ABSTRACTS OF PAPERS

Monday, September 8

OPENING CEREMONY

Morning Session (Chairman - J.T. Hougen)

L M1. Infrared Spectroscopy, Applications of Laser-Sideband, Raman and Photoacoustic Spectroscopy
W.L. Meerts

L M2. Laser Frequency Synthesis: Direct Frequency Measurements and Ultra High Resolution Spectroscopy from the Far Infrared to the Visible
K.M. Evenson

L M3. High Precision Infrared Spectroscopy
L. Henry, A. Valentin

L M4. The High Resolution Pursuit of the Isomers of Cynamide, H₂NCO
M. Winnewisser

Afternoon Session (Chairwoman - B. Winnewisser)

L M5. Critical Evaluation of the Calibration Standards in High Resolution Infrared Spectroscopy
K. Narahari Rao
The Infrared Spectra of $\text{H}_3^+$ and its Deuterium Isotopes

James K. G. Watson

This talk discusses the assignment and fitting of the infrared fundamentals of $\text{H}_3^+$, $\text{H}_2\text{D}^+$, $\text{D}_2\text{H}^+$ and $\text{D}_3^+$. From measurements by various groups, about 100 lines of each of these species are now known and all the allowed fundamentals are well characterized. Centrifugal effects are large, and it is important to formulate the theory so that the centrifugal distortion is well represented with a comparatively small number of parameters. In effective Hamiltonian fits, this has been achieved by the use of a Padé formulation of the centrifugal terms, which allows more reliable extrapolations to higher $J$ and is also found to give better fits than a truncated power series. An alternative fitting procedure uses the untransformed Hamiltonian and a large vibration-rotation basis set with numerical diagonalization. These fits are compared with the results of several recent ab initio vibration-rotation calculations.
This talk is a review of work I have been involved with concerning the calculation of rotation-vibration energy levels of triatomic molecules directly from the nuclear potential energy function (within the Born-Oppenheimer approximation). With the methods developed we can calculate transition frequencies of spectroscopic or astrophysical interest from ab initio potential energy functions, or we can refine analytical representations of the potential functions by fitting to experimental data.

The main objective of the work described is to develop methods through which the calculation of spectroscopically interesting energy levels \((J \approx 10)\) is feasible using present-day computers. This is achieved by trying, for each type of molecule treated, to express the rotation-vibration Hamiltonian in coordinates that are "natural" to the system, i.e. coordinates that yield Hamiltonians with minimized couplings between different types of motion. Further, in diagonalizing these Hamiltonians we try to find basis functions that resemble the eigenfunctions of the system as much as possible.

I shall primarily discuss two methods to obtain the rotation-vibration energy levels of triatomic molecules: first the nonrigid bender model, in which the energies are obtained through a perturbation approach, and secondly a variational method using Morse oscillator basis functions that we have presently developed for equilateral \(X_3\) and \(Y_2X\) molecules only.
L M9. **Ab Initio Calculations as a Tool in High-Resolution Vibration-Rotation Spectroscopy**

P. Botschwina

L M10. **Diode Laser Spectroscopy of some Unstable Molecules.**

Harold Jones, Josef Lindenmayer and Gerhard Taubmann

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D-7900 Ulm, Federal Republic Germany.

Diode laser spectroscopy has been carried out on a number of relatively unstable molecular species. Results will be reported as follows:

a). The equilibrium structure of $S_2O$ from combination of results from the $v_1$ and $v_3$ bands of $S_2^{16}O$ and $S_2^{16}O$ with microwave data.

b). The $\text{NH}_2$-wagging, N-O stretching and the O-H torsional band of hydroxylamine.

c). Production and spectroscopy of radicals. (examples; FOO, etc.)
A Preliminary Determination of the Equilibrium Geometry and Inversion Potential in SH$_3^+$ from Experiment

V. Špirko, S. Civiš, J.L. Destombes, P. Čársky

A model anharmonic potential energy function of SH$_3^+$ is determined. This is done by fitting the infrared data of Amano [T. Amano, private communication], the infrared and Raman spectra of solid H$_3$S$^+$ - SbF$_6$ [K. O. Christie, Inorg. Chem., 14, 2230 (1975)] and ab initio data of Civiš [S. Civiš, Thesis, 1986] using the nonrigid inveror Hamiltonian. The rotation-vibration energies calculated with this potential are in a reasonable agreement with experiment and recent ab initio results of Botschwina et al. [P. Botschwina, A. Zilch, H.-J. Werner, P. Rosmus, E.-A. Reinsch, J. Chem. Phys., submitted].
P M2. Dipole Moment Function of $XY_3$ Molecules

P. Pracna, V. Špirko

The dipole moment expanded for the sake of isotopical invariance in curvilinear vibrational coordinates is used to calculate vibrational transition moments using the nonrigid inverter Hamiltonian (V. Špirko, J. Mol. Spectrosc. 101, 30 (1983)). The theory is applied to the analysis of accessible intensity and laser-Stark data on the NH$_3$ molecule and its isotopical species. It reveals, among others, a significant rotational dependence of vibrational transition moments which should not be neglected in intensity analyses.

A comparison of the dipole moment function based on experimental data on NH$_3$ and the dipole moment function and vibrational transition moments obtained from ab initio calculations show the possibility of using the latter approach for predictions in case of lack of experimental information (e.g., for the H$_3$O$^+$ molecule ion).

P M3. Ab Initio Spectra of Large-Amplitude Motions in Flexible Molecules

A. Boldyrev
CALCULATION OF VIBRATION-ROTATIONAL SPECTRA OF DIATOMIC MOLECULES TAKING INTO ACCOUNT THE ASYMPTOTIC BEHAVIOR OF THE POTENTIAL FUNCTION

A.V. Burenin and M. Yu. Ryabikin

A traditional method for calculation of vibration-rotational spectra of molecules is based on representation of the vibration-rotational Hamiltonian operator in the form of a Taylor series in dynamic variables and construction of the perturbation series, where the harmonic oscillator model and the rigid top model are used as zero-order approximation. The asymptotic behavior of this zero-order approximation is far from the real one, which results in a bad convergence of the perturbation series.

The present paper deals with further development of the approach [1], that enables one to take into account the asymptotic behavior of the potential function. The interaction of nuclei is treated in the zero-order approximation employing the potential $\mathcal{U}(\gamma) = \frac{A}{\gamma^2} - \frac{B}{\gamma}$, while the perturbation is represented in the form $\mathcal{V}(\gamma) = \sum D_n \gamma^n$.

As in [1], to construct the perturbation series, we used the Rikatti equation derived from the Schrödinger one (see, e.g., [2]). We applied algebraic procedure for the calculation of corrections in the perturbation series (cf. [3]). This permits to simplify the calculations of corrections for the excited vibrational states.

The results of the application of this approach to the treatment of vibration-rotational spectra of hydrogen halides and alkali halides are presented.

REFERENCES

High precision analysis of the molecular constants of the $B^2\Sigma^+$ and $A^2\Pi$ states in the CO isotopic molecules.

Z. Jakubek and M. Rytel

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Fifteen bands of the Baldet-Johnson ($B^2\Sigma^+ - A^2\Pi$) and Comet-tail ($A^2\Pi - X^2\Sigma^+$) systems in the $^{12}\text{C}^{16}\text{O}^+$, $^{13}\text{C}^{16}\text{O}^+$ and $^{14}\text{C}^{16}\text{O}^+$ isotopic molecules have been photographed at high resolution, measured and rotationally analysed. Each band was fitted via a nonlinear least-squares method with the effective Hamiltonian of Brown. The band-by-band results have been merged to give the "best" molecular constants. The precise molecular constants of the $B^2\Sigma^+$, $v=0$, 1 i.e. $B_\nu$, $D_\nu$, $\gamma_\nu$ and $A^2\Pi$, $v \leq 4$ i.e. $B_\nu$, $D_\nu$, $A_\nu$, $A_{D\nu}$, $p_\nu$, $q_\nu$ states have been obtained. The vibrational and isotopic dependence of the molecular constants has been discussed. Then, the spin-rotation coupling constant $\gamma$ and the centrifugal correction to the spin-orbit coupling constant $A_D$ in the $A^2\Pi$ state have been separated.
New high resolution studies of the spectrum of the CO molecule in visible and near IR region.

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Some new emission bands have been found in the visible and near IR region spectrum of the CO and CO$^+$ molecules. The spectra have been photographed at high resolution and calibrated by using Th standards. The estimated precision of the lines is considered to be 0.005-0.010 cm$^{-1}$ (internal precision) and 0.010-0.020 cm$^{-1}$ (absolute precision).

After a detailed analysis, the following unanalysed and unobserved bands have been identified:

1. (0-5) and (1-5) bands of the unobserved $B^1\Sigma^+ - d^3\Delta_1$ system
2. (0-5) band of the unobserved $C^1\Sigma^+ - d^3\Delta_1$ system
3. (0-5), (0-6), (0-7), (0-8) unobserved unanalysed bands of the Herzberg system ($C^1\Sigma^+ - A^1\Pi$)
4. (1-2), (1-3) unanalysed and (0-6) and (1-7) unknown bands of the Ångström system ($B^1\Sigma^+ - A^1\Pi$)
5. (0-2) and (1-3) unknown bands of the Baldet-Johnson system ($B^2\Sigma^+ - A^2\Pi_i$) of the CO$^+$ molecule.

For all these states the parameters of the molecular structure have been determined. Also a detailed analysis of the mutual perturbations of the $A^1\Pi (v=1)$ and $d^3\Delta_1 (v=5)$ states was performed.
The double-peaked structure measured in the one-photon spectrum from 920 cm\(^{-1}\) to 970 cm\(^{-1}\) investigating the Van-der-Waals dimer (SF\(_6\))\(_2\) could be well understood by the effects of dipole-dipole interaction /1/.

In the present contribution we have calculated the energy level structure of the dimer excited with two vibrational quanta considering the dipole-dipole interaction with respect to the \(\nu_3\) mode of the monomer. Molecular rotation was assumed to be slow. Further the strengths of the corresponding two-photon transitions were determined.

The obtained results are applicable, in principle, also for other dimers consisting of two high-symmetry molecules.

Determination of the potential function of inversion and the geometry of methylamine from microwave and infrared data

Lajos Sztraka

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The observed inversion splittings in the spectrum of methylamine are strongly effected by different rotation-internal rotation-inversion couplings. The potential function of inversion approximated by a Swalen-Ibers potential has been determined from microwave and infrared ($\nu = 0.045 \text{ cm}^{-1}$) transitions using a very complex nonrigid Hamiltonian. Parallelly the geometry of molecule in both ground and excited states had to be fitted. The barrier of inversion has been found to be higher than those published [1,2]. The heigth of barrier is close to the one of ammonia.

The infrared spectrum of the CH$_3^{79}$Br between 4200 - 4600 cm$^{-1}$ was recorded at an instrumental resolution of 0.0054 cm$^{-1}$ with the FT spectrometer at Laboratoire d'Infrarouge in Orsay. The band system analyzed is $\nu_2 + \nu_4$ (E) and $\nu_4 + \nu_5$ (E+A$_1$+A$_2$). Lines of $\nu_2 + \nu_4$ with $K \Delta K$ from -8 to 8 and $\nu_4 + \nu_5$ with $K \Delta K$ from -9 to 8, for a total of 2475 transitions, were assigned and used in a least squares analysis. Emphasis is given to all those features which can lead to the identification and localization of the $\nu_4 + \nu_5$ (A$_1$,A$_2$) system.
The Potential Surface and Rotation-Vibration Energies of the Silyl Radical SiH₃

V. Danielis, V. Špirko


The fitted potential function is used to predict all the lower rotation-vibration energies of SiH₃ and SiD₃ and the Franck-London factors for the SiH₃ → SiH₂ and SiD₃ → SiD₂ electronic transitions. The calculated quantities are in a reasonable agreement with experiment.

Tuesday, September 9

Morning Session (Chairwoman - M. Morillon)

L 11. Spectroscopy of Interstellar Molecules

R.D. Brown
L T2. The Infrared Spectrum of CH₂: An Update.

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In the last two years there has been much new spectroscopic data obtained for triplet methylene, and we have used new nonrigid bender (1,2) computer programs to fit all the extant data. In this process we have determined the shape of the potential surface from which we can predict all the rotation-vibrational energy levels of interest and deduce a refined value for the singlet triplet splitting. We also predict the stretching frequencies which are experimentally unknown.

Rotational energy levels of stretching vibrational states

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Vibrational dependence of various vibration-rotation parameters in \( \text{XY}_2 \) (\( \text{X}_2\text{Y}_2 \)), \( \text{XY}_3 \), and \( \text{XY}_4 \) molecules with \( C_{2v} \) (\( D_{2h} \)), \( C_{3v} \), and \( T_d \) point groups have been investigated as the function of \( |\omega x/\lambda| \) where \( \omega x \) is the diatomic-like bond anharmonicity parameter and \( \lambda \) describes the net coupling between the bond oscillators. The results at the local mode limit, where \( \omega x >> |\lambda| \), differ drastically from those in the normal mode limit, where \( \omega x << |\lambda| \). The rotational constants of the two lowest vibrational states in each overtone manifold (\( v = v_1 + v_3 = \text{constant} \)) are equal for \( v \geq 2 \) in the local mode limit. The effective Coriolis constants between these vibrational pairs disappear but the vibrationally off-diagonal \( H_{zz} \)-resonance terms remain important as the local mode limit is approached.

The vibrational dependence of the experimental rotational constants of the CC and CH (CD) stretching vibrational states in acetylene has been successfully analyzed. The \( \text{C}_2\text{D}_2 \) molecule (\( \omega x/\lambda = 0.17 \)) can be treated well using the customary series expansion for rotational constants

\[
B = B_e - \sum_r a_r (v_r + d_r/2) + \ldots
\]

where the summation is over normal vibrations, \( B_e \) is the equilibrium rotational constant, and \( d_r \) is the degeneracy of the \( r \)th mode. In the case of the \( \text{C}_2\text{H}_2 \) molecule, where \( \omega x/\lambda = 1.05 \), it is vital to couple vibrational levels by quartic anharmonic resonance terms in the normal coordinate space in order to obtain physically sensible results for the vibrational dependence of the rotational constants.
First results with a new tunable diode laser spectrometer

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This year, a new project has been started in our laboratory, aimed to measure high temperature- and transient species with our new tunable diode laser spectrometer. First results will be presented during the meeting.
During a stay in the laboratory of Dr. Oka in Chicago, we have measured the $\nu_5$ band of HCNH$^+$. The center of this band was determined at 645.925 cm$^{-1}$.

High-Resolution CARS Spectroscopy

H.W. Schrötter
Infrared Spectra and Excitation Temperatures of Molecules in a Supersonic Free Jet

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We have investigated the rotational and vibrational temperatures of several small molecules like OCS and NNO in a freely expanding supersonic jet using a diode-laser spectrometer. The temperatures were determined for various location in the jet and for various values of the quantum number J.

The molecules in the jet were found to be lower than 30 K for low-J states. However, the distribution of the molecules was non-Boltzmann.

Now we are trying to apply this technique to the infrared spectrum of 1,1-Difluorethylene (1,1-DFE) in order to identify the lines in the band center region of ν₄ near 926 cm⁻¹. Because of the very low excitation temperatures most of hot-band and high-J transitions disappear in the jet spectra; thus spectroscopy of a supersonic free jet should be helpful in this region, where the absorption lines are densely populated at room temperature.

However, in the observed jet spectrum using pure sample there are still too many lines to ensure the assignment. The measurement of the jet spectrum of 1,1-DFE seeded in Ar is now in progress. By this seeded molecular jet we expect even lower excitation temperatures and, therefore, lower line density in the spectrum.
A few years ago, a high energy hot band of OCS associated to the $v_1$ fundamental band, $(2,0^0,0)$, $(1,0^0,0)$, was detected in a glow discharge in a region of 2045-2060 cm$^{-1}$ by diode laser spectroscopy (1). In the present work, we have extended the measurements in the low frequency direction, where a few more hot bands were expected to be observed.

A 1.5 m long glass tube of 10 cm inner diameter was used as an absorption cell. The dc discharge was applied to a flowing OCS/N$_2$ gas mixture: typically 20 mA across the electrodes separated by 120 cm. The total pressure was about 100 Pa with mixing ratios of 1/1 to 1/2. The second derivative spectra were recorded by modulating the laser frequency. The sensitivity of the spectrometer was improved by employing multi-reflection optics; the minimum detectable OCS density at 44 m path-length was about 10$^9$ molecules/cm$^3$. Using path-length of 37 m, more than 20 lines were recorded in a region from 1997 to 2038 cm$^{-1}$.

Among them we could newly identify the hot bands arising from the $(1,1^1,0)$, $(1,2^1,2,0)$, $(0,3^1,3,0)$, and $(0,4^4,0)$ states in addition to the high J transition of the bands known previously. Analysis together with the microwave data will be presented.

Study of Absorption Spectra Dynamics in Nonequilibrium Excited Gases with Diode Lasers Spectroscopy Methods

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IR-IR double-resonance spectrometer for simultaneous measurements of translational, rotational and vibrational temperatures instant values of nonequilibrium excited gas is described. Rapid diode laser wavelength scanning together with high spectral resolution is the principal feature of the method /1/. In SF$_6$ gas, exited by pulsed CO$_2$ laser, translational and vibrational temperatures were measured and collisional relaxation processes considered. Translational temperature measurement accuracy is about 10K while temporal resolution is better than 1μsec. Spectral and temporal properties of pulsed discharge in CO$_2$-laser were investigated. By the use of pulsed-periodical GaAs diode laser the translational temperature of high-frequency discharge was measured through the Doppler-shape Kr absorption line.

The Role of Rotational Freezing in the Polarization-Dependent Two-Photon Excitation of Triply Degenerate Vibrational Modes

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Under certain circumstances at low rotational temperatures the multiphoton excitation probabilities of vibrational-rotational levels in high-symmetric molecules do not depend on the rotational quantum numbers J and M of the initially populated levels. This has the consequence that during the absorption process the photon spin is not transferred to the molecular rotation but to the molecular vibration. In more detail the two-photon \( A_g(v_3=0) \rightarrow A_g(v_3=2) \) transition in SF\(_6\) at 944.5 cm\(^{-1}\) is theoretically studied: If the average "lifetime" in the \((v_3=1)\)-level is small compared with the effective molecular rotation period the transition is forbidden for circularly polarized light \(/1/\). Further the excitation process of the \( E_g(v_3=2) \) and \( F_{2g}(v_3=2) \) vibrational levels is investigated; it is discussed under which conditions it is not necessary to consider the rotational degrees of freedom in a calculation of the transition dipole moments.

Microwave-optical double resonance has been found to provide a powerful method for probing high rovibronic levels of the ground states of molecules (1). Experiments will be described in which specific rovibronic levels in the $\tilde{A}^1A_2$ excited state of thioformaldehyde (H$_2$CS) are pumped with a dye laser and microwave transitions to high rovibronic levels of the ground state are detected by the decrease in fluorescence observed when a microwave source is scanned through a resonance. The number of transitions observed in a given frequency range will be compared with the results obtained from a calculation of level densities. The question will be addressed as to what are the good quantum numbers for these high rovibronic levels of the ground state.

High Resolution Infrared Spectrum and Rovibrational Analysis of the N=N Diazo Bond Stretch in $d_2$-Diazirine.

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and

Manfred Winnewisser
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The infrared spectra of diazirine and its isotopomers containing carbon-13, nitrogen-15, and deuterium were recorded in Giessen at a resolution of about $0.08 \text{ cm}^{-1}$ with a Digilab FTS 20 between 450 and 3800 $\text{cm}^{-1}$. The infrared spectra of $H_2CN_2$, $H_2^{13}CN_2$, and $D_2CN_2$ in the range 1000-2500 $\text{cm}^{-1}$ were recorded in Orsay at resolution Doppler limited (about $0.005 \text{ cm}^{-1}$) with a high information Fourier transform interferometer.

The $d_2$-diazirine molecule belongs to the $C_2v$ point group, and the $v_2$ fundamental centered at 1610 $\text{cm}^{-1}$ of symmetry species $A_1$ gives rise to an A-type band. This vibrational mode in all the other isotopomers investigated undergoes to a Fermi resonance with the $2v_7$ overtone.

We report here the results of the rovibrational analysis of the $v_2$ fundamental of $D_2CN_2$ which is the starting-point for a more complete analysis of the N=N stretch in the others diazirines investigated. Using Watson'A-reduced Hamiltonian, the rotational and centrifugal distortion constants were determined for the $v_2=1$ state. Spectra, details of the interpretation and results obtained from the analysis will be presented.
The detection of CH$_3$Cl in the terrestrial atmosphere by infrared techniques is a topical subject. The $\nu_3$ band, centered at 732 cm$^{-1}$, has lines as strong as those of $\nu_4$ band, centered at 2970 cm$^{-1}$, and thus may be useful in this detection. The most effective instrument to use in the region of $\nu_3$ would be the tunable diode laser spectrometer.

A complete study of the range 640–800 cm$^{-1}$ has been undertaken in order to supply accurate values of frequency and intensity of individual lines.

On spectra recorded on a tunable diode laser spectrometer, we have assigned four bands: $\nu_3$, and $2\nu_3 - \nu_3$ for both isotopic species CH$_3^{35}$Cl and CH$_3^{37}$Cl. The parameters obtained for the level $\nu_3 = 2$ will improve the accuracy of the interactions in the triad $2\nu_3$, $\nu_2$ and $\nu_3$ in the region of 1450 cm$^{-1}$. For the bands $\nu_3$, the band centers have been found to be:

- 732.842 cm$^{-1}$ for CH$_3^{35}$Cl
- 727.029 cm$^{-1}$ for CH$_3^{37}$Cl
L T13. THE MICROWAVE SPECTRUM OF MONO FLUORO AMINE, FNHz.

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Only last year did Minkwitz and Nass, at the University of Dortmund, BRD, succeed in preparing mono fluoroamine FNHz, the last link in the chain of Fluorine substituted ammonias: NH3, FNHz, HNF2 and NF3.

In order to determine the molecular structure, barrier to inversion, dipole moment and nitrogen-14 quadrupole coupling constants, the microwave spectrum was analyzed for the three isotopic species: FNHz, FNHD and FND2 between frequencies of 7 and 105 GHz using a standard 100 kHz stark modulated spectrometer with BWOs or klystrons as frequency sources.

In order to interpret structural data and changes in the barriers to inversion, ab initio calculations (6-31G* / MP2) were carried out for the complete series of amines. Centrifugal Distortion constants are being used to refine the harmonic force field.

Preliminary data resulting from this investigation are:

Rotational and quadrupolar coupling constants (MHz):

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<td>C</td>
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Structural Parameters (Å and deg.):

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<tr>
<td>NH</td>
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<td>FNH</td>
</tr>
<tr>
<td>(NH - ND)</td>
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Barrier to Inversion: 15 kcal/mole

Dipole moment: \( \mu_a \) 2.0, \( \mu_c \) 2.1 \( \mu_{\text{total}} \) 2.9 Debye
The rs structure of cyclopropenylidene C₃H₂ from its millimeter and submillimeter wave spectra.

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The cyclopropenylidene C₃H₂ has been recently discovered by THADDEUS and coworkers [1] both in the interstellar medium and in the laboratory. We have been able to produce C₃H₂ in a very weak R.F. discharge in allene with a fractionnal abundance as high as 1 %. The two ¹³C substituted forms have been observed in natural abundance and the deuterated form by adding small amounts of Deuterium in the discharge.

A detailed analysis of the rotational spectrum of each isotopomer has been performed leading to an accurate determination of the molecular parameters.

A substitution structure has been derived which is in very good agreement with recent ab initio calculations by LEE et al [2].

Millimeter wave spectrum of the NS free radical in excited vibrational states up to $v = 5$.

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The NS free radicals are produced in a R.F. discharge in $\text{N}_2 + \text{H}_2\text{S}$ mixture. The rotational spectrum in the $\chi^z_{\Pi}$ state has been measured in the vibrational levels up $v = 5$. The experimental data are fitted together to obtain rotational as well as fine and hyperfine structure parameters and their vibrational dependence is investigated.
3. Line Strengths of Methane in the 7.5 µm region

M. Loëte, J.C. Hilico and O. Ouardi
Laboratoire de Spectrométrie Moléculaire et Instrumentation Laser, DIJON-FRANCE

In the 7.5 µm region there are two main polyads of methane CH₄:

- The dyad: \((v_2, v_4)\)
- The pentad-dyad: \((v_1, v_3, 2v_2, v_2+v_4, 2v_4) - (v_2, v_4)\)

This paper is especially devoted to the hot polyad strengths calculation, and it is shown how the results of the dyad strengths analysis may be used at this end.

To illustrate this extrapolation method, the more simple cases of the isolated hot bands: \(2v_4-v_4\), \(v_2+v_4-v_2\), \(2v_2-v_2\) and \(v_2+v_4-v_4\) are presented as preliminaries. The two first bands have been studied from the dipole moment parameters of the \(v_4\) isolated band, and the two last bands from those of the \(v_2\) isolated band.
Resonances in the Rotational Spectrum of HCNO: Ten Years Later

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Just over ten years ago, K. Yamada et al. (1) reported on the resonances between the \( v_1v_2v_3v_4v_5 = 0001^{10} \) and \( 0000^{20} \) vibrational states and between the \( 00100 \) and \( 00004^0 \) states of HCNO, as revealed in the pure rotational spectrum of molecules in these excited states. As a result of an improved preparation, high resolution infrared data and new millimeter wave measurements, it has now been possible to assign rotational transitions of all the component levels of the \( 0000n \) stack up through \( n = 4 \), the \( 0001n \) stack through \( n = 3 \), and most of the levels of the \( 0002n \) stack up to \( n = 2 \). Resonances corresponding to those observed earlier are found, and others are indicated. The resonances have been analyzed as extensively as the data allow.

CO-laser-Stark and high-resolution infrared spectroscopic studies of the $v_3$ fundamental of deutero-formic acid.

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Using a carbon-monoxide laser-Stark intracavity spectrometer at the National Research Council of Canada [1], we have recently carried out Lamb-dip spectroscopy to determine the $v_3=1$ fundamental excited state vibration-rotation constants of end-deuterated formic acid: HCOOD.

High resolution Fourier-transform infrared spectra were also taken in a limited frequency interval around the $v_3$ band-origin at 1773 cm\(^{-1}\) at apodized resolution level 0.004 cm\(^{-1}\). Preliminary results of the analysis of the $v_3=1$ excited state - as based on the infrared spectra - shall be reported along with a discussion of the electric dipole moment components of HCOOD.

Ground-state rotational constants of HCOOD were taken from the work of Willemot et al. [2].


The predominantly a-type $\nu_1$ band (N=S stretch) of NSF centred near 1375 cm$^{-1}$ has been studied with Doppler-limited resolution. The analysis of the band is complicated by a Coriolis-type perturbation. Judging from the energies of $(0,1,0)$ and $(0,0,1)$, the state interacting with $(1,0,0)$ appears to be $(0,2,1)$.

A further difficulty with this spectrum is produced by the fact that it is essentially impossible to prepare a sample which is free from $SO_2$ impurities. As a consequence of this, a large number of very intense $SO_2$ lines, belonging to the near-infrared band, are mixed into the NSF spectrum.

Despite these difficulties a set of effective constants for the $\nu_1$ band of NSF has been determined. The effects of the perturbation will be discussed.
Rotational relaxation processes in polar gases under low pressure are dominated by long range dipolar interactions that lead to collision-induced rotational transitions. Previous works [1, 2, 3, 4] have shown that for some pure polar gases, collision-induced transitions will lead to detectable microwave double resonance signals. In this paper microwave-microwave double resonance technique is used to study rotational transitions in ammonia molecule induced by collisions.

Inversion doublet of ammonia with rotational quantum numbers J=4, K=1 is "pumped" and the intensity of absorption between components of the /3,1/ doublet is monitored. The deviations of the molecular populations from those of Boltzmann distribution, produced in the upper and lower levels of the pump transition are transformed to the signal levels /3,1/ by collision-induced transitions. Measuring changes of signal amplitude /3,1/ versus gas pressure yields dependence which rapidly increase reaching maximum at about 20 mTorr and than decrease. Sign of changes of signal amplitude indicates that for this four level system /3,1/,/4,1/ of the inversion state in ammonia prefered transitions induced by collision are that of dipol-dipol type transitions.

References.
1-doubling in a Microwave Spectrum of the Linear Molecule, Interacting with a Resonant IR Radiation

A.A. Kiselev, A.V. Liapzev, A.N. Zuev

A linear triatomic molecule driven by a strong monochromatic electromagnetic field is considered. The driving field is assumed to be resonant with the quantum transition to the first excited state of the bending vibration. The corresponding Stark splitting of the vibrational-rotational levels is supposed to be as large as the 1-doubling and the quasi-energy method is applied to investigate the influence of the driving field on the microwave spectrum of the molecule.

Classification of the quasi-energy states is carried out basing on the permutation-inversion group with the inversion operation changed by the half-period time translation operation times inversion operation. Using this classification selection rules for the microwave transitions are derived.

The microwave absorption spectrum of the driven OCS molecule is calculated with the help of the density matrix method. The results obtained may be useful for the infrared-microwave double resonance investigations of linear molecules.
THÉ ROVIBRONIC SPECTRA OF EXCITED $XY_6$ MOLECULES

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Advances in high-resolution laser spectroscopy have made it possible to observe individual vibrational-rotational lines in the infrared spectra of vibrationally excited molecules. The theory of rovibronic spectra of spherical top molecules in their ground and first excited vibrational states have been formulated earlier by Hecht and Moret-Bailly in the terms of spherical tensors and have been exploited to describe vibrational overtones. The purpose of this work is to re-examine this theory to obtain an adequate picture of rovibronic spectra of highly excited vibrational states. This is useful as well as for analyses of vibrational-rotational spectra of molecules and for understanding of the behaviour of the molecule in intense laser fields.

The vibrational-rotational hamiltonian of the IR-active modes of spherical top molecules was written in terms of spherical tensor operators to third order of approximation. It was shown, that sextic order anharmonicity terms must be included into the hamiltonian. Included terms are significant for vibrational states $v \geq 3$. They are: two scalar, two four rank and one six rank spherical tensor operators. The formulae were obtained for reduced matrix elements of those tensor operators.

Inclusion of new operators made it possible to account for weak differences in the SF$_6$ molecule $\nu_3$ mode anharmonicity constants obtained recently from the overtone spectra ($2\nu_3$ and $3\nu_3$). The vibrational-rotational spectra of single photon and multiphoton transitions both from the ground and from the excited vibrational states of SF$_6$ molecule $\nu_3$ mode were calculated.
STUDY OF THE $v_1$ AND $v_1 + v_3$ BANDS OF $^{18}$O$^{14}$N$^{35}$Cl

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Infrared low-resolution spectra of this near-prolate asymmetric top can be found in the literature, and intensive studies of rotational spectra, obtained in Bologna by the microwave technique, have been published these last years.

The present work is the first infrared study in high resolution: the spectra were recorded by H. HUBBARD at Kitt Peak National Observatory on the Fourier Transform interferometer built by Urault. The $v_1$ band is very dense, almost all the rotational lines lying between 1760 and 1830 cm$^{-1}$: 498 A-type rotational lines have been assigned and a r.m.s. deviation of 0.0015 cm$^{-1}$ has been obtained through a least squares calculation carried out over them, according to the Watson's hamiltonian in $l^F$ representation [1]. For the much weaker $v_1 + v_3$ band, lying between 2105 and 2155 cm$^{-1}$, similar calculation over 435 A-type lines has given a r.m.s. deviation of 0.0016 cm$^{-1}$.

Since these publications, new lines have been assigned for both preceding bands, and a systematic study of the infrared spectrum of the ONCl molecule has been planned: rotational study of the $v_2 + v_3$, $2v_1$ and $3v_1$ bands, and vibrational study of the excited states close to the dissociation of the molecule.

[1] M. Cheikh, C. Alamichel, J.P. Chovillard and R. Hubbard

[2] M. Cheikh et R. Hubbard,
High Resolution and High Sensitivity Microwave Fourier Transform Spectroscopy at Zürich

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Two types of microwave Fourier transform spectrometers are currently in use in Zürich. The first type, where static gases in rectangular waveguides are subjected to short microwave pulses, is mainly used for substances with very small permanent electric dipole moments. The existence of a dipole moment in asymmetrically isotopically substituted species allowed the detection of the pure rotational spectra of allene-d₁ (H₂C=C=CHD), allene-1,1-d₂ (H₂C=C=CD₂) and s-trans glyoxal (HCO-CDO) in their vibrational ground states. The centrifugal distortion of symmetric, nonpolar molecules can give rise to a dipole moment which is strongly \( J \) dependent. This allowed the observation of the rotational spectrum of BF₃. More precise molecular constants could be deduced. Symmetric, nonpolar molecules which are in a vibrationally excited state of a degenerate mode can possess a permanent electric dipole moment as well. This effect allowed the detection of the 1-0 rotational transitions of different excited states of allene-d₀ (H₂C=C=CH₂).

A second type of microwave Fourier transform spectrometer has recently been completed in Zürich. It is based on Flygare's design. A pulsed molecular beam is injected into a bifocal cavity which is simultaneously subjected to microwave pulses. First results will be shown which indicate its superior resolution compared to the spectrometer mentioned above.

Title not yet delivered
G. McRae
The millimeter wave spectrum of $\text{H}_2\text{CO}--\text{HF}$ has been observed in a conventional microwave absorption cell. Rotational transitions in excited vibrational modes of the complex were observed in the spectrum. With the assistance of dynamical information that we obtained from ab initio calculations it was possible to fit the semirigid bender model to the observed rotational structure of levels involving the in-plane bending motion of the complex. The results of the fitting include the equilibrium geometry of the complex (the geometries of the constituent molecules were fixed in the fitting), the prediction of the in-plane bending vibrational energies, and the in-plane bending potential function of the complex.
The Rovibrational Spectrum of Carbodiimide, HNCNH

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The first identification of HNCNH in the gas phase was made in the Giessen laboratory last year from the medium resolution infrared spectrum of the molecule, which exists in equilibrium with cyanamide in the gas phase. Two of the three band systems in the spectral region from 2000 cm\(^{-1}\) to 2250 cm\(^{-1}\) which are parallel bands have now been recorded at a resolution of 0.004 cm\(^{-1}\) with the FT-IR spectrometer of the Laboratoire Spectrométrie Moléculaire in Paris. The present status of the analysis of these bands will be presented.

Structure of Rotameric Forms of Allylamine

K.-H. Wiedenmann, I. Botskor
Adiabatic method for solving of the inverse spectral problem of the ring-puckering vibration coupled with small amplitude vibrations

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In the Mid-infrared spectra of some molecules the combination bands are observed. They appear due to couplings between the low- and high-frequency vibrations/LFV and HFV/ of a molecule. In analysis of these couplings the adiabatic method is very convenient. This method allows the calculation of the effective potential for LFV. However, it depends on quantum numbers of the HFV states. We use this fact to propose the simple method for determination of the parameters of the total potential function for LFV and HFV. First, the effective potentials for LFV in each observed state of HFV are obtained by the fitting procedure using appropriate frequencies of the combination bands. Then, the total potential is derived directly from the known LFV potentials. This method is applied to molecules in which the LF-ring-puckering vibration is coupled with some HFV.

The Absorption Band of HNO₃ Around 7.2 μm

A. Perrin

Linewidth Parameter of the Rotational Transition

\[ J = 0 \rightarrow 1 \] in the first excited state \( v = 1 \)

of Methyl Cyanide

S. Gierszal, J. Galica, B. Mil-Kuźmińska

The linewidth parameter for the rotational transition \( J = 0 \rightarrow 1 \) of acetonitrile in the ground and the first excited state has been measured. Using the lines overlapping model [1] the quadrupole hyperfine structure for both states has been taken into account. Experimental results for the \( J = 0 \rightarrow 1, v = 0,1, F = 1 \rightarrow 2 \) of CH₃CN gives following values of the linewidth parameters:

\[ v = 1, \quad \Delta \nu / p = 43.3 \text{ kHz/Tr} \]
\[ v = 0, \quad \Delta \nu / p = 45.1 \text{ kHz/Tr} \]

The experiments have been made with the conventional microwave Stark spectrometer [2] while the pressure in the absorption cell was varied from 4 to 10 mTr.

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   Fiz. Diol. Radioosp. 11, 115 /1979/
Dipole Moment Functions of CH$_3$NCO and CH$_3$NCS

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The Stark effect of some rotational transitions of two quasi-symmetric top molecules, namely methyl isocyanate (CH$_3$NCO) and methyl isothiocyanate (CH$_3$NCS), has been measured and analyzed in terms of a five-dimensional quasi-symmetric top model. The electric dipole moment is expressed as a function of coordinates of the large-amplitude motions, the CNC bending and internal rotation. The function parameters have been determined using the experimental data combined with the results of ab initio SCF calculations.
Methylene Chloride rotational spectra were recorded in the range 10-75 cm\(^{-1}\), with a practical resolution of 0.002 cm\(^{-1}\), using a Michelson Interferometer.

Commercial grade methylene chloride was used. This consists of an isotopic mixture of 56% CH\(_2\)\(^{35}\)Cl\(_2\), 38% CH\(_2\)\(^{35}\)Cl\(^{37}\)Cl and 6% CH\(_2\)\(^{37}\)Cl.

In the spectra Q-branches belonging to all three isotopic species are clearly visible for low k values. However assignments for R branches can be reasonably made only for the two major isotopic species.

We began to analyze CH\(_2\)\(^{35}\)Cl\(^{37}\)Cl, since for the ground state only the rotational constants have been previously determined.

So far we have been able to analyze \(^r\)R branches with 5\(\leq k \leq 31\) and J up to 79.

Final results will be presented.

As far as CH\(_2\)\(^{35}\)Cl\(_2\) is concerned, from a first incomplete analysis of the data, we think that we should be able to obtain an improvement in the distortion constants previously determined from microwave data\(^1\).

In the spectra are clearly visible Q-branches which presumably are due to rotational spectra of \(\nu_4\) (\(\sim 280\) cm\(^{-1}\)) which we hope to be able to analyze in the near future.

High Resolution Infrared Laser Spectroscopy of Molecular Beams

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Several examples of very high resolution, coherent, spectroscopic measurements carried out recently in Waterloo on CH$_3$F, NH$_3$, CH$_3$OH and CO$_2$ in electric fields, at wavelengths around 10μm will be presented.

This will include the resolution of Ramsey fringes in the $\nu_3$ band of CH$_3$F, the precise determination of the transition dipole moment for the fundamental vibration of the same band and for the $\nu_2$ vibration of NH$_3$ via the measurement of Rabi oscillations and the resolution of the Stark splittings for some of the lasing transitions of CO$_2$.

If time permits recent work on the Stark spectroscopy of CH$_3$OH will also be presented.
HIGH RESOLUTION FAR-INFRARED SPECTROSCOPY ON SMALL MOLECULAR IONS

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We present the observation of rotational transitions in the electronic and vibrational ground state of the small molecular ions \( \text{OH}^+ (X^3\Sigma^-, N=1+0) \), \( \text{OD}^+ (X^3\Sigma^-, N=2+1) \) and \( \text{NH}^+ (X^2\Pi, J=3/2+1/2) \) with resolved hyperfine structure. Until recently, these species, which are of astrophysical interest, were only known by their optical or UV emission spectra.

Spectroscopic information has been obtained by using a laser sideband spectrometer. Tunable narrow band far-infrared radiation in the frequency range from 700-1200 GHz is generated in Schottky barrier diodes by frequency mixing of the radiation of a klystron with lines of a HCN laser. Molecular ions are produced in a temperature controlled hollow cathode discharge tube. Modulation of the discharge current was applied for phase sensitive detection with a liquid helium cooled bolometer.

The resolved hyperfine structure in the spectra allowed us to determine the hyperfine constants for \( \text{OH}^+ \), \( \text{OD}^+ \) and \( \text{NH}^+ \) in their ground states. Improved values of rotational and fine structure constants have been obtained for \( \text{OH}^+ \) and \( \text{OD}^+ \).
The stimulated Raman spectrum of $^{13}$CD$_4$ is presented in the region of the pentad, thus covering the $v_4(A1)$, $2v_2(A1)$, $2v_4(A1)$ and $v_2 + v_4(F1 + F2)$ Q-branches. This investigated wide frequency range is spread out to 45 cm$^{-1}$ and contains more than 300 lines with accuracy better than 1.10$^{-3}$cm$^{-1}$. This spectrum has been recorded on the stimulated Raman spectrometer of Dijon, at room temperature and at a pressure of 30 to 150 Torr, allowing an effective resolution of 10 to 40 10$^{-3}$cm$^{-1}$.

The interpretation of the spectrum is based on the tensorial hamiltonian for tetrahedral molecules [1] developed up to the 6th order for the ground state, 5th order for the dyad and the 3th order for the pentad levels. The ground state and dyad parameters are fixed to the values of the dyad $v_2/v_4$ infrared analysis [2].

The Hamiltonian parameters are determined by a simultaneous analysis of infrared [3] and Raman transitions of the pentad.

The standard deviation obtained for this Raman spectrum is of the same order of magnitude than the experimental wave numbers (1.2 10$^{-3}$cm$^{-1}$).

The Method for Improving the Convergence of Effective Rotational Hamiltonian of Nonrigid Molecules

V.I. Starikov

The method for improving the convergence of the effective rotational Hamiltonian $\mathcal{H}_{\text{rot}}$ is based on the account in the zero-order approximation $H_0$ of the component $\hbar$ from the perturbation $W$, completely describing the vibration-rotation interaction in molecule. For this purpose the following calculations are made.

1. When solving the Schrödinger equation

$$H_0 \Psi(\rho) = E \Psi(\rho)$$

the potential function $V_0(\rho)$ is chosen in such a way that Eq.(1) should have the analytical solution for $\xi$ and $\Psi$.

We use the potential function $V_0(\rho)$ in the form:

$$V_0(\rho) = C_0 + C_1 \cdot f(\rho) + C_2 \cdot [f(\rho)]^2$$

2. The term $\hbar = A(\rho) Z^2 + B(\rho) J^2$ is deleted from $W$, where the functions $A(\rho)$ and $B(\rho)$ are approximated by the segments of the series $A(\rho), B(\rho)$

$$A(\rho) = \sum_{k=0}^{\infty} A^{(k)} [f(\rho)]^k$$

$$B(\rho) = \sum_{k=0}^{\infty} B^{(k)} [f(\rho)]^k$$

then the operator $\mathcal{H}_1 = A(\rho) J^2 + B(\rho) J^2$ is considered in the zero-order approximation that results in

$$\{ H_0 + \mathcal{H}_1 \} \Psi_{j,k}(\rho) = C_y (Z J^2, B J^2) \Psi_{j,k}(\rho)$$

and the operator $\mathcal{H} = [A(\rho) - A(\rho)] J^2 + [B(\rho) - B(\rho)] J^2$ is considered in $W$. For $f(\rho) = \text{th} \cdot J_\rho$, $e^{-\alpha \rho}$, $1/\rho$ [1] the analytical form of $G(Z J^2, B J^2)$ is obtained. Under definite conditions in $\hbar$ we can find the values of $z$ and $b$. The same values are calculated from the approximation (3) by the least-square-method. The operator $G$ can serve as the zero-order approximation for $\mathcal{H}_{\text{rot}}$. Different applications of $G$ are considered in this paper.

The effective Hamiltonian for Coriolis interaction of \( \nu_n \) and \( \nu_t \) bands in \( C_{3v} \) molecules has been derived using contact transformations. The formulas for spectroscopic parameters of the types \( q^2j^2 \) and \( q^2j^3 \) in terms of molecular constants \( \omega, B, \zeta, K_{ij} \) have been obtained.

It has been found that the procedure of the "reduction" of effective Hamiltonian should be carried out to make the correct interpretation of the fitted parameters in terms of molecular constants. The procedure of the reduction has been considered for both degenerated isolated band \( \nu_t (E) \) and interacting \( \nu_n (A_1) \) and \( \nu_t (E) \) bands.

By the use of this procedure we succeeded in interpreting variations of the results on simultaneous fitting of interacting \( \nu_2 \) and \( \nu_5 \) bands of \( CH_3F \) [1,2].

<table>
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<th>Transf. Param.</th>
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THE USE OF VARIOUS NONPOLYNOMIAL FORMS OF THE EFFECTIVE
ROTATIONAL HAMILTONIAN \( \mathcal{H}_{\text{rot}} \) FOR DESCRIBING ROTATIONAL
ENERGIES OF MOLECULES

V.I. Starikov, V.F. Golovko, Vl.G. Tyuterev

The nonpolynomial forms of \( \mathcal{H}_{\text{rot}} \) are based on exact solution \( G \) of the Schrödinger equation \( H\Psi = \mathcal{E}\Psi \) which takes into account the vibration-rotation interaction within \( H_0 \). This paper presents the following forms of the operator \( G \):

1. \[
G_t = - \frac{[C_{1}^{jk}]^2}{4} \left[ \frac{1}{\varepsilon} \beta_t^j + \frac{C_0^j}{\varepsilon} \right] \beta_t^j = - \left( \alpha + \frac{0.5}{t} \right) \varepsilon \beta_t^j + \frac{0.25}{\varepsilon} \beta_t^j \] (1)

2. \[
G_t = - \alpha \left\{ \frac{C_{1}^{jk}}{4} \frac{\sqrt{\varepsilon}}{\varepsilon} C_{2}^{jk} - (t+0.5) \right\}^2 + C_0^{jk} \] (2)

3. \[
G_t = - \frac{[C_{1}^{jk}]^2}{4} \left[ \frac{1}{\varepsilon} \beta_t^j + \frac{C_0^j}{\varepsilon} \right] \frac{1}{\varepsilon} \beta_t^j \] (3)

where \( t = \frac{v_2}{2} \) for the \( X_2Y \) molecules and \( C_i = C_i + \varepsilon \mathcal{H}_i \mathcal{H}_r \), \( \mathcal{H}_i = 0,1,2 \), \( \mathcal{H}_i \) are the parameters of the potential function \( V_0(\rho) \in H_0 \).

The operator \( G \) is the zero-order approximation for \( \mathcal{H}_{\text{rot}} \). The use of various expansions of \( \mathcal{H}_{\text{rot}} \) with enables one to describe many experimental energies of nonrigid molecules with high accuracy.
In recent years, several very precise experimental spectra become available for molecules of the type CH₄, CD₄, SiH₄, GeH₄ and for their isotopic species, this suggests elaborate development of associated theoretical models.

The problem of unambiguous processing of such type experimental data is studied on the basis of series of fits of $\nu_S$, $2\nu_t$ and $\nu_t + \nu_t'$ bands using the tensorial formalism [1].

It is shown that correct handling of the transformation of effective Hamiltonians to reduced ones [2] is even more important for $2\nu_t$ and $\nu_t + \nu_t'$ then for fundamentals [3, 4], since the ambiguities become more pronounced with increasing vibrational degeneracy and increasing order of the expansion.

The spectroscopic constants of the upper states are determined as well as the experimental values of d-coefficients which are involved in the definition of invariant parameters [4].

The isotopic dependence of invariant parameters is examined.

ON THE PROCESSING OF VIBRATIONAL-ROTATIONAL SPECTRA OF 
LIGHT H₂X TYPE NONRIGID MOLECULES USING RATIONAL EXPAN-
SIONS IN ANGULAR MOMENTUM AND RELATED MODELS.

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Several versions of processing of experimental spectra of nonrigid H₂X type molecules on the basis of reduced effective molecular Hamiltonian $H_{\text{rot}}$, which is rational in angular momentum operator $J$, are discussed. The particular attention is payed to the version of the calculations suggested in (1,2). In this version of calculations one deals with usual rotational and centrifugal distortion parameters, however the operator form of the Hamiltonian is fractional-rational. The quality of description of experimental data is generally improved with respect to conventional polynomial model whereas the same parameters $A, B, C, \Delta, H, \cdots L, \cdots$ are adjusted. The typical example for (000) of $H_2O$ is the following:

$$\frac{\Sigma_{\text{rational}}}{\Sigma_{\text{polynom.}}} \quad \text{FIT} \quad \text{DIRECT CALC.}$$

$$2.10^{-2} \quad 3.10^{-4}$$

with 24 parameters in both calculations up to $L$-parameters (i.e. up to $J^8$-terms in $H_{\text{polynom.}}$). Here

$$\Sigma = \sum (E_{\text{obs.}} - E_{\text{calc.}})^2 \text{ with } J, K \text{ up to } 20.$$ 

The first number 0.02 refers to the case when all 24 parameters are adjusted in the fit to 428 experimental energies and the second number 0.0003 refers to the direct calculations with known parameters (3). In this approach 28 parameters are sufficient to achieve st.deviation $\sigma = 0.06 \text{ cm}^{-1}$ up to $J, K_a = 20$. (ref. (4)). The use of models with constraints imposed on denominator and numerator enables one to get further improvement of the fit.

THIRD GENERATION RAD SPECTROMETER

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A model of a submillimeter scanning RAD spectrometer of the third generation (RAD-3) is reported. The spectrometer allows to measure spectral line frequencies in gases in the 150-650 GHz range with a relative accuracy of 10^{-6} to 10^{-7} avoiding use of complex frequency measuring apparatus. RAD-3 preserves high sensitivity and wide range of a conventional RAD [1,2] and has a resolution of 1 MHz.

Analysis of possible sources of errors in measuring spectral line frequencies holds promise to increase the accuracy of frequency measurements in RAD-3 by one more order and to enhance its resolution up to 10^{-7}.

The design of RAD-3 makes it possible to fully automatize measurements throughout the spectrometer frequency range and to rapidly investigate absorption spectra of molecules in the submillimeter spectrum range.

MICROWAVE SCANNING CSR SPECTROMETER WITH A NEAR-LIMITING SENSITIVITY

L.I. Gerstein, S.I. Pripolzin and V.L. Vaks

The present paper deals with further improvement of the spectrometer based on coherent spontaneous radiation (CSR spectrometer), in which time separation of CSR and generator radiation initiating gas polarization, is provided by frequency switching of the radiation source /1/.

The detailed analysis of the reasons limiting the sensitivity of the first variant of this spectrometer, enabled us to develop an optimum reception system ensuring the sensitivity close to the theoretical limit. The sensitivity was checked using the rotational transitions of the OCS molecule /2/.

A unified microwave spectrometer, whose sensitivity exceeds the sensitivities of the spectrometers available in this region, can be realized on the CSR basis due to its frequency independence of the reception method.

To provide wide-range tuning with exact frequency measurement and necessary frequency stability of the CSR-spectrometer radiation source, a frequency synthesizer /3/ has been created, that is an improved submillimeter frequency synthesizer /4/.

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In principle, the optical alignment of cube corner interferometers is very simple compared to conventional plane mirror interferometers. This is true, because small tilts of the cube corner have no influence on interference. However, the lateral shifts of the moving cube corner create small distortions of a line shape. In this work we propose a new method that gives the possibility to adjust perfectly the direction of the movement of the cube corner. With the help of the Fourier transform of a recorded spectral line we are able to calculate very accurately the phase error between the main signal (IR) and the reference signal (laser). It is easy to adjust the interferometer so that the phase error function is linear as a function of the optical path difference. The linearity of the phase error function indicates a perfect optical alignment.
Contact Transformation in the Mixed Matrix-Operator Scheme: Effective Rotational Hamiltonians in Degenerate Vibrational States, Line Strength of the Allowed and Forbidden Vibrational-Rotational Transitions in Symmetric Top Molecules

D. Papoušek, Š. Urban

It is well known that it is possible to apply rotational contact transformations to the effective rotational Hamiltonians

$$H_{\text{rot}} = H_{02} + \lambda H_{04} + \lambda^2 H_{06} + \cdots$$

such that certain off-diagonal terms are eliminated from the lower order terms of the expansion of $H_{\text{rot}}$ in terms of the "smallness" parameter $\lambda$.

Such reductions are important in least squares fits of the experimental data; unless the Hamiltonian is fully reduced, correlations between the spectroscopic parameters lead to numerically ill-behaved problems.

So far the reduction of the effective rotational Hamiltonians has been discussed mainly for nondegenerate vibronic states of molecules. We have extended this treatment to the doubly degenerate fundamental levels of symmetric top molecules with special emphasis on the $XY_3$ nonrigid molecules.

The reduction of the effective Hamiltonians will be discussed which concerns two types of terms: i) $H_{\text{split}}$ term which is diagonal in all the vibrational quantum numbers $v$ and $l$ but off-diagonal in the rotational quantum number $k$ ii) operators of the $"2, \, \pm 2"$ and $"2, \, -1"$ $l$-type interactions which are diagonal in $v$ but off-diagonal in $l$.

The results have been used i) to discuss the correlation between the effective spectroscopic parameters of the degenerate fundamental levels ii) to develop a third order theory of the intensities of the allowed and "forbidden" transitions to the fundamental vibrational levels of symmetric top molecules.
IR-MW Double Resonance Spectroscopy of the $v_2/v_4$ Band System of SnH$_4$

Using a Tunable Diode Laser

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This paper reports high resolution study of the $v_2/v_4$ band system of SnH$_4$ and observation of pure rotational transitions in the ground vibrational state by IR-RF double resonance. The $v_4$ band of SnH$_4$ is known to have a strong Coriolis interaction with $v_2$. Vibration-rotation lines of the $v_4$ and perturbation-allowed $v_2$ bands were measured using tunable diode lasers provided by Fujitsu and Laser Analytics. Approximately 800 lines were assigned in the $v_4$ band for seven major isotopic species of SnH$_4$ up to $J = 20$. The observed lines were analyzed with a Hamiltonian which included the Coriolis interaction with $v_2$. An uncoupled basis set was used for diagonalizing the Hamiltonian. A preliminary analysis of the assigned lines led to the determination of 17 spectroscopic constants for the $v_4$ and $v_2$ states of each isotopic species.

Prior to double resonance experiment, Stark effect on the infrared absorption lines was examined to confirm the existence of induced dipole moments. Many lines showed first- and second-order Stark effect under the electric field of 3 kV/cm. Direction of the frequency shift in the second-order Stark signal indicated that the Stark effect arose primarily from the centrifugal-distortion-induced dipole moment in the ground vibrational state. Pure rotational transitions allowed by this dipole moment were then measured by IR-RF double resonance with a laser diode provided by Laser Analytics as pump source. Eventually 15 rotational transitions were measured below 530 MHz, from which three tensor constants, $D_t$, $H_{4t}$, and $H_{6t}$, were determined accurately. The induced dipole moment in SnH$_4$ was much larger than those of other tetrahydrides of group IVb elements due to lower vibrational energy and larger transition dipole moment of the $v_4$ mode. Further work is in progress.
Fourier transform spectra of $^{14}\text{ND}_3$ have been recorded in the region 450 - 850 cm$^{-1}$ at a resolution of approximately 0.005 cm$^{-1}$.

Transitions belonging to the $2\nu_2 \leftrightarrow \nu_2$ vibration-inversion-rotation band have been assigned with the $s \leftrightarrow a$ and $a \leftrightarrow s$ band origin at 609.9 cm$^{-1}$ and 684.5 cm$^{-1}$ respectively. The position of the $2\nu_2 \leftrightarrow 0$ transitions has been calculated by means of these transitions together with the $\nu_2 \leftrightarrow 0$ transitions and the inversion splitting in the ground or $\nu_2 = 1$ states.

All the experimental data have been analyzed simultaneously to provide a quantitative description of the inversion-rotational pattern of the $\nu_2 = 2$ vibrational state up to $J = 17$.

The effective Hamiltonian used includes the $\Delta k = \pm 3$ interaction terms between levels having opposite parity with respect to inversion.
A High Resolution Infrared Study of the $v_4$ Band of CH$_3$I

R. Paso, R. Anttila, and G. Guelachvili

The infrared spectrum of the $v_4$ band of CH$_3$I around 3060 cm$^{-1}$ was studied at a resolution of 0.0054 cm$^{-1}$. The recordings were performed using the Fourier spectrometer at Laboratoire d'Infrarouge in Orsay. About 1850 transitions were assigned including 350 $Q_{K(J)}$ lines. The $K$ range was from $K\Delta K = -7$ to $K\Delta K = +9$ and the highest $J$ values were about 75.

The $Q$-branches $RQ_5$ and $RQ_7$ are split into two parts with a crossing around $J = 30$ in both cases. $RQ_6$ is sharp and the rotational structure is resolved only above $J = 50$. The anomalous rotational structures observed in these subbands $K\Delta K = +5 - +7$ were explained with the aid of Coriolis and Fermi interactions with the combination level $v_2 + 2v_6 \pm 2$. In $PQ_6$ a smaller Coriolis-type resonance, caused probably by $v_2 + 2v_6^0$, was observed.

The standard deviation of the least squares fit with 19 free parameters was 0.00083 cm$^{-1}$.

In addition to the fundamental band the hot band $v_3 + v_4 - v_2$ was also studied. Almost 400 lines were assigned to the subbands with $K\Delta K$ from -4 to +6 and they could be fitted with a standard deviation of 0.0013 cm$^{-1}$ using seven free parameters.

VIBRATIONAL DEPENDENCE OF SPECTROSCOPIC PARAMETERS OF MOLECULES AND CONVERGENCE PROPERTIES OF HAMILTONIAN EXPANSION FOR INTERACTING VIBRATIONAL STATES.

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The expansions in rational functions of the angular momentum components are successfully employed recently to construct effective rotational Hamiltonian operators. The possibility to reduce these Hamiltonian operators to the form with phenomenological parameters unambiguously determined from experimental data, is considered in /1-4/. As a result of this procedure, one obtains free-parameter families of effective Hamiltonian operators. It is important that selection of free parameters influences the convergence of the effective Hamiltonian operator when treating experimental data. Therefore, we deal with the problem of optimum selection. To solve this problem, we use the variational Ritz method. The application of the obtained optimum form of the effective Hamiltonian operator has greatly improved the treatment of experimental data.

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Some New Developments in One-Dimensional Approximation of Effective Hamiltonians

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It is shown numerically that Watson's perturbation series is of Stieltjes type [1] and its one-dimensional approximation [2] convergence is a consequence of its analytical properties. Using rotational constants of the water ground state obtained by Johns [3] we have shown that Borel approximants [2] are about ten times more rapidly convergent than the Padé [2] ones.

Borel approximants [2] are expressed in terms of standard special functions and fit of high precision MW and FIR data [3] is made to compare predictability of various models. Padé model [2] of 31 constants with the terms up to $J_{12}$ give fit to experimental uncertainty and prediction of the levels of $K$ up to 20 [4] with discrepancy less than 0.8 cm$^{-1}$, that is about 50,000 times better than in a standard model [3]. Prediction of levels of high $K$ in a model of 24 parameters up to $J_8$ terms yields the discrepancy less than 5 cm$^{-1}$ for Borel and 73 cm$^{-1}$ for Padé approximants.

Joint fit of all available MW, FIR data and levels of Ref. [4] in the model of 24 constants gives standard deviation of about 30 times better in Padé and 200 times better in Borel approximation than in a conventional model with the same number of parameters.

Nuclear Hyperfine Structure of Molecular Rotational Levels
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Theoretical and experimental study of nuclear hyperfine structure of rotational levels of various molecules is presented.

Complete hyperfine Hamiltonian of a $C_3v$ molecule with off-axis nuclear spins $1/2$ and $1$ is formulated, including all the quadrupole couplings, spin-rotation and spin-spin interactions, as well as centrifugal distortion of quadrupole couplings. Matrix elements of the Hamiltonian are evaluated by the irreducible tensor method.

Forbidden transitions $\Delta J=\pm 2$ and $\Delta K=\pm 1, \pm 2$ allowed by quadrupole couplings, as well as centrifugal contributions in the case of strong quadrupole coupling ($\Delta J>0$) and in the cases of two and three quadrupole nuclei are discussed.

Pure quadrupole spectra of $\text{CH}_3\text{I}$, $\text{CD}_3\text{I}$, $^{13}\text{CH}_3\text{I}$, $\text{CH}_3^{79}\text{Br}$, $\text{CH}_3^{81}\text{Br}$, and some K-type transitions of the HCOOD and DCOOH molecules, have been studied by the RF-MW double resonance method at resolution ~1 KHz in the region 80-500 MHz. Spectra of halomethanes have been fitted using above-mentioned Hamiltonian, and all the hyperfine constants have been determined, which obey newly developed isotopic relations. An interesting example of spin-rotation compensation of deuterium quadrupole coupling in DCOOH is illustrated.

The Pure Rotational Spectrum of Silicon Tetrafluoride
L. Jörissen, W.A. Kreiner, T. Oka
POSTER SESSION

P. Thla. Studies of isobutanol rotational isomerism fromMW absorption spectra
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The possibility of studies from microwave spectra of rotational isomerism due to azimuthal rotations of asymmetrical atomic fragments permits to obtain data on the internal molecular dynamics, to study the nature of intramolecular interactions, and matter structure at atomic and molecular levels.

To investigate rotational isomerism, microwave absorption spectrum of isobutanol, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$, has been studied, which is the following step in comprehensive search of physical and chemical behaviour of one-atomic alcohols and mercaptans. The frequencies, intensities and Stark effects for about 500 spectral lines are measured at the Stark-modulated double-resonance gas spectrometer at $-30$ to $-40^\circ\text{C}$ and at $10^{-2}$ to $10^{-3}$ Torr within 10+30 GHz frequency range. Several series of doublet transitions with $J = 3 : 12$ and splitting of about 10+20 MHz have been identified. Assigned transitions are listed; average rotational constants and approximate values of dipole components along the principal axes are obtained. Structural parameters are found by the computer program and correlated with the similar ones for allied molecules. The data obtained provide evidence on the spectral belonging to one of the five conformational-analysis predicted coiled conformers, whose realization is associated with the azimuthal rotation of heavy atomic fragment $\text{OH}_2\text{OH}$ about the frame of molecule by $2/3\pi$. 
Design features of the modified measuring cells for Stark-modulated MW gas spectrometer
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Studies of microwave absorption spectra in substance molecules by Stark-modulated gas spectrometer are associated with recurrent measuring cell cleaning for sample renewal or substitution by another substance. Present technique of cell degassing has low efficiency due to the process duration and cleaning degradation.

Both our and foreign scientists' research on some organic molecules with chemically unstable atomic fragments and their isotopically substituted species such as OH, SH, NH, OD, SD, ND established a dramatic drop in concentration for the samples, liquid-phased in ampoules, distilled into conventional evacuated waveguide cell; simultaneous formation of exchange by-products whose strong lines overlap the spectrum of the sample under study, is detected, which greatly hinders spectral identification.

Basing on the analysis of the possible reasons for these undesirable phenomena, the modified technique and construction of the waveguide measuring cell are proposed (author's certificate No.1183873 of 08.06.85) which promote to accelerate by the order of magnitude the process, and to improve cleaning as well as to preserve initial concentration of molecules with chemically unstable atomic fragments and to increase labour productivity.
Some aspects of multiisomerism in one-atomic alcohols
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Internal dynamics and intramolecular interactions which stabilize rotational isomers in free molecules are the keystones of understanding the nature of matter structure. Microwave spectroscopy combined with other spectroscopic and physico-chemical methods makes possible the high-precision determination of molecular structure according to the given model, or data accumulation and generalization for new concepts of matter structure at various organizational levels. Investigations of MW spectra of ethanol, propanol, isopropanol, butanol, iso-butanol and their isotopically substituted species demonstrated the occurrence of isomers associated with the internal rotation of asymmetrical atomic fragments. Comprehensive research revealed, besides conformational analysis predicted spectra, the existence of such spectra that could be assigned neither to the theoretically allowed conformers nor to the excited states of allowed conformers. The origin of these spectra was found to be conditioned by some peculiar structural conformations. The phenomenon caused by the "excessive" amount of isomers and called "multiisomerism" was detected by the author not only in alcohols and mercaptans but also in some other substituted hydrocarbons. Therefore we are to solve the problem of generation of "forbidden" conformers and the related necessity to introduce additional types of intramolecular interactions which enable us to correlate conformational calculations with the experimental data. These and other aspects of "multiisomerism" in one-atomic alcohols are discussed in the paper.
Increasing of Sensitivity of Submillimeter RAD Spectrometer by Cavity Cells and Application to Molecular Chemical Analysis


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In conventional cells of RAD [1] there is single-pass interaction of radiation with gas molecules and small part of the BWO power is transformed into acoustic signal. A multipass cell is a simple method of increasing efficiency of radiation - gas interaction [2, 3].

We report on a highly sensitive submillimeter gas RAD spectrometer [4] (\( T_{\text{min}} \approx 3 \times 10^{-11} \text{ cm}^{-1} \) at \( T \sim 1 \text{ s} \) and \( \nu = 200 - 380 \text{ GHz} \)) with quasi-optical cavity absorption cells. Weak absorption lines of \( \text{N}_2\text{O} \) molecule in states 001, 200, 040 and 030 are studied. The results are used in the molecular analysis of monogermane for phosphine small species down to the 50 ppb level [4]. Comparative analysis with the gas chromatographic method proves that low concentrations of polar gaseous species have been determined correctly. Range of applicability of the proposed method for the investigation of weak line submillimeter molecular spectra is discussed.

A further development of the investigations of molecular pressure line shifts initiated in [1,2] is presented. The shifts of lines $2_{20}^{11}$ of molecules $H_2^{32}S$, $H_2^{33}S$, $H_2^{34}S$ by the pressure of various gases are studied experimentally. The temperature dependences of line shifts investigated in [3] are extended now to the lines of asymmetric tops $H_2S$ and $H_2O$. The validity and the general character of the before obtained dependences of shifts on quantum numbers $J$ and $K$ are confirmed by the experiment. The measured self-shift parameter
\[
\Delta \chi (I_{01} - 0_{00}) = 4.8 \text{ MHz/Torr}, \text{ self-broadening (HWHM)}
\]
\[
\Delta \gamma (I_{01} - 0_{00}) = 27 \text{ MHz/Torr}. \text{ The estimates of the line shifts of the molecular ions are obtained. The Ritz combination principle is used to analyze the line shifts by pressure. An example of centimeter, submillimeter and infrared spectra of ammonia is considered. Some applications of the phenomenon of the line shift by pressure[4] are considered.}

Ground and Excited Vibrational States of Water. Pure Rotational and Fundamental Band Spectrum Investigation

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New line frequencies of pure rotational spectra of H$_2^{16}O$ and H$_2^{18}O$ in both ground and first excited 010 vibrational states were measured. In particular, 5 submillimeter line frequencies of 010 pure rotational spectrum of H$_2^{16}O$ in the region between 230 and 600 GHz were measured and fitted to a model of 24 parameters of one-dimensional Borel approximation [1] of Watsonian. All known rotational data [2,3,4] and about 200 energy levels up to K=14 [5] were used in the fit and for the first time all of them were fitted to within experimental error for rotational data and $\sigma = 500$ MHz for the energy levels of Ref.[5]. The attempt to fit all these data in a conventional model resulted in standard deviation 60 times greater than in our model.

The investigation of H$_2^{18}O$ spectrum resulted in 24 rotational constants for both ground and 010 states which reproduce the newly obtained MW and known pure rotational [6] and $\nu_2$ fundamental band data [7] to experimental uncertainty. Some of the constants were fixed to the values of H$_2^{16}O$ constants.

REANALYSIS OF $\nu_1$ FUNDAMENTAL BANDS OF DEUTERATED $\text{H}_3^+$ MOLECULAR IONS AND ITS PREDISSOCIATION SPECTRUM INTERPRETATION

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Reanalysis of $\nu_1$ band frequencies of $\text{H}_2\text{D}^+$ [1] and $\text{D}_2\text{H}^+$ [2], 2 MW frequencies of $\text{H}_2\text{D}^+$ and about 20 combination differences from $\nu_2$ and $\nu_3$ bands of $\text{H}_2\text{D}^+$ [3] is performed. It is shown that poor fit in [1] and [2] is due to misassignment. The following reassignment is done: for $\text{H}_2\text{D}^+$ the line 3168.702 cm$^{-1}$ is assigned as 505 - 404 and for $\text{D}_2\text{H}^+$ the line 2990.154 cm$^{-1}$ as 441 - 330; assignment of the lines 2899.242 and 2899.362 cm$^{-1}$ is interchanged and the line 2832.859 cm$^{-1}$ is presumably attributed to 515 - 514 of $\text{H}_2\text{D}^+$. This reassignment results in about ten times better fitting than in Ref. [1] and [2] in the model of up to J$^6$ terms and in the standard deviation of about 7.10$^{-3}$ cm$^{-1}$ (IR data) for both $\text{H}_2\text{D}^+$ and $\text{D}_2\text{H}^+$ in the model of up to J$^4$ terms. A model of one-dimensional approximation [4] of Watsonian is used in both cases.

The predissociation spectrum of $\text{H}_3^+$ [5] based on the approach of Ref. [4] is interpreted as pure rotational and rovibrational forbidden transitions of high J levels in various vibrational states.

Analysis of pentad and pentad-dyad of \(^{13}\)CD\(_4\) from FT-IR spectra.

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The infrared spectrum of the \(^{13}\)CD\(_4\) molecule in the dyad region (920-1200 cm\(^{-1}\)) and pentad region (1800-2300 cm\(^{-1}\)) has been recorded on the Fourier Transform Spectrometer of Laboratoire de Spectrométrie Moléculaire de Paris. The FWHM of the unblended lines is of the same order to the Doppler-Fizeau width (3 \(\times\) \(10^{-3}\) cm\(^{-1}\) for the dyad and 6 \(\times\) \(10^{-3}\) cm\(^{-1}\) for the pentad). The accuracy of the frequencies is 1.1 \(\times\) \(10^{-4}\) cm\(^{-1}\) for the dyad and slightly worse for the pentad.

The pentad consist of the two fundamental bands \(\nu_1\) (A1) and \(\nu_3\) (F2). The overtone and combination bands 2\(\nu_2\) (A1 + E), 2\(\nu_4\) (A1 + E + F2) and \(\nu_2 + \nu_4\) (F1 + F2). The analysis of the infrared data is achieved with the tensoriel Hamiltonian [1] developed for tetrahedral molecules up to the 6th, 5th and 3rd order for the ground state (10 operators), dyad (40 operators) and pentad (63 operators) respectively. The 40 ground state and dyad parameters of the reduced Hamiltonian [2] are fixed to the values resulting from the dyad \(\nu_2/\nu_4\) infrared analysis [3]. The parameters of the pentad are determined by simultaneous analysis of the pentad and pentad-dyad infrared spectra and the pentad Raman spectra [4].

The standard deviation obtained for the infrared data is about 1 to 2 \(\times\) \(10^{-3}\) cm\(^{-1}\).

P Th8. Effective Rotational Hamiltonians for Molecules With Large Amplitude Motions

K. Sarka

P Th9. Derivation of the Nonrigid (Effective) Rotation-Large-Amplitude Internal Motion Hamiltonian of the General Molecule

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A nonrigid (effective) rotation-large-amplitude internal motion Hamiltonian of the general molecule is developed to order of magnitude $k^2 T_{\text{VIB}}$ providing a method for accurate ab initio calculation of rotation-large-amplitude internal motion spectra of nonrigid molecules the large-amplitude internal motion frequencies of which are much less than their small amplitude vibration frequencies.
Investigation of Forbidden Submillimeter Spectrum of $\text{AsH}_3$ in $V_2=1$ and $V_4=1$ States and Joint Analysis of Submillimeter and Infrared Data

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An experimental study by RAD spectrometer [1] of both allowed ($J=0,1,2,3$) and weak "forbidden" (for example, $K=3\leftrightarrow0$, $3\leftrightarrow1$, $2\leftrightarrow0$) rotational transitions of $\text{AsH}_3$ in the $V_2=1$ and $V_4=1$ states in the frequency range 200 - 940 GHz is described. The observation of weak ($\gamma\approx10^{-7}-10^{-8}\text{cm}^{-1}$) "forbidden" transitions of $\text{AsH}_3$ became possible due to the use of multipass cavity absorption cells [2,3]. A theoretical analysis was carried out taking into account the interaction between $V_2$ and $V_4$ states and new submillimeter data together with known experimental results [4,5,6,7]. A set of rotational constants of $\text{AsH}_3$ molecule in excited vibrational $V_2=1$ and $V_4=1$ states was obtained which refined the values of spectroscopic constants determined earlier.

In some previous works the term "common beam spectroscopy" was adopted for measurements in which an anisotropic sample is introduced into the common optical path of a double beam spectrometer, both sample and reference beams being variously polarized. In this measurement the spectrometer ignores the overall absorption of the sample and records only the difference in absorption or the transmission ratio with respect to both beams. The corresponding measurement with FTIR spectrometers is simply the difference spectrum from two records with variously polarized beams. In the latter case, however, the common beam principle remains exactly the same as in the case of the dispersive instruments. Four basic optical phenomena in the IR region could be measured on the basis of the common beam principle: linear and circular dichroism, linear and circular birefringence. The design of the measuring device permits one to compensate for side phenomena if they are present. The resolution of the instrument turns out to be very important for obtaining reliable spectral features and for calculating optical parameters. Although common beam measurements are considered to be a typical medium resolution task, increasing the resolution up to 0.06 cm$^{-1}$ leads to a considerable improvement of the spectral features especially in the cases when dispersion and interference curves are recorded. Some typical examples are shown.
p Th12. Reduction of the Effective Rotational Hamiltonian for the Degenerate Vibrational States of Symmetric Top Molecules

Š. Urban, D. Papoušek, M. García Hernández

A mixed matrix-operator form of the effective rotational Hamiltonians has been discussed for the degenerate vibrational states of symmetric top molecules. In this scheme, a contact transformation can be applied to the effective Hamiltonian such that the operators of the $2,\pm 2$ and $2,\pm 1$ $\ell$-type interactions as well as the operators of the $\Delta k = \pm 3$ and $\pm 4$ interactions are eliminated from the first order terms of the expansion of the rotational Hamiltonians in terms of the small parameter $\lambda$.

The results have been used to discuss the correlation between various interaction parameters in the effective rotational Hamiltonians with the special emphasis on the $XY_3$ semirigid and nonrigid pyramidal molecules.
P Th13. Third Order Theory of the Line Intensities in the
Allowed and "Forbidden" Vibrational-Rotational
Bands of C$_{3v}$ Molecules

M. R. Aliev, D. Papoušek, Š. Urban

A third order theory of the intensities of the
allowed and "forbidden" (perturbation allowed)
transitions to the fundamental vibrational levels
of C$_{3v}$ semirigid molecules has been worked out
by using the method of contact transformations
applied to the electric dipole moment operator.
Explicit expressions have been obtained for the
line strengths of the allowed ($\Delta k = 0, \pm 1$) as
well as forbidden ($\Delta k = \pm 2, \pm 3, \pm 4$) transitions
from the ground vibronic state to the fundamental
vibrational levels of C$_{3v}$ molecules.

The treatment takes into account all the
important Coriolis and anharmonic interactions in
a C$_{3v}$ molecule including the effect of the "2,2"
and "2,-1" $\xi$-type and $\Delta k = \pm 3$ interactions on
the intensities of the allowed and forbidden
vibrational-rotational transitions.

The expressions for the line strengths of the
allowed and forbidden transitions are given here
in a form suitable to fit the experimental data on
the intensities in the vibrational-rotational
spectra of C$_{3v}$ molecules.
Microwave Dielectric Relaxation of Aqueous Silicic Acid Solutions.

K.E.Zulfugarzadeh, A.A.Tevosov

The rotational relaxation processes in water diluted by silicic acid have been studied using microwave dielectric spectroscopy. Complex permittivities of the silicic acid solutions with the sodium hydroxide and ethanol additives were measured in the microwave range as a function of concentration and temperature. Comparative measurements were also performed for the aqueous sodium hydroxide solutions. Irrespective of any model considerations experimental data corrected for the frequency independent ionic conductivity are reproduced quantitatively by superposition of three Debye-type bands.

Obtained relaxational spectra are analyzed in the framework of the three-level water structure organization based on the earlier results for the aqueous aminoacid solutions (Proceedings of VII-th International Conference on High Resolution IR Spectroscopy, Prague, 1982, p.45). According to this approach the pure water spectrum being observationally unresolved consists of three virtual bands reflecting the two-mode local structure rearrangements and the single molecule reorientations, respectively. All solutes considered influence only the low-frequency band leaving unshifted spectral positions of the two others. This feature corroborates the assignment of that band to disturbed regions of the three-dimensional hydrogen bond network.

Effect of charged species on the spectra is explained by the rotational dielectric friction mechanism. It is established that besides monomers and small anions, silicic acid also exists (at concentrations up to 0.6\% by mass) in neutral form as 'highly polar ion pairs.'
Study of $\text{H}_2\text{O}$ Molecule Overtones Using Diode Lasers in the Near IR Range

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Parameters of third overtone lines of water in the near IR range (0.89 μm) were studied with pulse diode laser spectroscopy methods as a function of temperature and pressure of the buffer gas (air).

On the basis of this data a laser device for measuring of atmospheric humidity was created and was tested in expedition.
Resonance Peculiarities in SF$_6$ Absorption Lines

Collisional Broadening

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Using diode laser spectroscopy methods, a part of $^{32}$SF$_6$ spectrum at 950 cm$^{-1}$ was studied for collisional broadening by buffer gases: He, Ne, Ar, Kr, Xe, N$_2$, CO, H$_2$, $^{32}$SF$_6$, $^{34}$SF$_6$.

It was found out that Weisskopf's cross section $\sigma_w$ of collisional broadening processes was quite larger than that of gas kinetical processes.

It was shown that at distances $r = \sqrt{\sigma_w/\pi}$ the dispersive interaction contributes mainly to broadening and at low pressure inelastic collisions accompanied by nonradiational transitions between rotational sublevels of SF$_6$ take part.

Considerable differences were found between experimental and calculated (in the approximation of classical trajectories /1/) values of cross sections of transitions (normalised to Born's cross section) as a function of parameter of adiabaticity of collisions $\chi$. The resonant increasing of experimental cross sections in the region of $\chi = 1$ appears to be the most significant.

That resonance peculiarity is explained by the quantizing of the angular momentum of colliding particles relative motion, which usually is not considered in the calculated models /1/.

In the quantum case quasicrossing of rotational terms of SF$_6$ molecule appears leading at certain conditions to increase of efficiency of relaxation processes and consequently to more effective line broadening at collisions.

High Resolution Far Infrared Spectra of the Molecules S=C=C=C=S and O=C=C=C=S

F. Holland, M. Winnewisser and J.W.C. Johns

The far infrared spectra of the molecules S=C=C=C=S and O=C=C=C=S were measured with a Bomem FT spectrometer at an apodized resolution of 0.004 cm⁻¹. The latest results of the analysis of these spectra will be discussed.

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The results of CARS-spectroscopy studies of collisional processes of vibrational energy exchange in polyatomic molecules, resonantly excited by IR laser field, are presented. CARS spectra of SF$_6$, SiF$_4$ and CF$_3$I molecules have been recorded at resolution of 0.15 cm$^{-1}$. This vibrational excitation of molecular states has been carried out at different frequencies with the TEA CO$_2$-laser, the intensity of this laser being varied up to 1 J/cm$^2$.

In the experiments on collisional $\nu - \nu$ and $\nu - \nu'$ energy exchange processes in SF$_6$ and SiF$_4$ molecules the shape of the vibrational distribution function and its time development has been determined; also a few characteristic energy exchange time constants have been measured. In the experiments with CF$_3$I spectral lines of CF$_3$ radicals have been recorded.
Residual Rovibrator Branches in the Infra-Red Spektrum of Liquid Carbon Disulfide and its Solutions

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To our knowledge the infra-red spectrum of liquid CS$_2$ has never been scrutinized so much as to arouse concern for a weak side-band at the short wave flank of the absorption at 392 cm$^{-1}$ (bending CS$_2$). It is observed with more intensity with CS$_2$ dissolved in cyclohexane (C$_6$H$_{12}$) and some other solvents - equivalent of the branch of the gas phase! The P-branch is almost hidden by the strong central band, but appears at low concentrations in C$_6$H$_{12}$ as shoulder. CS$_2$ antisymmetric stretching shows at low concentrations in C$_6$H$_{12}$ a residual P-branch as a shoulder at 1518 cm$^{-1}$, separated 12 cm$^{-1}$ from the main absorption (gas phase: PR = 18 cm$^{-1}$).

CH$_2$Cl$_2$ combined with C$_6$H$_{12}$ almost quenches the rovibrator contributions, but a shoulder near 400 cm$^{-1}$ remains even in pure CH$_2$Cl$_2$. CCl$_4$ (and n-heptane almost so) produces a symmetric absorption around 1520 cm$^{-1}$, but acts just as C$_6$H$_{12}$ around 390 cm$^{-1}$.

It was thought at first that the additional bands could arise from some structure in the liquid. But when a CS$_2$-C$_6$H$_{12}$ mixture is heated from 20 to 80° C only small losses in peak intensities coupled with broadening occur (constancy of integral intensities).

To account for the residual rovibrator contributions, theories starting from CS$_2$-dimers etc. appear to be rather distant from reality. Different effects from solvents upon bending and stretching, resp., may be expressed by interaction coefficients, related to average time of free rotation with different vibrational excitation in different solvents.
Ph20. Hyperfine Structure of $^{127}\text{I}_2$ at 640 nm and 612 nm Wavelength Measured in the Gain Profile of the He-$^{22}\text{Ne}$ Laser

J. Blabla

Ph21. On the Determination of the Parameter of the Hamiltonian and Dipole Moment for Highly-Excited Vibrational States of the $\text{H}_2^{16}\text{O}$ molecule

A.D. Bykov, O.N. Ulenikov, and A.S. Zhilyakov

The method for investigating the spectra of highly-excited vibrational states of the $\text{H}_2\text{O}$-type molecules has been developed based on the model taking into account the presence of resonance interactions. Using this method the analysis has been made and the inverse problems have been solved for the second hexade of $\text{H}_2\text{O}$ (states $(111)$-$(031)$-$(012)$-$(210)$-$(130)$-$(050)$). The study of the energy spectrum and the line intensities has been carried out and the parameters of the transformed dipole moment have been found.

The similar analysis of the system of vibrational bands whose absorption lines are in the range of 0.59 $\mu$m has been made based on the experimental data from Refs. (1, 2). Both the energy spectrum and the vibration-rotation line intensities have also been investigated.

References

Higher-order Dipole Moments for pure Rotational Transitions of Methane-type Molecules

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Explicit expressions in terms of molecular parameters and angular momentum components have been obtained for the effective dipole moment operators $\tilde{M}_{05}$ and $\tilde{M}_{22}$ determining the higher-order contributions to the intensity perturbation allowed rotational absorption spectra of methane-type molecules. The calculations have been performed by the method of sequential contact transformations. The term $\tilde{M}_{05}$ is essential only for the ground vibronic state, while the term $\tilde{M}_{22}$ may be significant for the excited states of degenerate vibrations.

Diode Laser Spectroscopy of Pulsed-Jet Cooled SF$_6$ and NH$_3$ Molecules Subject to Vibrational Excitation by High-Intensity IR Laser Radiation

V.M. Apatin, V.M. Krivtsun, Yu.A. Kuritsyn, G.N. Makarov, and I. Pak

To understand the physics of multiphoton excitation of molecules in a strong laser field, it is essential to reveal the excitation mechanism of low-lying vibrational-rotational levels. In this paper, we will present the experimental results of double IR-IR resonance investigations into the excitation dynamics of SF$_6$ and NH$_3$ molecules cooled in a pulsed supersonic jet. The probing radiation used was that of a tunable diode laser. The absorption spectra obtained with the aid of this laser were used to register the depletion of the rotational sublevels of the molecules under the effect of a pulsed CO$_2$ laser.

We have measured the portion $f_j$ of molecules excited from various rotational sublevels by the CO$_2$ laser radiation and studied the laser fluence and exciting pulse frequency dependences of $f_j$. Diode lasers were used to probe transitions from both the ground and vibrationally excited states upon single- and multiple-frequency excitation of the molecules by the strong IR laser field.
The determination of dipole moment function (DMF) of semirigid molecule from various experimental data is considered. The data include the integral intensities of infrared fundamentals, first and second overtones and binary combination bands as well as the Herman-Wallis factors, intensities forbidden rotational and vibrational-rotational transitions and the precise data on the dipole moments of various vibrational and rotational states. Expressions for these data are presented for linear and symmetric top molecules in terms of tensor $\Theta$-parameters; exact relations of $\Theta$-parameters with basic molecular parameters and dipole moment derivatives are also presented. The relations for the empirical parameters in the dipole moments and DMF parameters are applied for OCS molecule. DMF OCS thus determined well reproduced the observed values of average dipole moments$^1$ and transition dipole moments. Some applications DMF OCS are considered. In particular the dependence of average dipole moments on the quantum numbers is obtained in the form:

$$\mu_{st}(V_1, V_2^l, V_3, J, L) = 0.70344(402) - 0.020426(57) (V_1 + 1/2) - 0.010921(30)(V_2 + 1) + 0.0738(123)(V_3 + 1/2) - 0.000278(15)(V_1 + 1/2)^2 - 0.000060(5)(V_2 + 1)^2 + 0.000204(10)(V_1 + 1/2)(V_2 + 1) + 0.000107(7)L^2 + 0.0000005J(J+1).$$

Limiting Ordering Schemes of Vibrational-Rotational Interactions in Theory of Molecular Spectra

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Various ordering schemes ((g)-grouping) of vibrational-rotational interactions in expansion of molecular Hamiltonian $H_{vr} = \sum H_{mn} (r^{m} J^{n})$ - schemes with final $\lambda$-order/1,2/ and limiting schemes /3,4/ - are considered from the point of view of choice of optimal ordering scheme for calculation of certain $\tilde{H}_{mn}$ (or $\tilde{M}_{mn}$) in effective rotational Hamiltonian (or effective dipole moment operator). Various groupings are presented through the conventions on the $\lambda$-orders of vibrational and rotational operators and commutators; in groupings /1-4/ $\lambda$-orders of $H_{mn} (\ell, m + \beta n)$ are presented in the following way:

$N = m + 2n \rightarrow N = m + 2n$ - Oka/2/, $N = m + n$ - Amat-Nielsen/1/, $N = m + 5 n$ (E $\rightarrow$ O) - Watson/3/(W), $N = \ell m + n$ (E $\rightarrow$ O) - Mikhailov/4/(M).

The relations between $S_{mn}^{(g)} (m+n\leq 5)$ operators of the contact transformation (CT) method in various groupings were obtained by "unravel" the exponential operator technique. The calculation algorithm of high-order transition dipole moment operators by CT method in the limiting ordering schemes ((W), (M)) is suggested. Expressions for the reduced $\tilde{M}_{mn} (m+n=5)$ operators are obtained in terms of $\tilde{H}_{mn}^{(g)} (m+n \leq 4)$ and $S_{mn}^{(g)}, S_{mn}^{(R)}$ operators. Some aspects of effective rotational Hamiltonian construction in various groupings for the case of accidental resonances are discussed.

/1/G. Amat, H. H. Nielsen, G. Tarrago, Rotation-Vibration of Polyatomic Molecules, Marcel Dekker, N.Y., 1971
LINE INTENSITY AND COLLISIONAL BROADENING OF WATER VAPOR
IN THE REGION OF 0.59 \mu m
V.A. Kapitanov, V.P. Kochanov, V.P. Lopasov, I.S. Tyryshkin

The paper describes the results of measuring the absolute values of the water-vapor absorption coefficient in the region of 0.59 nm. The measurements were carried out using an automatized spectrophotometric complex based on a 30-m multipass cell and a CW dye laser with linewidth as low as 0.007 cm$^{-1}$. The coefficient $\kappa_{\nu}$ was determined at room temperature and absorbing path of 2 km. The automatization involves the real time recording, the input and output emission intensities and primary data processing providing for the restitution of the values $\kappa_{\nu}$. The subsequent processing of the data was carried out using a computer BESM-6. The fitting of the theoretical expressions for $\kappa_{\nu}$ to the experimental ones was carried out using the least-squares method and extracting the values of intensities, line broadening parameters and their confidence intervals.

The nitrogen and oxygen pressure-broadenings in the 0.59 nm region were investigated. The Voigt profile and the contour in the high-speed collisions model were used to describe the spectral line shapes. As a result, the values of intensities with the $<5\%$ error (for the lines with the absorption coefficient $\geq 10^{-6}$ cm$^{-1}$) as well as the values of the impact-collision and self-broadening constants were obtained.
The impact theory of line broadening developed with taking account of collision-induced relaxation connection between the components of rotational doublet lines enabled one to determine the strong relaxation connection between the doublet lines of the symmetric top molecules. For the molecules with large inversion splitting, the spectral exchange results in the composite dependence of the line contour shape on the diagonal and off-diagonal matrix elements of the impact relaxation operator $\hat{A}$. The numerical computer realization of these elements calculation enables one to determine that for the molecules with high potential barrier and large inversion splitting the collision effect of spectral exchange together with the appearance of the cross-relaxation parameter $\xi$ results in essential additional narrowing and shift of spectral lines.
On the Calculation Method of Spectral Line Gases Half-width in Microwave and Infrared Spectral Regions Using Linear Molecules and Asymmetric Top Molecules

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A new high-speed algorithm of calculating the spectral line halfwidths of atmospheric gases was determined on the basis of the Anderson impact theory and the method of estimating the average impact parameter between the interacting gaseous particles. As an example, the broadening of spectral lines of H$_2$O, CO$_2$ and CO was considered. As a whole, a good agreement of the calculated values of halfwidths and the experimental data is obtained. The study of temperature dependence of the line halfwidths enabled one to find out a series of physical regularities of spectral line broadening. In particular, the resonance collisions have been estimated to affect essentially the H$_2$O molecule spectral lines broadening, and the role of the above collisions is more important in the case of water vapor self-broadening as compared with the H$_2$O broadening by the N$_2$ molecules.
On Investigation of Water-Vapor Highly Excited Rotational Transitions
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The measurements of water-vapor spectral bands 000 $\rightarrow$ 000, 000 $\rightarrow$ 010 in the region 8 to 12 $\mu$m have been carried out using a diffraction spectrometer. Taking into account the calibration function of the spectrometer by fitting the experimental results the intensities of 71 H$_2$O lines formed by transitions between the states with large values of rotational quantum numbers ($J \gg 10$) were determined.

Based on the projection perturbation theory the obtained values of line intensities have been interpreted and the parameters of vibration-rotation interaction of $F$ factor have been found ($F = (1 + \sum C_i f_i)^2$). The comparison with the data from the literature has been made.
The results of measurements and processing of the absorption coefficients $\chi(\nu)$ of isotopes of the CF$_2$Cl$_2$ molecule within the 915-930 cm$^{-1}$ frequency range are presented. The absorption spectrum is measured using a laser spectrometer with the resolution $\sim 10^{-4}-10^{-3}$ cm$^{-1}$.

The conditions of the experiment are the following: partial pressure of CF$_2$Cl$_2$ varies within 0.25-0.9 torr, the cavity length $L = 12-28$ cm, $T = 130$ K and 296 K, the error of measurement $\chi(\nu)$ $\approx 20\%$.

The centers of vibration-rotation (VR) lines are calculated according to the model of effective rotational Watson's Hamiltonian [1]. When calculating the line intensities the VR effect of the interaction is neglected. The value of the integral intensity of the band $\nu_6(S\nu_6)$ is taken as a varied parameter. The value of $S\nu_6 = 292$ cm$^{-1}$ is found for the CF$_2^{35}$Cl isotope (T=296 K). In this case, the mean ratio of the calculated values $\chi(\nu)$ to the measured ones is $\approx 15\%$ that on the average is within the limits of the experimental error. The values of intensities of separate lines are in good agreement with those measured in [2,3].

References
Transmission windows in IR-spectra of some molecular gases are of great practical interest. The absorption in these spectral regions is caused by far wings of strong spectral lines.

A survey of the line wing theory developed by the authors is reported. The essential points of the theory are the consistent use of the semiclassical approximation for molecular mass center motion and the asymptotic evaluation of integrals at frequencies far removed from the line center. The result is that the probability for molecules to be at definite separations depends on their interaction. The potential of intermolecular interaction is the main physical cause determining the spectral and temperature behavior of absorption coefficient. The line wing theory gives the quantitative interpretation of available data on absorption in vibration-rotation spectra in the troughs between lines and in the band wings for different gas mixtures. The examples of the interpretation are reported.

The clear conceptions underlying the theory and its numerous applications allow one to treat this approach as a separate branch of spectroscopy named the line wing spectroscopy.
The results of experimental investigations of the isolated and overlapped lines contour shapes of the dipole $\text{H}_2\text{O}$ molecule vibration-rotation spectrum in the fields of disturbing particles and laser radiation are discussed. The measurements have been carried out using a two-channel opto-acoustic laser spectrometer in the range of disturbing-gas pressures 10 to 760 torr at the laser-radiation intensity $\lesssim 10^8 \text{ W/cm}^2$.

The effect of the following factors: Pressure and type of a broadening gas, frequency, intensity and laser radiation polarization, on the absorption-line contour shape and the line center shift has been investigated.
Numerous hot band transitions in the long-path Fourier transform spectra of ammonia* have been identified and assigned. Results of intensity measurements on some of these transitions using a tunable diode laser, as well as optogalvanic measurements using a line tunable CO2 laser will be presented and discussed.

* Spectra were recorded at the Kitt Peak National Observatory, Tuscon, Arizona.
Reduced Hamiltonian for $^{12}\text{CD}_4$ pentad and dyad (at third order)

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The V.R. Hamiltonian expansion involves a lot of coefficients which appear strongly correlated, as more as it describes larger polyads of interacting vibrational states. These coefficients are not unambiguously defined because of possible contact transformations which preserve the Hamiltonian form, as shown by Perevalov et al.

In $XY_4$ molecules, the contact transformations which have to be taken into account in a 3rd order study involve:
- for the (0100 and 0001) dyad one 1st order and one 2nd order generators
- for the (0002, 0101, 1000, 0200 and 0010) pentad four 1st order and ten 2nd order generators. These generators can be fixed using a reduced Hamiltonian expansion in which are fixed to zero an equal number of coefficients. The choice of such coefficients in much more difficult for the pentad than for the dyad, and can be determined only after many numerical trials.

Applied to $^{12}\text{CD}_4$, these formulation has led to a reduced Hamiltonian describing the pentad and dyad levels treated simultaneously with only 63 adjusted parameters. The fit of the levels until $J'=20$ is as good as in the case of a separated reductionless polyad analysis with 63 and 16 adjusted constrained parameters for the pentad and the dyad respectively.
VIBRATIONAL AND ROTATIONAL RELAXATION IN GASES AND SHAPE OF Q-BRANCHES IN HIGH-RESOLUTION CARS SPECTRA

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The characteristic dependence of isotropic Raman spectra Q-branches shape on density enables collisional rotational and vibrational relaxation contributions into the broadening and shift of the contour to be separated and the crosssections of corresponding processes to be determined. However, in case of polyatomic molecules high spectral resolution and high precision of frequency calibration, inaccessible to spontaneous Raman spectroscopy, is needed to obtain the information of that kind.

The present study deals with isotropic coherent Raman spectra Q-branches shape behaviour in dense molecular gases such as N₂, C₂H₂, CH₄, SiH₄, SF₆ at pressures up to 150 atm. The research has been carried out by means of CARS-spectroscopy with the resolution as high as (1-3)·10⁻³ cm⁻¹. Effects of collisional narrowing of the Q-branches, due to rotationally inelastic collisions, and broadening due to vibrational dephasing have been observed for molecules of different types. The rate constants and crosssections of these processes have been determined.

Rotational Assignment of Higher Vibrational States of NH₃, Using Microwave-Optical Double Resonance

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The $v_2$ Band of HOBr

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Recently the gas phase infrared and microwave spectra of HOBr and DOBr have been identified by Koga, et al. (1) As part of a collaborative effort, the submillimeter and far infrared laser sideband spectra have been observed at JPL. In addition, the 1162 cm$^{-1}$ $v_2$ band of HOBr has been observed at 0.0056 cm$^{-1}$ resolution using the McMath Solar Telescope Fourier transform spectrometer at Kitt Peak National Observatory. In spite of a very low sample concentration, $v_2$ transitions were assignable for $K_a$≤5 and $J$≤42. Coriolis resonances have been observed between the $K_a$=2 levels of $v_2$ and the otherwise unobservable $K_a$=1 levels of $2v_3$. A total of 889 infrared features have been fitted with a rms deviation of 0.00057 cm$^{-1}$. These are approximately equally divided between the two main isotopic species and represent 1272 assigned transitions. Features from which frequencies for the individual species could not be obtained were excluded from the fit but are well determined by the parameter set. Microwave data (1) as well as submillimeter and far infrared laser sideband measurements have been incorporated in the fit to improve the ground state parameters. The spectrum will be described. Molecular parameters for $v_2$, $2v_3$ and their interaction will be presented.

1. Y. Koga, H. Takeo, S. Kondo, M. Sugie, and C. Matsumura, personal communication from C. Matsumura
Hierarchic structure of permutation-inversion group and dynamics of molecular motions

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The symmetry of the potential function determining the motions of the molecule nuclei is described by the permutation-inversion group $G_{PI}$ \(^1,2\). However, if the nuclei move only in the vicinity of some local minimum $M$ of the potential, then some subgroup of $G_{PI}$ is sufficient to classify the molecular wavefunctions. We have found, that the smallest local subgroup is a "reduced point group" $\hat{G}$ different from the point group of a molecule. $\hat{G}$ is the little group of $M$, i.e.: $\hat{G} = \{ g \in G_{PI} : gM = M \}$. This group determines the structure of $G_{PI}$ because it generates chains of subgroups $G_k \subseteq G_{PI}$ such that $G_{PI} = \{ G_n \ldots G_1 \hat{G} \}$. For a given $\hat{G}$ and $G_{PI}$ many generating chains may exist. They are associated with trajectories on potential hypersurface connecting equivalent local minima. In consequence, they determine the possible hierarchies of the energy levels splittings due to the tunnelings between the minima. The decomposition of $G_{PI}$ on the chains of subgroups is the systematic way of the derivation of all possible feasible groups for a molecule.

The goal of the present work is to indicate what sorts of rotation-vibration spectra might be expected for protonated acetylene when the three protons in the molecule are allowed to interchange roles in a cyclic manner by migrating around an elliptical orbit enclosing the two carbon atoms, as suggested by ab initio calculations.\(^1\)

\[ \begin{align*}
&\text{H}^+ \text{C} = \text{C} - \text{H} \quad \text{H}^+ \\
&\text{C} = \text{C} - \text{C} \quad \text{H}^+ \\
&\text{H}^+ \text{C} = \text{C} - \text{H} \\
\end{align*} \]

On the one hand, approximate rotation-vibration-tunneling energy levels can be obtained by mapping the protonated acetylene problem onto an internal rotation problem already discussed in the literature\(^3\) in terms of numerical calculations in a Principal-Axis-Method treatment. On the other hand, semi-quantitative rotation-vibration-tunneling energy levels can be obtained for the high barrier limit by applying to protonated acetylene an Internal-Axis-Method-like formalism originally set up to treat the water dimer. The agreement between the numerical PAM calculations and the algebraic IAM results serves as a check on both.

Unfortunately, the development of this formalism, with its tunneling splittings, statistical weights, selection rules, etc., has not yet led to an assignment of the spectrum of \(\text{C}_2\text{H}_3^+\) reported at the 1985 Columbus Symposium by Crofton and Oka\(^4\).


