

Infrared–Radiofrequency Double-resonance Spectra and Pressure Broadening in the Enantiomers and Racemic Mixture of Gaseous 1,2-Dichloro-2-fluoroethanone

Daniel Hennequin, Pierre Glorieux and Ennio Arimondo†

Laboratoire de Spectroscopie Hertzienne, associé au CNRS, Université de Lille I, France

Myron W. Evans*‡

Department of Physics, University College of North Wales, Bangor, Gwynedd LL57 2UW

The frequencies and pressure broadening of some infrared–radiofrequency double-resonance absorptions are reported for the (–) enantiomer and racemic mixture of 1,2-dichloro-2-fluoroethanone at mTorr§ pressures. This is the first study of its kind, aimed at discerning spectral differences between an enantiomer and its racemic mixture at sub-Doppler resolution. The different frequency dependence of the lineshape in the enantiomer and racemic mixture as a function of pressure (*i.e.* collision rate) is a source of information on the statistical cross-correlation between vibration, rotation and translation during the intermolecular collision. Some differences in intensity have been found for the infrared–microwave double-resonance lines at 736 and 588 MHz on the 10 R32 CO₂ laser line, but these differences could be due to chemical and/or absorption phenomena or to a genuine intensity difference between the enantiomer and the racemate. Another radio-frequency resonance at 273 MHz was also investigated and the results are given in this paper together with their equivalents in all three lines in the racemic mixture. This high-resolution spectroscopic investigation does not show with a clear level of confidence the differences expected from the different statistical correlation between vibration, rotation and translation in enantiomer and racemic mixture.

It is probable that the highest frequency resolution in contemporary absorption spectroscopy can be reached by saturated absorption¹ and to a lesser degree by infrared radiofrequency double-resonance (i.r.r.f.d.r.).² This property has been exploited recently by Arimondo *et al.*^{2b} in a careful gas-phase study of the *R* and *S* enantiomers of camphor. An experiment was designed to try to detect those minute spectral differences in the laboratory frame absorption spectra of *R* and *S* enantiomers, predicted by nuclear (lepton) theory.

In this paper, we use the same technique to explore the i.r.r.f.d.r. spectra of the (–) enantiomer of 1-fluoro-1,2-dichloro-2-ethanone and its racemic mixture at mTorr pressure in the vapour phase. The purpose of the experiment is to try to observe with precision fundamental spectral differences between enantiomer and racemic mixture in the laboratory frame. Recent computer simulations^{3–9} have shown that the cross-correlation function (c.c.f.), $\langle v(t)J^T(0) \rangle_m$ for an *R* enantiomer is not the same as that for the *S* enantiomer. Two elements out of nine in the matrix $\langle v(t)J^T(0) \rangle_m$ are mirror images in time dependence. Here v is the molecular centre-of-mass linear velocity and J the

† Present address: IBM Corporation, Department 48B/428, Neighborhood Road, Kingston, New York 12401, U.S.A.

§ 1 Torr = 101 325/760 Pa.

molecular angular momentum, both defined in the frame of the principal molecular moments of inertia, a moving frame of reference.¹⁰ These same two elements vanish for all t in the racemic mixture, so that the symmetry of $\langle v(t)J^T(0) \rangle_m$ for the mixture is different from that of each enantiomer.

The experiment by Arimondo *et al.*^{2b} on the two enantiomers of camphor vapour showed that the i.r.r.f.d.r. spectra of both R and S enantiomers in the vapour phase were essentially identical at limiting frequency resolution. This resolution, although orders of magnitude greater than that obtainable in conventional microwave spectroscopy, was still not enough to detect the differences predicted by lepton theory. However, this experiment demonstrates with great precision that the moving frame differences in $\langle v(t)J^T(0) \rangle_m$ between R and S enantiomers do not affect the absorption frequencies of double resonance and inverse Lamb dip frequencies in the laboratory frame.

On the other hand, it is well known that the general physical properties of a racemic mixture are not the same as those of an enantiomer. The differences, *e.g.* in the refractive index, may sometimes be small, but may also be very large, especially as regards the freezing point. It is therefore reasonable in this context to expect that laboratory frame time correlation functions, such as the orientational autocorrelation function (a.c.f.) are also different. It is also well known that this a.c.f. is related by Fourier transformation to spectral lineshapes, broadened by collision.^{11,12} There is reason to suppose, therefore, that high-precision spectroscopy will reveal that the lineshapes (and possibly the frequencies of double resonance) of enantiomers are different from those of their racemic mixture.

This brings us to the point of this paper, which is to try to detect these differences⁹ and trace them to the difference in symmetry in c.c.f.s such as $\langle v(t)J^T(0) \rangle_m$ for an enantiomer and its racemic mixture.

The link between the lineshape and the symmetry of a c.c.f. such as $\langle v(t)J^T(0) \rangle_m$ of the moving frame of reference may be established as follows. We have seen that there is a well defined statistical difference between the molecular dynamics of R and S enantiomers.¹⁰ Therefore an observable difference in lineshape between enantiomer and racemic mixture can be traced to the statistical cross-correlation (*e.g.* between v and J) and provides, in principle, information on this fundamental statistical quantity.

Note that this type of reasoning can be extended to the cross-correlation between modes of intramolecular vibration and molecular rotation or translation. There is also the possibility, in principle, of extending the analysis to triple cross-correlations between vibration, rotation and translation. These correlations are, of course, neglected in the Born-Oppenheimer approximation (and also in the Onsager reciprocal relations). Finally, we note that the known symmetry differences in $\langle v(t)J^T(0) \rangle_m$ from computer simulation are entirely based on classical dynamics. If we were able to extend the analysis to quantum mechanics, then it might well turn out that rotation-vibration cross-correlations affect the positions as well as shapes of quantised i.r.f.d.r. spectra in enantiomers and racemic mixtures at mTorr pressures.

This paper is arranged as follows. First, the experimental method is described and sources of experimental uncertainty are discussed, including possible sources of impurity in the material under investigation. Secondly, the results are summarised and finally a brief discussion of the first reported i.r.f.d.r. spectrum of 1,2-dichloro-2-fluoroethanone is given.

Experimental

The experimental set-up is shown diagrammatically in fig. 1. The basic spectroscopic technique is fully described elsewhere.² For this work, however, an interface with a computer was constructed for analysing the pressure broadening of the double-resonance lines. A preliminary series of measurements on methyl iodide was made to check the

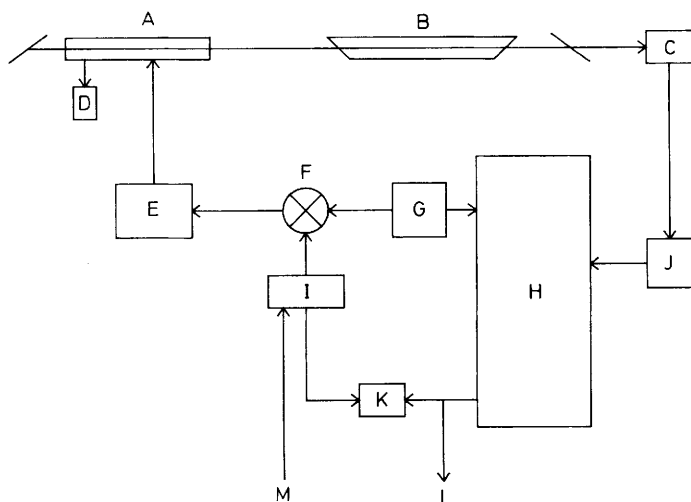


Fig. 1. Experimental set-up. A, Cell; B, laser; C, detector; D, attenuator; E, amplifier; F, mixer; G, low-frequency generator; H, synchronous detector; I, radiofrequency generator; J, 50 kHz selective amplifier; K, oscilloscope; L, information reduction; M, microprocessor.

set-up and uncertainty in the linewidth analysis before beginning a series of measurements on 1,2-dichloro-2-fluoroethane (CHFCICOCI).

I.r. radiation was produced by the rotation-vibration lines of a CO₂ laser. The gaseous sample under investigation is studied in a coaxial intracavity cell in which there is a radiofrequency field generated by a type 2000 Wavetek, covering the range of frequency from 10 to 1500 MHz. The signal is modulated by a square wave provided by a low-frequency generator at 50 kHz. The complete signal is amplified to *ca.* 1 W at the entrance to the cell.

The infrared radiation is detected by an HgCdTe cell cooled to liquid-nitrogen temperatures and the signal is amplified selectively with synchronous 50 kHz detection.

The sample pressure was measured with three separate types of gauge: (i) a digitised Datamatrix capacitor; (ii) a Penning gauge, which could be used to check the zero of the Datamatrix capacitor; (iii) Pirani gauges at different locations in the cell to check the pressure homogeneity.

An Ortec 9501 E lock-in amplifier with a time constant of 200 μ s meant that the total accumulation time could be reduced to *ca.* 1 min. This is important to counter any effects of sample degradation and pressure variations in the sample cavity.

Frequency control of the r.f. generator was assured with a microprocessor and the signal emerging from the synchronous detector was stored on 8 bits.

The microprocessor was interfaced to a Hewlett Packard 85 or 86 computer on which all this information making up the signal was stored, together with the measurement conditions: pressure, r.f. field, laser power *etc.*

Measurement Conditions for Methyl Iodide

The double-resonance spectrum of gaseous methyl iodide is already well known. The IOP4 line of the CO₂ laser was selected for use since it coincides with the ${}^{\pi}Q(11, 9)\nu_6 \leftarrow 0$ transition of CH₃I. Two r.f. frequencies at 246 and 400 MHz were used, corresponding, respectively, to a fundamental state and first rotational excited-state transition. The optimum conditions were attained with the maximum power of the r.f. generator (8 V cm⁻¹) and low power from the laser, <50 mW.

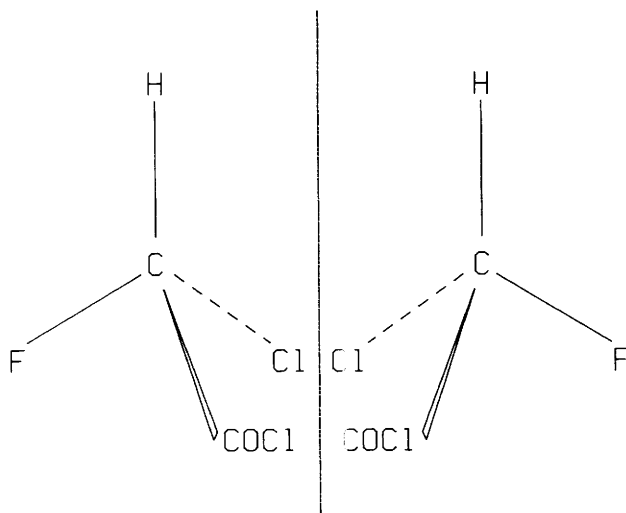


Fig. 2. The enantiomers of 1,2-dichloro-2-fluoroethanone.

Measurement Conditions for 1,2-Dichloro-2-fluoroethanone (CHFClCOCl)

The above trial run on methyl iodide indicated that the pressure broadening measurements on CHFClCOCl could be made with fixed laser and r.f. power because the broadenings of the double-resonance lines in CH_3I was found to be satisfactorily linear. (This is discussed in the results section.) In other words, pressure broadening (in MHz) with sample pressure (in mTorr) is a straight line with slope independent of laser and r.f. field power.

The CHFClCOCl molecule has seven atoms (fig. 2). Two samples were kindly synthesized by Mlle Molines of the Chemistry Laboratory of Thiais: *ca.* 1.5 cm^3 of the racemic liquid and *ca.* 0.05 cm^3 of the (-) enantiomer. This means that many more measurements were possible on the racemic species than on the enantiomer.

The vapour oxidises in the presence of water to form CHFClCO₂H. This is a fairly rapid process and meant that traces of water could not be allowed to contaminate the CHFClCOCl sample under investigation. Therefore, transfer of samples were made in an atmosphere of dry nitrogen, which was also used to try to keep the cells permanently free of water vapour.

It seems that the presence of chlorine in CHClCOCl produces an inherent instability at relatively high temperatures. This was observable by a colouring of the liquid and a degradation of the observed spectrum, notably in the (-) enantiomer. The spectrum disappears after a few hours of observation owing to thermal instability, water contamination or the effects of adsorption. Thus the measurements were performed with a total accumulation time reduced to *ca.* 1 min, in order to reduce the uncertainty in the sample pressure.

Results

Methyl Iodide

Treatment of Raw Data

At the end of a series of measurements the results stored on disk were treated as follows: the lineshape was fitted by least-mean-squares to a Lorentzian, with four adjustable

parameters for CH_3I : the central frequency, the maximum of the curve, the width of the Lorentzian at half peak height and baseline. Later the dependence of the Lorentzian width on the sample pressure was fitted by least-mean-squares to a straight line.

Precision of the Results

The precision of the linewidth estimates is affected by fluctuations in a number of experimental parameters and by uncertainty in their measurement. (i) The fluctuations in the power of the laser are small enough to be negligible. (ii) Uncertainty in frequency determination is introduced by thermal drift in the generator. This is usually sufficiently slow not to affect seriously the measurement of frequency difference between two lines. (iii) The greatest uncertainty is the measurement of pressure. In *ca.* 10 min the pressure changed by 1 to 2 mTorr, and for this reason total measurement time was reduced to 1 min or less as discussed already.

A number of different measurements were made on CH_3I in four groups (two groups for each radiofrequency used), one with a larger power ranging from 10–20 mW, the other with 40 mW. The measurements were spread over several days to test for reproducibility in the apparatus.

These results are summarized in fig. 3 for the two radiofrequency lines and different power levels in the laser.

In a range of pressure greater than 15 mTorr the linewidth appears to be a linear function of pressure. With different laser and radiofrequency powers, the straight line intersects the ordinate at different values. The displacement due to a change in laser power is comparable with that due to a change in r.f. power. The i.r. and r.f. Rabi frequencies have, therefore, the same order of magnitude. The data in fig. 3 have an estimated uncertainty of 15% in the experimental conditions under which the measurements are made.

CHFClCOCl

The CHFClCOCl molecule has not been observed previously by infrared-radiofrequency double resonance. Guided by some preliminary results due to Salomon,¹³ we investigated for the racemic mixture the region around the 10R34 line from 10R14 to 10R44. This exploratory work (fig. 4) showed that the 10R32 group has the advantage of isolated lines for the pressure-broadening measurements. A line at 736 MHz in the 10R32 group has the twin advantages of being nearly completely separated from its neighbours and being free of resonance satellite lines. A line at 588 MHz was also studied to provide an extra series of measurements in case the line at 736 MHz could not be used for the (–) enantiomer. When the latter sample became available this proved, indeed, to be the case; *i.e.* the 736 MHz line in the (–) enantiomer is so weak as to be almost unobservable in comparison with the equivalent line in the racemic mixture. Moreover, the spectra were also different at 588 MHz, *i.e.* this line also was vanishingly weak in the (–) enantiomer as compared with the racemic mixture.

However, this may not be definitely attributed to different intensities for the racemate and the enantiomer since the i.r.r.f.d.r. method proved to be very sensitive and the abovementioned lines could originate from contaminants in the sample or residues from the synthesis.

In contrast, the line at 273 MHz in the 10R32 group is similar in intensity in both the (–) enantiomer and the racemic mixture. The pressure-broadening results are summarised in fig. 5 for the three lines available for the racemic mixture (588, 736 and 273 MHz), and for the 273 MHz line in the (–) enantiomer. The best straight line for the racemic mixture gives $14.6 \pm 0.7 \text{ kHz mTorr}^{-1}$ for the two laser powers used. The 16 measurements available for the (–) enantiomer are more scattered than those for the

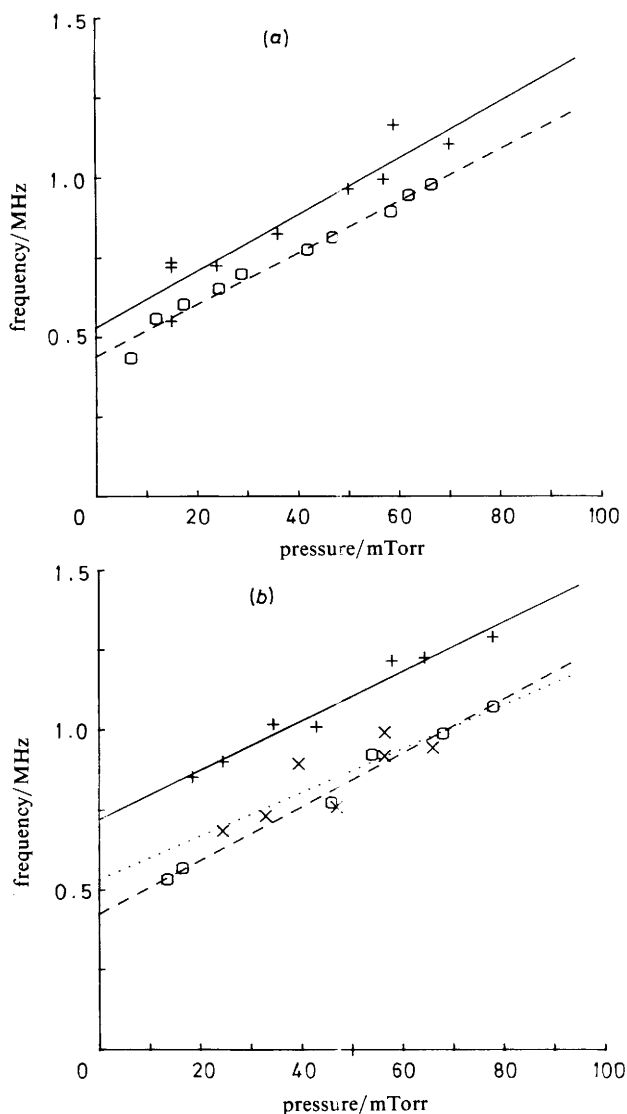


Fig. 3. Pressure broadening curves for methyl iodide. (a) 264 MHz r.f. line: (+) laser power 40 mW, r.f. power 1 W, slope, 8.7 ± 0.9 kHz mTorr⁻¹. (□) Laser power 20 mW, r.f. power 1 W, slope, 8.1 ± 0.9 kHz mTorr⁻¹. The full and dashed lines are the least-squares fits of the (+) and (□) experimental data, respectively. (b) 400 MHz r.f. line: (+) laser power 40 mW, r.f. power 1 W, slope 7.7 ± 0.7 kHz mTorr⁻¹. (□) Laser power 20 mW, r.f. power 1 W, slope 8.4 ± 0.5 kHz mTorr⁻¹. (x) Laser power 40 mW, r.f. power 0.1 W, slope 6.8 ± 1.9 kHz mTorr⁻¹. The full, dashed and dotted lines are the least-squares fits of the (+), (□) and (x) experimental data, respectively.

racemic mixture. If we take all 16 available points, the result is 10.8 ± 3.8 kHz mTorr⁻¹. If one point at low pressure is ignored, the slope is 14.4 ± 3.0 kHz mTorr⁻¹.

All in all, therefore, it seems that within experimental uncertainty there is no convincing evidence of a difference in the pressure broadening in the enantiomer and in the racemic mixture.

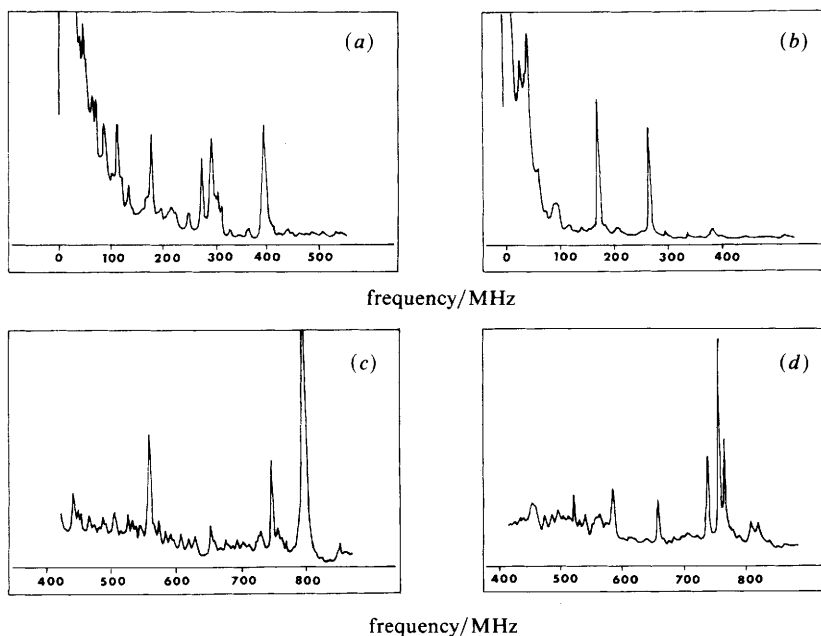


Fig. 4. R.f. lines measured with the $10R32CO_2$ laser line for different laser frequencies in different r.f. ranges. Spectra (a) and (b) cover the 0–500 MHz range, while spectra (c) and (d) cover the 400–900 MHz range, laser frequencies differing by *ca.* 25 MHz.

Discussion

It seems that there are no insurmountable problems in comparing the collisional broadening of optical isomers with i.r.f.d.r. The technical problems to be overcome are: sample purity and degradation, thermal instability, degassing, adsorption *etc.* However, to provide corroborative evidence for the spectral differences found in these observations, similar measurements are being made on the enantiomer and racemic mixture of camphor vapour, which is more stable chemically and whose i.r.f.d.r. spectrum is known from the work of Arimondo *et al.* on the separate enantiomers.^{2a}

Computer Simulation

In order to provide some qualitative and indirect theoretical support for these observations, which reveal the effect of cross-correlations such as $\langle v(t)J^T(0) \rangle_m$ in the laboratory frame, a series of computer simulations was carried out on the closely similar (but rigid) molecule fluorochloro-acetonitrile. These are reported fully in the literature^{6,8} in the supercooled liquid state because computer simulations in the dilute gas are not feasible for economic reasons. These simulations show clearly that the (1,3) and (3,1) elements of $\langle v(t)J^T(0) \rangle_m$ are mirror images in their time dependence, and the effects in the laboratory frame^{8,9} show up as differences in autocorrelation functions such as the rotational velocity autocorrelation function, the Fourier transform of the conventional far-infrared spectrum of the liquid phase. However, the infrared–radiofrequency double resonances recorded in this paper provide enormously greater precision as regards frequency resolution than conventional far-infrared absorption spectroscopy is currently capable of. However, there is experimental evidence¹⁴ to show that the conventional

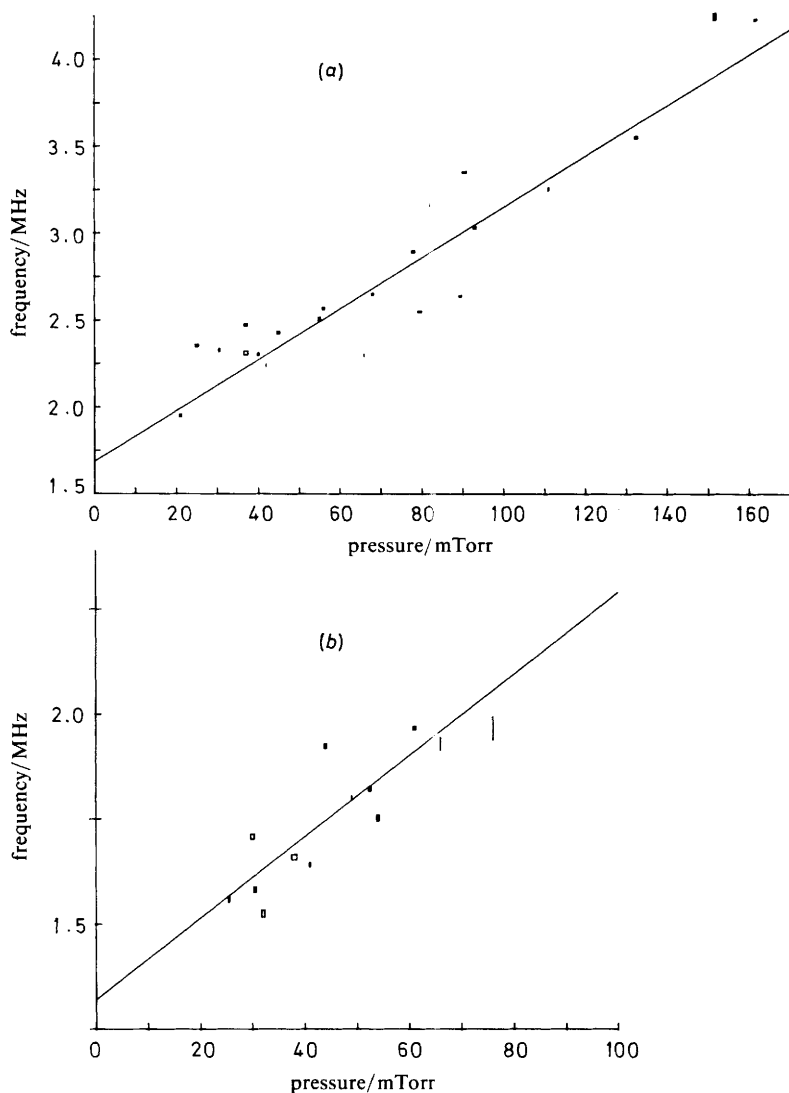


Fig. 5. (a) Pressure broadening for the racemic mixture of CHFCICOCl. Slope = 14.8 ± 1.1 kHz mTorr⁻¹; data from three double-resonance lines, see text. (b) As for (a), (-) enantiomer, data from one line only.

infrared power absorption of an enantiomer in the liquid state is significantly different from that of its racemic mixture. The lack of precision in resolution is offset by the fact that the density of the liquid is much greater than those of the dilute gases used here. These differences are again expected on the basis of symmetry differences in cross-correlations such as $\langle v(t)J^T(0) \rangle_m$.

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