ASSIGNMENT AND ANALYSIS OF COMPLEX ROTATIONAL SPECTRA

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Abstract. Rotational spectra of even simple molecules can pose serious interpretational difficulties, especially in the high-J conditions of spectroscopy in the environmentally relevant mm-wave region. In recent years several useful techniques for dealing with such spectra in the laboratory have become apparent. These include the choice of the most suitable experimental tools, more detailed understanding of the characteristic features of high-J rotational spectra of asymmetric top rotors, more confident prediction of centrifugal distortion and nuclear quadrupole splitting terms in the Hamiltonian, and the use of more powerful computer programs.

1. Introduction

Laboratory rotational spectroscopy is essential for understanding gas-phase environmental spectra, and it is also the source of key data for analytical applications in environmental spectroscopy. It is perhaps surprising that rotational spectra of even rather simple and rigid molecules of environmental importance can often pose severe interpretational difficulties. These may arise from lack of characteristic spectral features due to low molecular symmetry, overlaps of transitions allowed by several dipole moment components and of transitions in low lying vibrational states. In the mm-wave region of the spectrum, which is currently of particular atmospheric and astrophysical relevance there is the possibility of overlaps of transitions from plethora of transition rules and a broad range of quantum numbers. The presence of quadrupolar nuclei in the molecule may also introduce non-negligible nuclear quadrupole structure. In the room-temperature rotational spectrum of even some halogenomethanes, such as $CBrClF_2$ and CH_2I_2, such issues
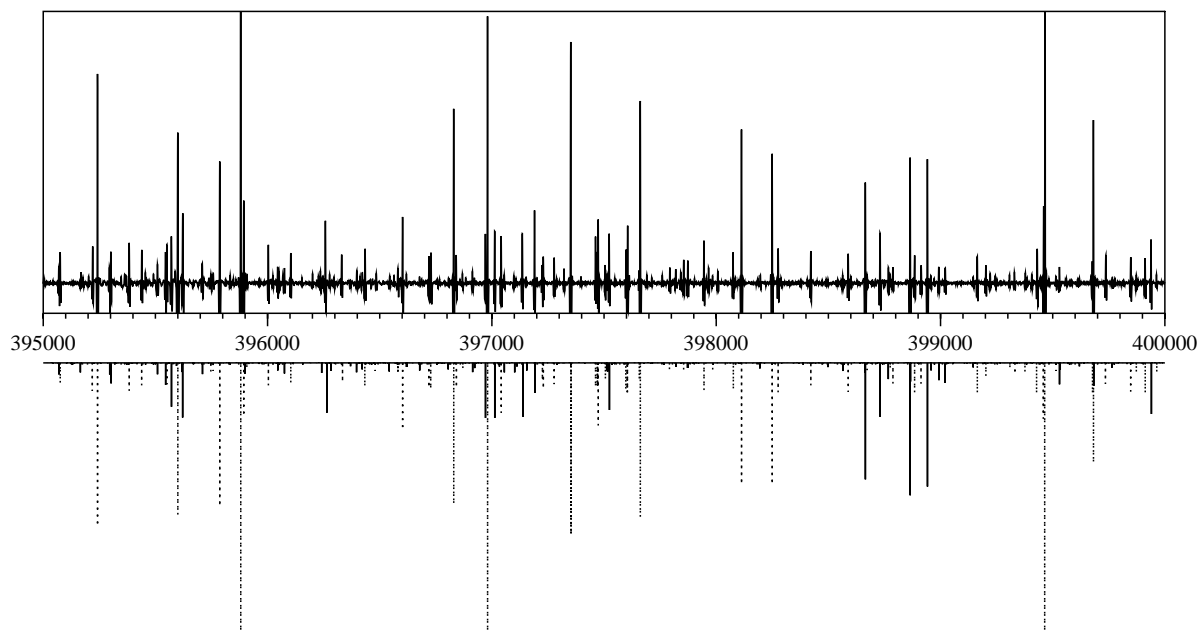
Figure 1. The observed (top) and predicted (bottom) room temperature spectrum of the HCFC-22 freon, CHF_2Cl in natural abundance. The experimental spectrum is a 5 GHz portion out of a single 10 GHz recording. The prediction encompasses the common isotopic species (dotted lines) and the ^{37}Cl isotopomer (continuous) lines and includes transitions in the ground states, and the low lying vibrational states $v_5 = 1$, $v_6 = 1$, and $v_9 = 1$.

precluded assignment with the popular Stark modulation spectrometers working in the 8-40 GHz region.

Over the recent years several molecules of this type have been successfully studied in the author's laboratory in Warsaw, and also in cooperation with several other research groups. These include the well known halon $CBrClF_2$ [1, 2], the freon HCFC-22 (CHF_2Cl) [3], trichloroethylene $Cl_2C=CHCl$ [4, 5] and 1,1,1-trichloroethane Cl_3CCH_3 [6, 7, 8]. Both serendipity and design led to the development of useful guidelines and techniques for facilitating such studies. The culmination of judicious application of these techniques has been the successful analysis of the rotational spectrum of methylene iodide, first of the normal isotopomer CH_2I_2[9], then of its deuterated isotopomer, CD_2I_2 [10], and finally of the extensive vibrational satellite structure [11].

2. The choice of a suitable spectrometer

Laboratory rotational spectroscopist has a powerful array of tools at his disposal. Currently some of the most useful appear to be broadband millimetre-wave rotational spectroscopy of a static sample, free-jet millimetre wave spectroscopy, and cavity Fourier transform spectroscopy of supersonic ex-

pansion. There are also many operational Stark modulation spectrometers for the region around 8-40 GHz, as well as several waveguide Fourier transform spectrometers operating at similar frequencies. In cases of complex spectra it is best to apply these techniques in an appropriate sequence to take advantage of a certain 'separability' of the spectroscopic problem, so that various parts of the spectroscopic Hamiltonian can be determined nearly independently.

Spectroscopy of the millimetre wave region is of most immediate relevance to environmental studies and the most powerful tools for this frequency region are based on broad-band backward wave oscillator (BWO) sources, and in particular on the excellent devices available from the Russian company Istok. Following the pioneering work of Krupnov and coworkers [12] and changes in the political climate spectrometers based on these sources have gained worldwide circulation. Operation well into the submillimeter region is possible and particularly active instrumental development is currently being pursued by G.Winnewisser and colleagues in Cologne [13]. A typical example of the capabilities taken from the spectrometer in Warsaw is shown in Fig.1 [3]. High resolution recordings over many GHz are possible, which is very desirable when dealing with complex spectra, since they may be either incompletely or altogether unassigned at the time of recording. Large regions of the rotational spectrum can be measured with relatively small demand on spectrometer time. If signal to noise ratio in such recordings is sufficiently high then appropriate software tools can be applied off-line in a process of analysis, which can reveal new features in the spectra for a long time after the recording. As an example the set of spectra originally recorded for the study of the ground states of $CBrClF_2$ isotopomers [1], was reprocessed in a second stage of analysis to assign transitions in three lowest excited vibrational states [2].

If the room temperature mm-wave spectrum is too rich owing to rotational transitions in low-lying vibrational states then the tool of choice is spectroscopy of a sample cooled on isothermal expansion through a nozzle. The free-jet, Stark-modulation technique pioneered by Brown and coworkers in Monash is attractive since the degree of rotational cooling (to *ca* 10-20 K) is still compatible with observation of spectra in at least the lower part of the mm-wave region. This method enabled the first analysis of the rotational spectrum of of $CBrClF_2$ [14] through elimination of transitions in vibrationally excited states. In combination with a broad-band BWO-based frequency synthesizer this technique becomes extremely useful and efficient as demonstrated in the spectrum in Fig.2 [10] obtained with the free-jet spectrometer developed by Favero and Caminati in Bologna. The difficulty in assigning the rotational spectrum of the structurally simple methylene iodide molecule was due to the combination of extensive nuclear
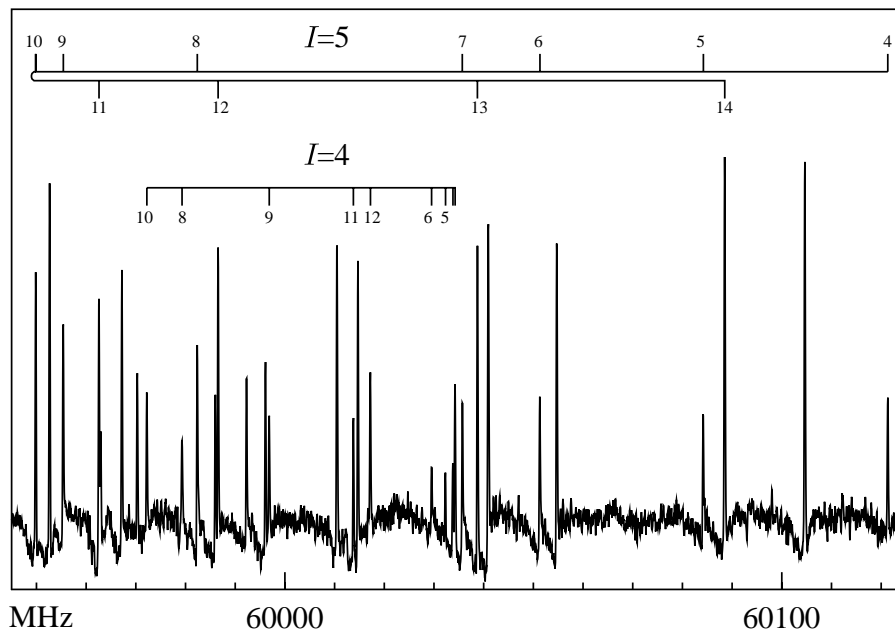
Figure 2. The $10_{2,9} \leftarrow 9_{1,8}$ rotational transition of CD_2I_2 at 60 GHz recorded with a free jet spectrometer at a rotational temperature of *ca* 10K. All of the expected 36 hyperfine components are visible, some of which are unresolved doublets. The spins are coupled using $I = I(I_1) + I(I_2)$, $F = I + J$ and the F quantum number assignment for the two highest values of the quantum number I is indicated.

quadrupole hyperfine patterns from the two iodine nuclei with rich structure of transitions in excited vibrational states of the ∠ICI bending mode, the frequency of which is only 121 cm^{-1}. Broad-band scans made with the free jet spectrometer eliminated the excited states, and were possible in a region in which hyperfine structure of rotational transitions was sufficiently compact so that complete, isolated quadrupole patterns of individual rotational transitions could be recorded, as in Fig. 2. This made assignment of the rotational quantum numbers reasonably straightforward. Comparison of broad band recordings of several transitions then made possible the identification of the effect of nuclear spin statistical weights on the intensities of the hyperfine components and assignment of the nuclear spin quantum numbers [9].

Finally the highest resolution and coverage of transitions with lowest values of J can be obtained if the sample is studied in full supersonic expansion, so that sub-Doppler spectra can be recorded. Since rotational cooling is typically to *ca* 1K the maximum in the rotational absorption envelope is usually well below 20 GHz. The microwave measurements can therefore be made with high efficiency with the cavity Fourier Transform (FTMW) method, as pioneered by Balle and Flygare [15]. The only drawback is that scanning is still not the strong point of such spectrometers.
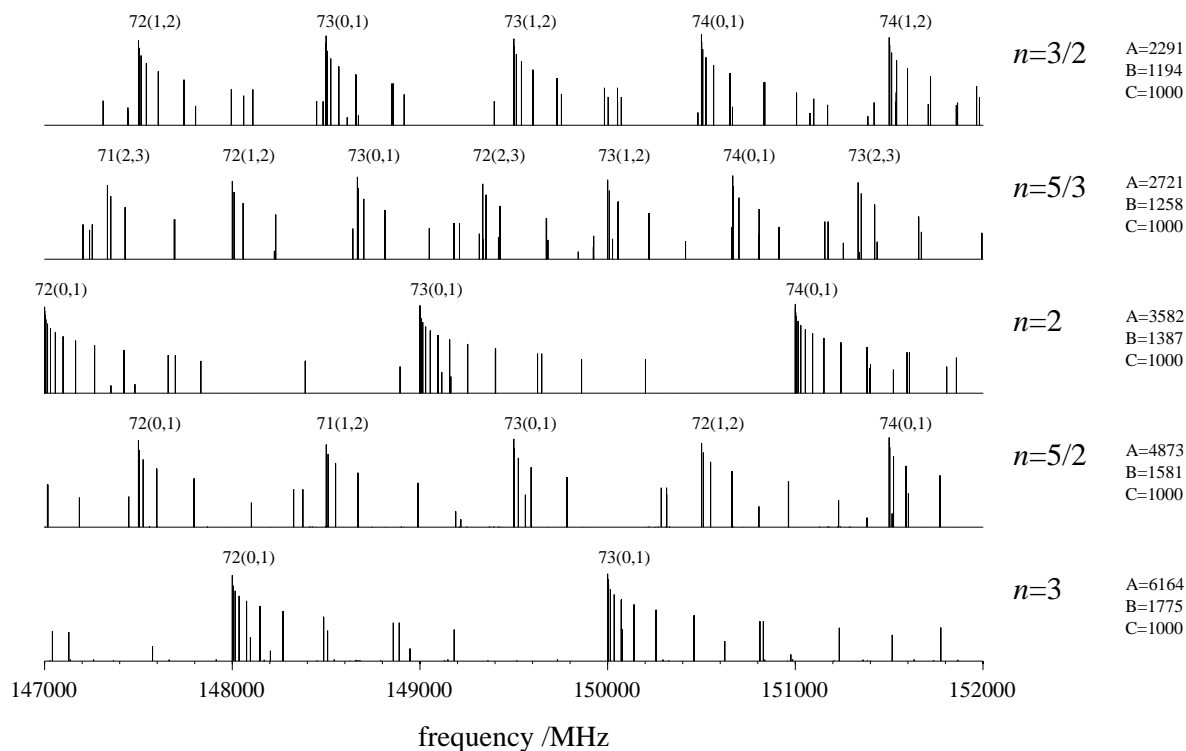
Figure 3. The oblate type-II$^+$ R-type bands, which arise for several values of the oblate limit condition $n = l/m = (A + B)/2C$. All plots are for a rotor with $\kappa = -0.7$ and C=1000 MHz. The quantum numbers $J(K_{-1}^a, K_{-1}^b)$ of the two degenerate lower energy levels for the leading lines in each band are indicated.

In connection with studies of complex spectra of halogenated molecules of environmental relevance they are, however, the most powerful tool available for accurate determination of the nuclear quadrupole splitting part of the rotational Hamiltonian. Such spectrometers can of course also be used for isolation of the ground vibrational state in difficult cases, and recent advances suggest that their application for measurement of electric dipole moments in molecules with quadrupolar nuclei should be on the increase [16].

3. Band spectra

The condensation of rotational spectra into bands is a well known phenomenon, which has seen much use in the assignment process for asymmetric rotor molecules. The best established band types are type-I R-type bands, arising from pileups of $J+1 \leftarrow J$ $^aR_{0,1}$ transitions for the higher values of K_{-1}, and Q-type bands arising from pileups of transitions for a fixed value of K_{-1} or K_{+1} and varying J. That various other types of equally spaced line pileups are also of importance has become apparent from Low Resolution Microwave (LRMW) studies [17]. Some time ago Borchert [18]

noted that in $^aR_{0,1}$ transitions strong lines arise from coalescence of transitions from the $J_{0,J}$ and $J_{1,J}$ levels. It turns out that in high-J rotational spectra much more extended pileups of this type can be of importance, with bandheads formed in such a way that successive lines are either increasing or decreasing in J. Such bands can arise from either accidental or symmetry induced relations between the three rotational constants in an asymmetric top molecule. In an extension of the nomenclature of Borchert type-II$^+$ bands can arise from properties of asymmetric tops extending from the oblate top limit $(A = B > C)$ when

$$(A + B) \approx n(2C). \tag{1}$$

in which each band subtype is defined uniquely by the quantity $n = l/m$ where l and m are integers such that $l > m$. Simulation of bands possible for several values of n is presented in Fig.3. The convergence properties of $n=2$ bands have been investigated in [19], and a more detailed analysis of general properties of type-II$^+$ bands has been made in [1]. Such bands are equidistantly spaced by $2C/m$, and the bands for $n = 2$ are of particular relevance since their convergence condition $(A + B) \approx 4C$ is equivalent to the planarity condition, $I_c = I_a + I_b$, expressed in rotational constants of the oblate symmetric top limit. Extended bands of this type have now been observed for several molecules, and an example for trichloroethylene can be seen in Fig.4. Even though this molecule is quite prolate ($\kappa = -0.7$) and the type-II$^+$ band in question will collapse completely only at the oblate top limit of $\kappa = +1$, the degree of convergence visible in Fig.4 is already considerable. Since these bands were the most easily identifiable feature in the mm-wave spectrum of trichloroethylene, an understanding of their properties allowed the assignment of this rather rich spectrum to be extended well beyond that of the ground state. In the end it was possible to assign all three singly substituted ^{37}Cl isotopomers, all three doubly substituted ^{37}Cl isotopomers and four low lying vibrational states in the rotational spectrum of normal trichloroethylene [4]. Since other band variants are not tied to particular molecular symmetry and are of accidental nature they are expected to be less frequent, although $n = 3/2$ type-II$^+$ bands have already been observed for CBrClF$_2$ [1].

The symmetry counterpart of type-II$^+$ bands are type-II$^-$ bands, which are possible from extension of properties extending from the prolate limit $(A > B = C)$. The band formation condition is

$$2A \approx n(B + C). \tag{2}$$

where, as before, $n = l/m$. Type II$^-$ bands occur at a spacing of $2A/l$. An example of bands of this type, for $n = 3$, has also been identified in the
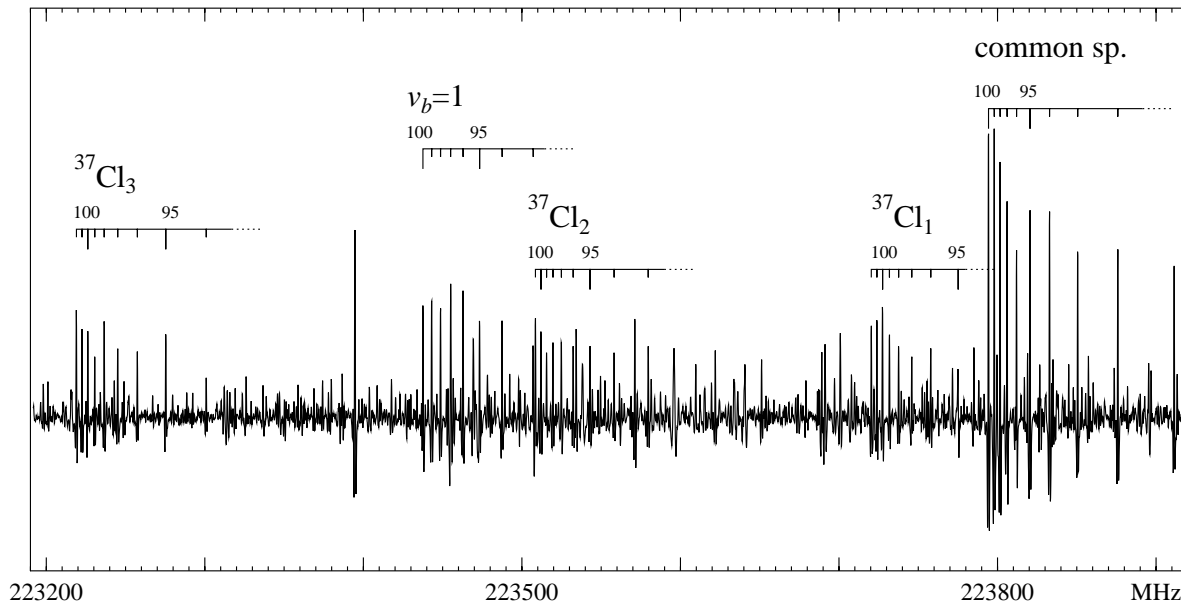
Figure 4. Type-II$^+$ $n = 2$ bands in the room temperature spectrum of trichloroethylene, visible here for the ground state, all three singly substituted ^{37}Cl species and a vibrational satellite. This band-type originates from rotor properties at the oblate rotor limit and the indicated values of J are seen to decrease away from the bandhead.

rotational spectrum of trichloroethylene, see Fig.5. A detailed discussion of properties of type-II$^-$ bands can be found in [4]. The observation of two different R-band types for trichloroethylene proved to be a bonus in determining spectroscopic constants. Transitions in the two types of bands exhibited complementary sensitivity to spectroscopic constants so that measurement strategy based on following lines along each band type was sufficient for determining decorrelated values for all constants in the sextic level rotational Hamiltonian.

A convenient summary of the properties of the four known families of R-type bands has been given in Table 9 of [4]. Actual relationships for maximum band convergence deviate somewhat from the simple form of Eq.1-2, but it was established in [4, 1] that sufficient diagnostic accuracy is obtained by replacing n with a quantity n_{eff} given by

$$\text{type} - \text{II}^- : \qquad n_{\text{eff}} = 1 + \frac{(n-1)(3+\kappa)}{2\sqrt{2(\kappa+1)}}, \ \kappa > -1 \qquad (3)$$

$$\text{type} - \text{II}^+ : \qquad n_{\text{eff}} = n \left(\frac{2 - b_p^2}{2 - n b_p^2} \right) \qquad (4)$$

where $b_p = (\kappa + 1)/(\kappa - 1)$.

For the most established type-I$^-$ bands there are examples in broadband mm-wave recordings for acrylonitrile [20], and chloroacetonitrile [21]. The much less common type-I$^+$ band can also be rather important in some
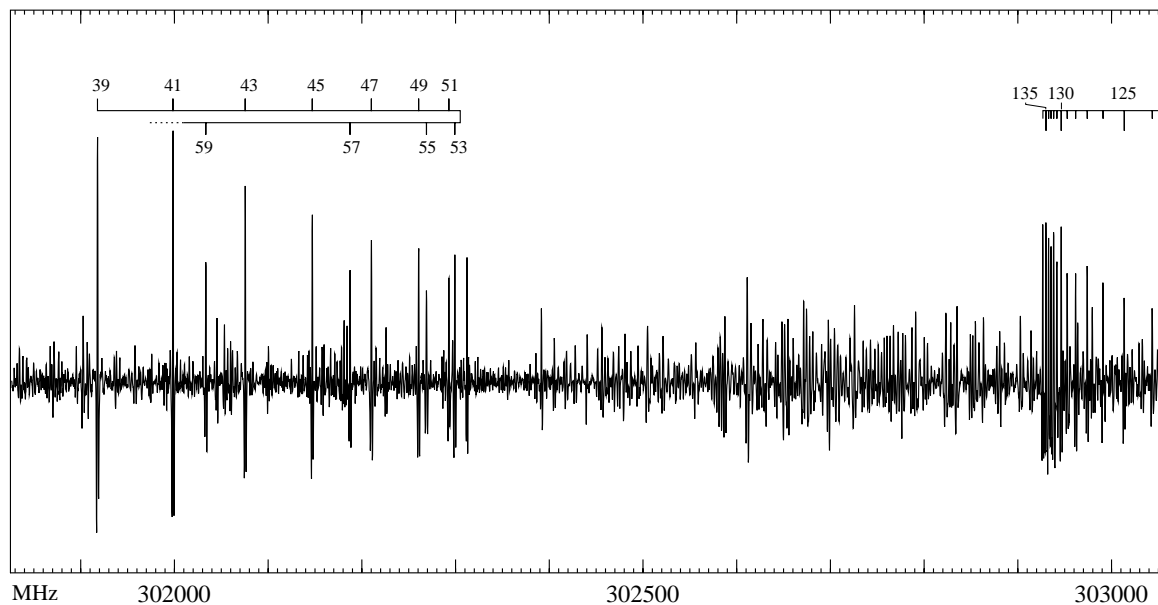
Figure 5. Type II$^-$ $n = 3$ R-type band for the ground state of trichloroethylene (left) which originates from rotor properties at the prolate limit and is characterised by J increasing away from the bandhead. A much more compact type-II$^+$ $n = 2$ band is also visible to the right.
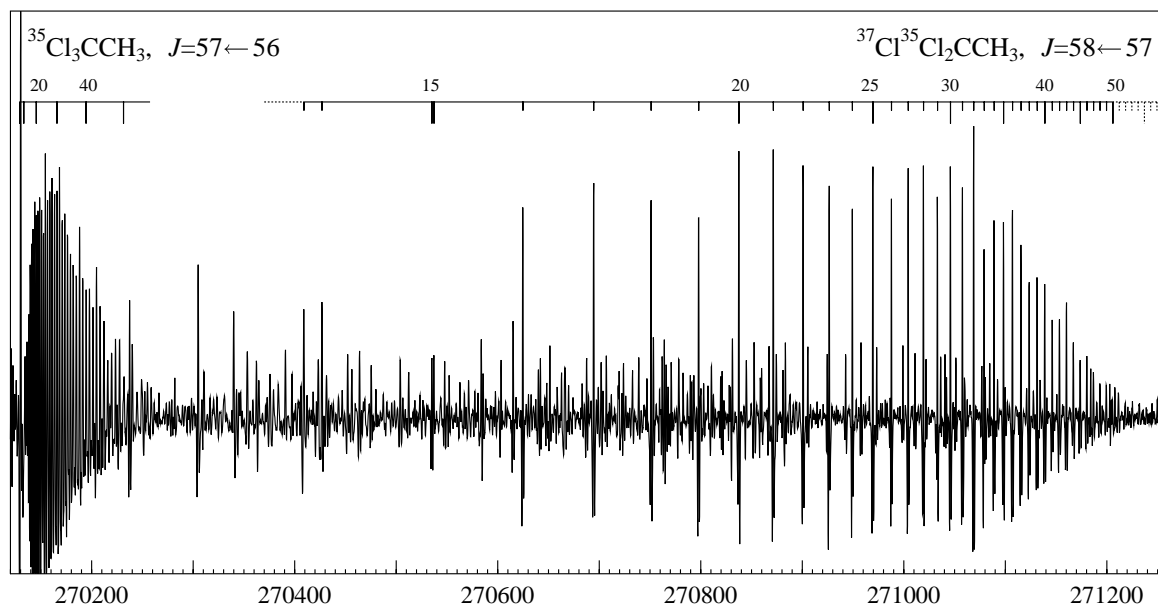

Figure 6. Type I$^+$ R-type band for the ground state of $^{37}Cl^{35}Cl_2CCH_3$ (right) compared with the symmetric top spectrum of the common isotopomer, left. The values of K_{+1} and K are marked for the two bands, respectively.

situations, for example for isotopomers of symmetric tops with a CCl_3 segment, as illustrated by the mm-wave spectrum of 1,1,1-trichloroethane in Fig.6 [7]. Note that in this case the possibility of three indistinguishable single ^{37}Cl substitutions results in comparable intensities for the common

and for the naturally substituted isotopomer. In addition, in both Fig.4 and Fig.6, the isotopic bands are not a reflection of the common isotopomer band in the same window, but of a band one or two such bands to the right.

4. Complex nuclear quadrupole coupling

Plural nuclear quadrupole coupling is relatively common in trace molecules of atmospheric importance. It is normally most convenient to commence assignment of their rotational spectra with high-J, R-type transitions in the mm-wave region. The hyperfine structure in such transitions is either completely or partially collapsed so it is easy to determine the parameters in the rotational part of the molecular Hamiltonian. It is then possible to investigate the nuclear quadrupole structure itself. For ground state transitions the tool of choice is FTMW spectroscopy of the supersonic expansion which, as stated above, gives sub-Doppler access to the lowest-J transitions, which are most affected by such splitting. In addition the high accuracy with which frequencies can be measured allows off-diagonal components in the quadrupole tensor to be determined routinely. An example is provided by studies of the spectrum of trichloroethylene, which proceeded in such *top-down* manner. The rotational part of the Hamiltonian was determined first from high-J spectra, and then the nuclear quadrupole splitting itself was analysed by starting from the simplest transition $1_{1,1} \leftarrow 0_{0,0}$ [5]. Since this molecule contains three non-equivalent chlorine nuclei the splitting structure is rather complex. This is illustrated in Fig.7 which shows how the pattern of three hyperfine components for the $1_{1,1} \leftarrow 0_{0,0}$ transition in a molecule with a single chlorine nucleus develops on addition of further one and two chlorine nuclei. The complexity of the pattern of the $3_{1,3} \leftarrow 2_{0,2}$ transition in trichloroethylene is even greater, although the cavity FTMW spectrometer allows the individual hyperfine components to be readily resolved. Even though the analysis was far from trivial it was facilitated by accurate prediction of nuclear quadrupole coupling constants for the three nuclei on the basis of constants available from the mm-wave study, the molecular geometry determined therein, and quadrupole tensor elements from 1,1-dichloroethylene.

Another case of complex hyperfine coupling for three chlorine nuclei in 1,1,1-trichloroethane has also been successfully investigated in Warsaw [8], for both the symmetric top species with three identical chlorine nuclei, and the singly ^{37}Cl substituted species in which two of the three chlorine nuclei are identical. Several double nucleus cases have also been studied including $CBrClF_2$ [2], CH_2I_2 [9, 10], and CH_2Cl_2 [22]. For all of these molecules the complete nuclear quadrupole tensor in inertial axes was determined which allowed, in turn, diagonalisation to the principal quadrupole axes.
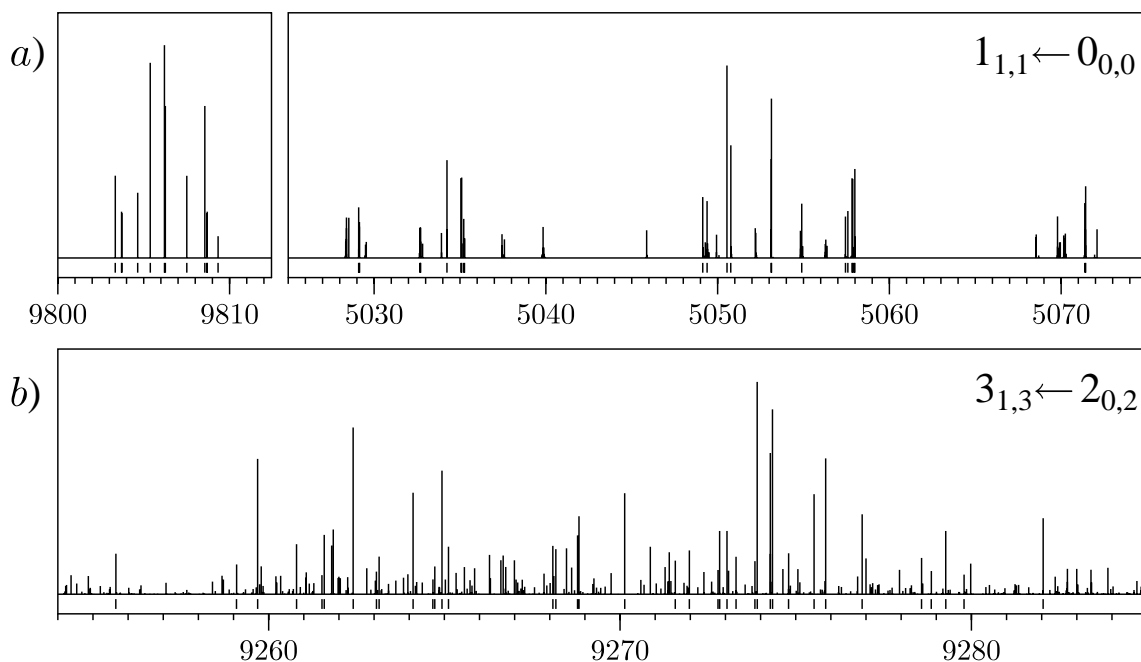
Figure 7. (a) The nuclear quadrupole splitting patterns for the $1_{1,1} \leftarrow 0_{0,0}$ rotational transition in $^{35}Cl_2C=CH_2$ (left) and $^{35}Cl_2C=CH^{35}Cl$ (right). (b) The central portion of the $3_{1,3} \leftarrow 2_{0,2}$ transition of $^{35}Cl_2C=CH^{35}Cl$. The splitting patterns are calculated from the final spectroscopic constants and the small ticks underneath each diagram denote the measured components. The frequency axes are in MHz.

If there is accidental near coincidence between suitable rotational levels then the strong perturbations in the hyperfine patterns allow considerable enhancement in the precision of measurement of the splitting constants. In this way the principal nuclear quadrupole tensor for ^{14}N, which is normally rather elusive in an asymmetric top molecule, could be determined precisely for 2-chloro-acrylonitrile [23].

Synthesis of such results allowed useful conclusions to be drawn concerning the relative orientation of the principal axes of the nuclear quadrupole coupling tensor and the principal inertial axes [5]. Diagonalisation of the inertial quadrupole tensor allows the angle between these two sets of axes to be determined accurately, often to better than $0.01°$. In the first approximation it was anticipated that, at least for a quadrupolar nucleus terminal to a chemical bond, the z axis of the principal quadrupole tensor will be aligned with the bond. Accurate experimental data revealed deviations between bond direction and the z axes at the level of *ca* $1\text{-}2°$. These deviations have been confirmed to be experimentally reliable and it was found that their magnitude and direction are easily reproduced in *ab initio* calculations [5]. The reason for the small deviations turns out to be distortion of the field gradient by electron density further away from the quadrupolar nucleus, and its understanding allows the use of quadrupolar angles as valuable data in determination of molecular geometry. In addition transfer

of quadrupole tensors between molecules for the purposes of prediction can be made with increased confidence.

5. Centrifugal distortion constants

In high-J rotational spectra the contributions to transition frequencies from even small values of quartic centrifugal distortion constants can be appreciable. For example for chlorobenzene $\Delta_J = 60$ Hz contributes 250 MHz at J=100 [19]. Estimates of centrifugal distortion constants are therefore most useful since their values may have a bearing even on the J assignment. In the absence of highly anharmonic motions, it is now possible to make routine, reliable predictions of quartic constants from the *ab initio* harmonic force field. This has been demonstrated quite some time ago for the rather rigid ring molecules furan, pyrrole, pyridine [24]. Equally encouraging results have been obtained for the environmentally relevant molecules $CBrClF_2$, trichloroethylene and 1,1,1-trichloroethane discussed presently, as summarised in Table 1.

TABLE 1. The observed and calculated quartic centrifugal distortion constants (kHz) for several selected molecules

| | $Cl_2C{=}CHCl$, [4] | | $^{35}Cl_2{}^{37}ClCCH_3$, [7] | |
	obs.	calc.	obs.	calc.
Δ_J	0.09309(3)	0.0962	0.26797(4)	0.2777
Δ_{JK}	1.2662(2)	1.266		0.0782
Δ_K	1.6268(8)	1.548	0.07021(9)	0.0722
δ_J	0.02098(2)	0.0222	0.06634(5)	0.0669
δ_K	0.6734(2)	0.680	0.05013(11)	0.0511
	$C^{79}Br^{35}ClF_2$, [1]		CD_2I_2, [10]	
	obs.	calc.	obs.	calc.
D_J	0.19872(3)	0.2029	0.067109(8)	0.0622
D_{JK}	0.0700(2)	0.0711	-4.3281(3)	-4.28
D_K	1.0988(2)	1.237	166.72(3)	176.9
d_1	-0.03939(3)	-0.0402	-0.003355(4)	-0.00306
d_2	-0.003034(8)	-0.00314	-0.0000430(5)	-0.0000324

In our laboratory we have routinely used theoretically predicted quartic constants in *top-down* assignment commenced from high-J transitions and it was particularly fortunate to find that the quartics for CH_2I_2 and CD_2I_2 were reliably calculated with even the rudimentary basis sets which are available for iodine, see Table 1 and [9, 10]. The reason for this success

is that appreciable contributions to quartic constants arise from only the several lowest frequency vibrational modes, so that only a small part of the total force field is of importance.

To further aid the analysis of rotational spectra it is also possible to use *ab initio* harmonic force fields to calculate reliable values of Coriolis coupling constants and inertia defects. Calculated Coriolis constants can serve as a check of the analysis of spectra in doubly degenerate excited states of symmetric top molecules, or of fitting of Coriolis perturbations between vibrationally excited states of molecules, as in $CHClF_2$ [25]. Although moments of inertia can contain appreciable anharmonic contributions, these are known to cancel on evaluation of inertia defects, so that calculation of harmonic contributions to moments of inertia can yield reliable inertia defects. This feature has been used, for example, to assign with confidence excited vibrational states in the mm-wave rotational spectrum of pyrimidine [26].

Encouraging progress has been made in the prediction of sextic centrifugal distortion constants and of the vibration-rotation α constants, but this is yet far from routine. That reasonably satisfactory results can be obtained has been demonstrated for several molecules, including $CHClF_2$ [27], but efforts in the direction of bringing such calculations closer to spectroscopist are still required.

6. Computer programs

The use of efficient software tools is always desirable, and becomes mandatory in spectroscopic problems involving many transitions, vibrational states, high values of quantum numbers etc. Appropriate computer programs are necessary to process spectra, fit data to determine spectroscopic constants, and to compare known data or predictions with spectra. Traditionally many computer codes have been circulated informally within the rotational spectroscopic community, but the internet age is bringing considerable improvement in access to such information.

The fitting side of the spectroscopic problem has benefited considerably from the availability [28] of the powerful package SPFIT/SPCAT written by H.M.Pickett [29]. These programs were originally written for the purpose of cataloguing rotational spectra of many different molecules. This requirement enforced a very general way of setting up the molecular Hamiltonian and efficient factorisation of its energy matrix. Easy scalability then allowed a multitude of research grade applications. An example from this discussion is that all studies of complex hyperfine splitting discussed above have been carried out with that package. The importance of the package is such that various accessory programs, worked examples and help files are now
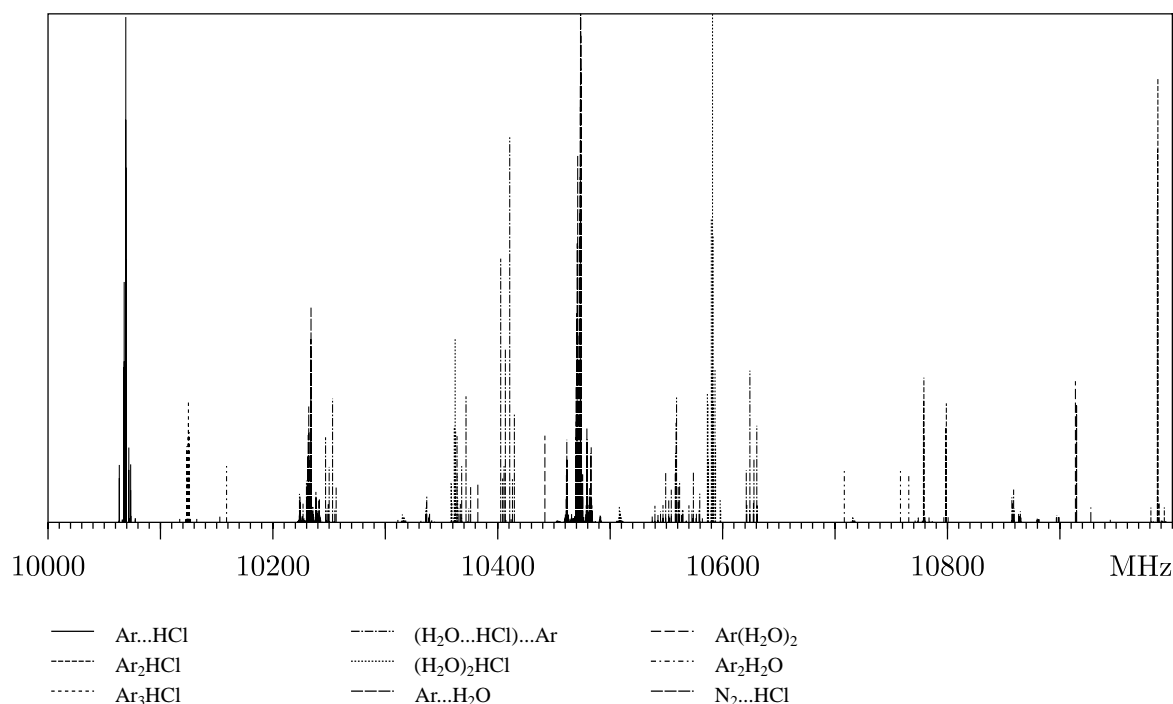
Figure 8. Illustration of common impurities observed during FTMW work involving HCl, as an example of the use of the graphics viewing program ASCP to inspect a catalogue of known spectra. The relative intensities of the various molecular species have been adjusted in the control file for the program to obtain comparable displayed intensities.

available [30, 31].

When it is necessary to deal with complex spectra flexible graphical display of spectroscopic predictions becomes essential. This is possible with the program ASCP [30], which can display predictions from SPCAT and, in fact any other predictive programs, once conversion to a standard input format is made. The program allows merged display of lines from many data files, and has been found invaluable in investigations ranging from complex hyperfine structure to overlaps of transitions from many vibrational states and isotopic species. A summary of some previous applications is given in [11]. The program has been used to produce the bottom part of Fig.1, reproducing the spectrum of CHClF$_2$, which is devoid of characteristic features. An example of the use of ASCP to display a catalogue of spectra is also shown in Fig.8.

ASCP is one of the programs available from the PROSPE (Programs for ROtational SPEctroscopy) web site, which has recently been established by this author. The aim of the site has been to make available well tested, clearly documented and satisfactorily commented computer programs in this field. The programs deal with various aspects of the rotational prob-

lem, including structure fitting and display, dipole moment determination, vibrational calculations. The programs range from state of the art for a given application, to simple, yet useful tools. Although the collection is based on programs of the author, contributions of well tested programs have also been made and further such contributions are encouraged.

7. Conclusions

The array of techniques described above provides a route to efficient, in-depth analysis of some types of complex rotational spectra. It may be anticipated that the much improving access to the mm-wave and submillimetre-wave parts of the rotational spectrum, and extension of such studies to those of successively heavier species will be creating a continuous demand on the refinement of such approaches.

Acknowledgements

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