectral parameters in Table 3 are adequate.

Following reports [4, 5] of complexes of DCl with argon and CO, we sought evidence of such complexes in our spectra of the supersonic jet, especially near 208,800 m⁻¹ (the location of both the P-branch of a band of ⁴⁰Ar²H³⁵Cl and the R-branch of the corresponding band of 40 Ar²H³⁷Cl) and 211,700 m⁻¹ (the location of a *O*-branch of another band of ⁴⁰Ar²H³⁵Cl); we found no evidence of matching lines. Explanations of these discrepant observations are that the diode laser [4, 5] enables a much greater sensitivity and that the pressure behind our nozzle was about one-tenth that in the reported experiments [4,5]. The former factor can be overcome by the use of more numerous scans, to improve the ratio of signal to noise and hence the sensitivity to minute absorptions: in the event the limited amount of sample available precluded such protracted measurements. The effect of the pressure before expansion of the sample is important because adiabatic cooling and formation of complexes proceed according to distinct molecular mechanisms: whereas cooling occurs on bimolecular encounters, formation of a complex requires a ternary collision (or the equivalent) during which the third body carries away the excess energy to effect stabilization of the complex. The rate of bimolecular collisions in the molecular jet near the nozzle is proportional to the product of the stagnation pressure and the width of the orifice, whereas the rate of ternary collisions depends on the product of the square of the molecular density and the width of the orifice; a relatively small pressure favours cooling whereas a large pressure favours formation of complexes. Although our use of helium instead of argon would have diminished further any susceptibility to form complexes, argon produces more efficient relaxation of the internal degrees of freedom of any complexes than helium because of the masses of argon and helium in relation to those of CO and DCl.

In the linear regression to determine the temperature we restricted the fit to the intensities of lines of small J. Although the resulting plots in Fig. 3 indicate extensive equilibration in the jet of free molecules, there are obvious deviations from linear behaviour at elevated values of J that we attribute to two effects. One is a gradual and systematic change of the shape of the spectral line with increasing J from a purely gaussian shape at small J to a flattened maximum at moderate J and even to a double maximum at J'' = 7 of CO; this phenomenon, which we have neglected in our analysis of the intensities, has been observed and explained previously [3, 10, 16, 17]. The other effect is absorption by background gas in the expansion chamber which has a correspondingly greater effective temperature than the gas in the jet; these molecules consequently contribute to absorption in particular lines according to their respective temperatures. Although there exists a further effect, namely orientational polarization in CO expanded from a slit nozzle [18], that might introduce an additional anomalous intensity for lines of small J in different branches, we found no evidence of this effect in our spectra.

That the rotational temepratures of CO and DCl in the same sample expanded through the nozzle were essentially the same provides qualitative information about the efficiency of the relaxation processes in the supersonic beam. Relative to a circular orifice in the nozzle, the rectangular orifice in our apparatus not only provided a greater length of absorbing path but also was less subject to less rapid decrease of density with distance from the orifice [19]. The relatively larger number of collisions consequently improved the equilibration between the internal and external degrees of molecular freedom; for this reason one expects the rotational temperature of the seeded gases, DCI and CO, to be nearer the translational temperature of the carrier gas, argon, if the orifice of the nozzle is rectangular rather than circular. The actual ratio of the length of the slit to its width was chosen as a compromise between the problems of precise mechanical manufacture of the metal slit and the fact that the attained aspect ratio-20-leads to hydrodynamic flow almost like that predicted to arise when the aspect of the slit has an infinite ratio [17]. A practical factor is that the area of the slit was limited by the throughput of the pumping system. Because there exists experimental evidence that CO in a supersonic jet can be cooled to less than 6 K [3] in appropriate conditions, the rotational temperature of CO in our experiment may represent accurately the effective temperature actually attained at the intersection of the radiant beam and the supersonic jet. Cooling in an expanded gas becomes inefficient when the temperature decreases to a value at which the thermal energy of the jet is comparable with the intervals of energy subject to non-radiative transitions in the process of relaxation [19]; for our molecules, $2hcB_0/k_B = 15$ K for DCl but 6 K for CO. Owing to the proximity of the atomic and molecular masses of argon, DCl and CO, the effect of velocity slip [20] should be minor in our conditions. A second factor that limits the cooling attainable in a seeded beam is the local temperature of the carrier gas. According to an empirical relation $M_T \approx$ $\theta(P_0w)^{0.4}$ [21], in which P_0 is the pressure of the gas at temperature T_0 upstream from the nozzle, w is the width of the orifice and θ is a proportionality factor that has a value 8.4 for $P_0/N \text{ m}^{-2}$ and w/m and we estimate the terminal Mach number M_T of the monatomic gas argon to be 8.4; from the definition of the Mach number M (the ratio of the average velocity of flow to the local speed of sound) and with $M = [5C_vT_0/(C_pT)]^{1/2} = M_T$, the terminal temperature becomes 13 K. Our application of this relation that was originally developed to treat the case of one-dimensional hydrodynamic flow from a circular orifice in a nozzle seems to be justified by the fact that the character of the pure planar flow of the expansion through a slit exists only a distance downstream equal to the product of the width of the slit and the ratio of the length to the width. The latter distance from the orifice in our experiment was 1 mm, much nearer the nozzle than the intersection with the radiant beam. Farther downstream the influence of axial symmetric flow prevails [16]. The agreement between the estimated translational temperature of argon from the jet and the experimentally derived rotational temperatures of the seeded species, both CO and DCl, demonstrates the efficiency of the processes of relaxation between translation and rotation that proceeded under the conditions prevailing in our expansion jet.

The data on the widths of lines in the spectrum of the supersonic jet require comment. The unapodized resolution in our measurements was 0.23 m⁻¹; thus the instrumental linewidth did not exceed $0.20 \,\mathrm{m}^{-1}$ because according to the weak function for our approximation the ratio of instrumental linewidth to resolution was in the range 0.6-0.9. When we deconvoluted the observed width (full width at half net maximum absorbance, 0.32 m^{-1}) by the instrumental linewidth, we found that the dopplerian broadening/m⁻¹ was $(0.32^2 - 0.20^2)^{1/2} = 0.25$ which corresponds to a translational temperature about 100 K. Three prospective explanations arise. If the various degrees of freedom are not in equilibrium, then one expects the effective temperatures to decrease in the order $T_{\rm vib} > T_{\rm rot} > T_{\rm transl}$, contrary to the observed order. The interferometer possibly failed to yield the intended resolution, which is related to the difference of the optical path multiplied by 0.9, but probably not to the applicable extent; under great magnification of a particular spectral line we discern a small but significant asymmetry that indicates only a small loss of resolution. A more likely explanation is that a non-uniform translational temperature exists in the free jet; what one measures under these conditions is a convolution of lines of various widths characteristic of molecules in different zones of the free jet at varying temperatures. This effect would yield a misleading estimate of the linewidth for molecules in the cold core of the jet. In test spectra of CO_2 on the same

apparatus, lineshapes were found to depend on the particular conditions of the gaseous expansion, the specific nozzle and the rotational state [10]. Hence the value 0.25 m^{-1} of the linewidth reflects the convolution of the effective resolution of the interferometer under the conditions of operation with the dopplerian width of the cooled molecules. If we suppose equilibration of the translational and rotational degrees of freedom at 12 K, we calculate the linewidths/m⁻¹ 0.10 for CO and 0.08 for DCl. The expected observable linewidth would therefore be 0.23 m^{-1} , just the effect of instrumental distortion. The increase by 30% to 0.32 m^{-1} is due to contributions from not only the inhomogeneous cooling [10] but also a residual Doppler shift resulting from a diverging flow in the planar jet [22].

The spectrum of ${}^{2}\text{H}{}^{35}\text{Cl}$ in the supersonic jet at 12 K contains essentially four measurable lines, conventionally labelled P_1 , R_0 , R_1 and R_2 . The number of lines discernible, or equivalently the effective rotational temperature, reflects to some extent the magnitude of the pressure in the reservoir behind the nozzle through which adiabatic expansion occurred. If deployment of the gaseous sample behind the nozzle had been practicable at a greater total pressure, then one might have expected that an effective temperature less than 12 K—and correspondingly fewer observable lines—would have been achieved; with increasing total pressure in the reservoir, only the line near 210,000 m⁻¹ might then eventually have remained. From spectra of complexes of HCl or DCl there exists indirect evidence that the terminal temperature in a jet is about 10 K, independent of both the pressure behind the nozzle and whether HCl or DCl is involved: expansion of DCl and argon from 5.2×10^5 N m⁻², a pressure about 25 times that in our experiments, led to a temperature about 13 K [4], whereas expansion of HCl and CO in argon from 1.7×10^5 N m⁻² yielded temperatures in the range 10–15 K [17].

Even containing four lines of ²H³⁵Cl, the spectrum in Fig. 2 has heuristic value, by contrast with the spectrum in Fig. 1, because clearly the most intense line under the conditions of the least attainable temperature is expected to represent transitions of molecules from the vibration-rotational state of least energy that is accessible. One line is dominant; this fact demonstrates the operation of a selection rule for the transitions. Moreover we envisage a further experiment that, although not implemented here, is certainly practicable: the analogue has long been performed in microwave spectroscopy. One could apply to the jet intense illumination from a monochromatic source (such as a klystron or an appropriate laser) of frequency equal to that of the pure rotational transition from J = 0 to J = 1 in the ground vibrational state; thus most molecules already relaxed to the state J=0 would be transferred to the state J=1 in the region of space in which the absence of collisions (under conditions of a sufficiently small background pressure) effectively precluded further relaxation again to J=0 by non-radiative means. Then interception of the sample in this prepared condition with the (relatively weak) beam of light for analysis by means of the absorption spectrum would enable observation of essentially two lines, P_1 and R_1 , instead of the single line R_0 dominant in the spectrum before application of the radiation from the laser. Clearly by this means one might progressively assign the lines of the absorption spectrum purely empirically, without reference to any particular quantum theory; on the other hand the few and narrow lines in Fig. 2 certainly indicate the applicability of quantum laws [23]. As molecular spectroscopy remains an experimental science, the fundamentally simple experiments that we can now perform, even if sophisticated instruments are required, illuminate the molecular mechanisms of spectral processes far better than the invocation of any particular quantum theory ex cathedra.

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