Strong Coriolis coupling between v_5 and v_{11} states of CH_3CCl_3 studied by millimeter-wave spectroscopy

Zbigniew Kisiel [a,*], Lech Pszczółkowski [a], Gabriele Cazzoli [b], Luca Dore [b]

[a] *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*
[b] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, via F. Selmi 2, 40126 Bologna, Italy*

ABSTRACT

Rotational transitions in vibrational states $v_5 = 1$ and $v_{11} = 1$ in the oblate $CH_3C^{35}Cl_3$ molecule have been studied at frequencies from 69 to 332 GHz. The two states belong to the second lowest wavenumber *A*-symmetry, and *E*-symmetry normal modes, and are accidentally very close in energy. They are thus strongly coupled by $(x - y)$ Coriolis interaction, in addition to the *l*-type resonance in the degenerate $v_{11} = 1$ state. The resulting rotational transitions form three characteristic band series, which show many manifestations of strong interstate coupling. Frequencies of well over 1000 transitions have been measured and fitted to within experimental accuracy, resulting in $\Delta E_{5,11} = 2.41204(3)$ cm^{-1}, first values of the axial constants for this molecule, $C_5 = 1709.966(7)$, $C_{11} = 1712.462(7)$ MHz, and of values for the pertinent Coriolis coupling coefficients, ζ^c_{11} and $\zeta^b_{5,11}$, which are in good agreement with results of *ab initio* calculations.

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1. Introduction

1,1,1-Trichloroethane (methyl chloroform, CH_3CCl_3) is in widespread industrial use and many of its gas-phase spectroscopic studies were stimulated by interest in atmospheric monitoring. The rotational spectrum of CH_3CCl_3 is now known in considerable detail, with the ground state of the parent species studied at room-temperature up to 678 GHz in the quest for the elusive $K = 3$ splitting [1], and in supersonic expansion in the analysis of fully resolved nuclear hyperfine structure [2]. Rotational transitions in the lowest frequency *E*-symmetry mode, v_{12}, and the lowest frequency *A*-symmetry mode, v_6, have also been assigned [3]. The v_6 torsional mode has recently been revisited and a global fit of rotational transitions in the ground state, v_6, and $2v_6$ has been reported [4]. Since CH_3CCl_3 contains three symmetry equivalent chlorine nuclei the spectrum of the single ^{37}Cl isotopologue is as intense as that of the parent, which stimulated a detailed study of all species containing ^{37}Cl [5].

It would thus appear that the room-temperature rotational spectrum of CH_3CCl_3 should hold no major surprises. Many measurable excited state species still remain to be assigned but those would be expected to give rise to weak groups of lines positioned

close to ground state bands of the respective isotopologues. It was therefore with some surprise when broadband millimeter-wave spectra of CH_3CCl_3 revealed the presence of two intriguing band series positioned midway between successive $J + 1 \leftarrow J$ transitions of the parent species, Fig. 1. The two band series, given working designations X_1 and X_2 were, after a time, complemented by a third, X_3, and evidence was obtained that the three series constitute a joint set. The band series, at least near the bandhead, exhibit apparent symmetric top character, but with effective values of D_{JK} that may exceed that in the ground state by well over an order of magnitude, and can also differ in sign. The assignment and successful analysis of these band series in terms of rotational transitions in strongly coupled $v_5 = 1$ and $v_{11} = 1$ states of the parent isotopic species of CH_3CCl_3 is presented below.

2. Experimental details

The mm-wave spectra were recorded over the frequency region 69–332 GHz by using two different millimeter-wave spectrometers: the BWO-based, broadband spectrometer in Warsaw [6,7], and the harmonic generation spectrometer in Bologna [8]. Measurements were performed on a static, room temperature sample of standard commercial origin. The sample was contained at pressures from 5 to 30 mTorr in absorption cells of 3 to 4 m length.

* Corresponding author. Fax: +48 22 8430926.
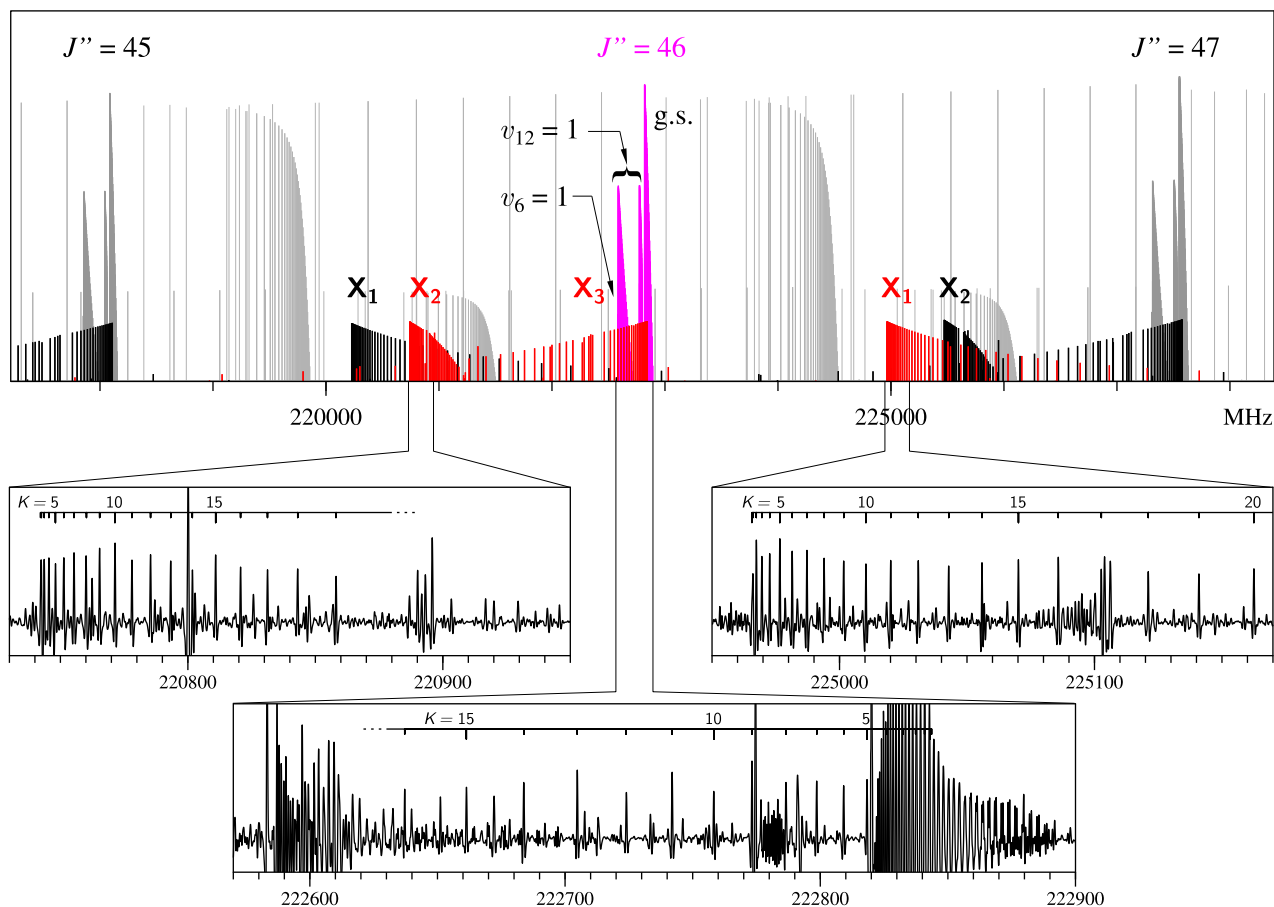 *E-mail address:* kisiel@ifpan.edu.pl (Z. Kisiel).

Fig. 1. The location and the appearance of the three new symmetric top-type bands in the rotational spectrum of CH_3CCl_3. The first two bands, given working designations X_1 and X_2, were identified midway between successive $J+1 \leftarrow J$ transitions of the parent species, but exhibited an order of magnitude greater dispersion in K than the ground state lines. An even more diffuse band, X_3, was then found with origin close to that of the ground state, but evolving to low-frequency. The top pane collects predictions based on final fits and the three new bands for $J'' = 46$ are identified with the same color. The strong faint bands are formed by ground state transitions of the $^{37}Cl_1$ isotopologue, and the weaker ones are due to the $^{37}Cl_2$ isotopologue.

In the final stage of the analysis all of the recorded spectra were combined into a single spectral file and were processed using the recently developed AABS software package for Analysis and Assignment of Broadband Spectra [9]. This package allows efficient operation on a spectrum composed of spectral segments that are not necessarily contiguous in frequency. The spectrum can be compared against collected predictions for as many spectroscopic species as desired, and data sets for several different fitting programs can be constructed rapidly. Loomis–Wood type display options allow graphical assignment of the spectra. Detailed documentation and the package itself are freely available on the PROSPE website [10], and recent examples of the use of the AABS package can be found in [11–13].

3. Rotational spectrum

The first task in the analysis was to derive some clues as to the origin of the new bands. It was not immediately clear which isotopic species they belonged to, which is the pertinent vibrational state, and finally what is the quantum number assignment. The evidence that bands X_1 and X_2 belong to $^{35}Cl_3CCH_3$ as well as for their J assignment was derived from the Fortrat type diagram shown in Fig. 2. The assumption of the same J value for adjacent X_1 and X_2 bands would require the presence of another band or bands positioned on the other frequency side of the ground state (normal or isotopic) species with the same J. This was not supported by observation since we observed only two and not three

new bands at frequencies well removed from the strongest isotopic ground state bands. On the other hand assumption that in an adjacent X_1, X_2 pair the X_2 band is for J'' corresponding to the ground state transition to high frequency from it, and X_1 has J'' of the ground state transition to low-frequency from it, leads to a more promising picture. The values of $B_{eff} = v/[2(J+1)]$ for the two bands are symmetrically disposed around that for the ground state of the parent species, and the correspondence becomes even closer if frequency differences between successive J transitions are used. This argument, when combined with relative intensity considerations, made it possible to assign new bands to the next higher unassigned excited vibrational states in $^{35}Cl_3CCH_3$, namely second lowest A-symmetry mode, v_5 and the second lowest E-symmetry mode, v_{11}. Ab initio calculations and the available information on the infrared spectrum [14] indicated that the wavenumbers for these modes are both in the 350 cm^{-1} region. There is still a problem in that it was unlikely that the bands X_1, X_2 reflected interstate interactions completely since the progressions of lines away from the bandheads were in both bands in the same direction.

At this point further analyses of the problem were performed with program MILLI [15,16] of G. Graner, which allowed exploration of the effect of the major interaction terms anticipated to couple the v_5 and v_{11} states. The values of the relevant Coriolis coupling coefficients were calculated using program VIBCA [10], from the harmonic force field evaluated with the PC-GAMESS version of the GAMESS package [17,18]. It is at that stage that the third band series, X_3 in Fig. 1, was located. The J assignment did not cause any problem since this band originated very close to the ground state