ABSTRACTS OF PAPERS

Monday, September 3

Opening Ceremony

Morning Session (Chairman - D.H. Whiffen)

K. Narahari Rao

L A2. Higher-order Effects in Vibration-Rotation Line Intensities
M.R. Aliev and V.M. Mikhailov
Institute of Spectroscopy, Troitzzk, Moscow region, 142092

Effective dipole moment operator \( \tilde{M} \) obtained by Contact transformation method is the sum of operators \( \tilde{M}_{mn} \) with vibrational degree \( m \) and rotational degree \( n \) including direction cosine. The expressions of \( \tilde{M}_{03}, \tilde{M}_{12}, \tilde{M}_{13}, \) and \( \tilde{M}_{22}(\text{Rot}) \) have been evaluated previously. In the present report we will discuss new results for the operators \( \tilde{M}_{22}(\text{Vib}) \) and \( \tilde{M}_{31}; \tilde{M}_{22}(\text{Vib}) \) describes higher-order effects and forbidden transitions in first overtones and binary combination bands, \( \tilde{M}_{31} \) is the dominant term in the dipole moment of second overtones and ternary combination bands, while the \( \Delta V=1 \) matrix elements of \( \tilde{M}_{31} \) contribute to infrared fundamentals. The coefficients of these operators are expressed explicitly in terms of the coefficients of the ordinary dipole moment and Hamiltonian expansions. The new formula for the higher-order centrifugal distortion moment \( \tilde{M}_{05} \) will also be given. The line strength formulas for various molecular models will be presented, and the problem of the determination of higher-order dipole moment derivatives from observed line strengths will be discussed.
Microwave Fourier Transform Spectroscopy
Helmut Dreizler
Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel, D2300 Kiel.

The development and performance of our Microwave Fourier Transform Spectrometer from 5 to 20 GHz will be given in detail. Advantages and disadvantages with respect to conventional Stark spectroscopy will be discussed. The extension to two photon spectroscopy in the form of microwave-microwave and radiofrequency-microwave double resonance spectroscopy will be demonstrated.

The performance will be illustrated by the determination of barriers to internal rotation, nuclear hyperfine coupling and relaxation times.
Ab initio calculations with configuration interaction have been performed to obtain the potential energy surface of the ground electronic state of the following molecules: C$_3$, CNC$^+$, CCN$^+$, NH$_3$, SiH$_3$ and H$_3$O$^+$. In each case the rotation-vibration energy levels have been determined and, for the triatomic molecules, the dipole moment and vibrational transition moments have been calculated. The results of these calculations and the comparison with the experimental data (only available for C$_3$, NH$_3$ and H$_3$O$^+$) will be reported.

Of particular interest is the finding that the equilibrium structure of C$_3$ is bent (r$_e$ = 1.290 Å and $\alpha_e$ = 162°) with a barrier to linearity of only 20 cm$^{-1}$.

The equilibrium structure and inversion barrier in H$_3$O$^+$ has been determined from the experimental results.
Afternoon Session (Chairman - W. L. Meerts)

L A5. Non-Rigidity and Large Amplitude Motions in van der Waals Molecules and Hydrogen Bonded Species
W. Klemperer

A. Pine

L A7. Internal Rotation in Symmetric Tops
I. Ozier

L A8. Laser Spectroscopy of Some Small Molecules
H. Jones
INITIAL STUDIES WITH A BOMEM FTIR SPECTROMETER: THE IR SPECTRUM OF \( \ce{C2N2} \)

Alfons Weber, Walter J. Lafferty, and W. Bruce Olson

Molecular Spectroscopy Division
National Bureau of Standards
Washington, D.C. 20234
USA

Initial experiments done and experiences gained with a recently acquired BOMEM DA3.002 Fourier transform spectrometer are described. To facilitate testing of the new instrument we chose to record and analyze the spectrum of cyanogen which is known from previous studies at low resolution to have a relatively dense but theoretically well behaved spectrum. The region of the \( \nu_3 \) band near 2157 cm\(^{-1} \) was recorded with an apodized resolution of 0.004 cm\(^{-1} \) using gas pressures of 1, 5, and 20 torr and a path length of 20 cm. The \( \nu_3 \) band as well as several associated hot bands were analyzed. The \( \nu_3 \) band of OCS near 2062 cm\(^{-1} \), present as a trace impurity in the \( \ce{C2N2} \) gas, was also observed up to \( J \sim 40 \) and was used to calibrate the \( \ce{C2N2} \) spectrum using measured OCS frequencies reported elsewhere [1]. The \( \nu_5 \) band of \( \ce{C2N2} \) near 233 cm\(^{-1} \) was recorded using a gas pressure of 3 torr and path length of 20 cm.

THEORETICAL METHOD FOR PREDICTION OF MW SPECTRA

J. KONARSKI, Faculty of Chemistry, A. Mickiewicz University, Poznan, Poland.

Using fully canonical approach to the rotational-vibrational Hamiltonian a method for predicting the MW spectra of molecules is proposed.

Applying variables which are invariant under transformation from molecule fixed coordinate system to space fixed coordinate system the Hamiltonian has the form:

\[ H = H_V + E^{\text{ROT}} \]

where

- \( H_V \) = vibrational Hamiltonian
- \( E^{\text{ROT}} = E_R + E_{\text{COR}} \) - operator describing rotational energy.

For a triatomic molecule the Hamiltonian has the form:

\[ \frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial \lambda_1^2} - \frac{\hbar^2}{2\mu_2} \left( \frac{\partial^2}{\partial \lambda_2^2} + \frac{1}{\lambda_2^2} \frac{\partial}{\partial \lambda_2} + \frac{1}{\lambda_2^2} \frac{\partial^2}{\partial \theta^2} \right) + V \]

\[ + \frac{1}{2} \left[ \frac{1}{\lambda_1} (\lambda_1 K_x^2 + \frac{DK_z}{\lambda_1^2}) + \frac{1}{\lambda_2} (C_{\text{CK}_x^2} + K_{\text{K}_x^2}) \right] \]

\[ + FL_z K_z \]

where

- \( \lambda_1, \lambda_2, \theta \) - are the vibrational variables,
- \( A, D, C, F \) - rotational constants,
- \( K_x, K_z \) - components of overall rotational angular momentum
- \( L_z \) - components of vibrational angular momentum.

This equation has been applied to the prediction of MW spectra of a few triatomic molecules.
Methyl Isocyanate: An Analysis of the Low-J Rotational Spectrum Using the Quasi-Symmetric Top Molecule Approach

Jacek Koput
Department of Chemistry, A. Mickiewicz University, Poznań, Poland

The low-J rotational spectrum of methyl isocyanate (CH₃NCO) has been analyzed in terms of the quasi-symmetric top molecule model accounting explicitly for the large-amplitude CNC bending motion, internal and overall rotation. An assignment of the 25 J = 1 → 0 and 2 → 1 rotational transitions arising from the various CNC bending and torsional states is proposed. The molecule is found to be a nearly freely internally rotating quasi-symmetric top with the barrier to linearity of the CNCO skeleton of 1049 cm⁻¹ and equilibrium CNC valence angle of 140.2 degrees. The calculations have shown that the large centrifugal distortion effects observed in the microwave spectrum are mainly due to strong CNC bending-internal rotation-overall rotation interaction.

J. Makarewicz

Department of Chemistry, A. Mickiewicz University, PL 60-780 Poznań, Poland

A generalized adiabatic method is presented which can be used for description of multi-level hierarchical systems. This method applied to the coupled molecular vibrations reduces the multi-dimensional problem step by step to the problem of a lower dimension and allows to obtain effective potentials for large-amplitude-motions. A simple method of determination of the multi-dimensional potential parameters in the fitting procedure based on this method is proposed.

P A5. Application of Adiabatic and Born-Oppenheimer Methods in Calculations of Energy Levels of Multidimensional Hamiltonian for Molecular Vibrations

A. Wierzbicki, J. Makarewicz

Born-Oppenheimer method and adiabatic Born-Oppenheimer method are shown to work efficiently in solving multidimensional problem of coupled vibrations in molecules. A simple way of estimation of the errors in energy level, implied by the methods, is given. The considerations are exemplified by 1,3-disilacyclobutane molecule.
Vibrational-rotational analysis of the infrared fundamentals $\nu_6$, $\nu_8$ and $\nu_9$ of diazomethane

L. Nemes, Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budapest, Hungary

J. Vogt, H. Mirk and M. Winnewisser, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Gießen, West Germany

Low pressure gas-phase infrared spectra of diazomethane, CH$_2$NN, have been recorded on a Digilab Fourier-transform spectrometer in the spectral range: 1200-150 cm$^{-1}$ at a resolution level 0.06 cm$^{-1}$. The K-type rotational structure of the c-type perpendicular modes $\nu_5$ and $\nu_6$, and the b-type perpendicular modes $\nu_3$ and $\nu_9$ has been assigned.

A preliminary analysis is attempted for the strong z-axis Coriolis interactions among these low frequency modes. The rotational analysis is based on recent, high-precision ground-state rotational constants derived from mm-wave studies (ref. 1), while a normal-coordinate analysis utilizing all available information is applied as a physically limiting model-calculation for the vibration-rotation data derived (ref. 2). A computer-simulation of the infrared band-contour is used analogously to a treatment for similar perturbations in the ketene, CH$_2$CO molecule (ref. 3).

2. L. Nemes and B. Gellai, to be published
EXCITED VIBRATION STATES OF 1,1-DIFLUOROETHYLENE

O.L. Stiefvater, Coleg Prifysgol Gogledd Cymru
Bangor, Wales, U.K.

Although the majority of pure rotational transitions observed in microwave spectroscopy arises from molecules in vibrationally excited states, microwave spectroscopists have focussed their attention predominantly on the determination of molecular constants of the vibrational ground state, thereby ignoring a great deal of information valuable to the high resolution I.R. spectroscopist. The resulting separation between infrared and microwave studies was mainly due to the difficulties that used to be encountered in assigning pure rotational spectra.

Our exploration of the potential of Double Resonance Modulation (DRM) in microwave spectroscopy has shown that this difficulty now belongs to the past, and work on the rotation spectra of rare isotopic species has indicated that the sensitivity of DRM microwave spectroscopy is sufficient to detect the pure rotation spectra of all vibrationally excited states up to $\nu 1000 \text{ cm}^{-1}$ for substances with a dipole moment in excess of 1 D, and often beyond that limit. The data emanating from such studies reduce the analysis of I.R. bands in that range to the fitting of the pure vibration frequency $\nu^0$ only, as band structures are calculable to an accuracy of about 0.00003 cm$^{-1}$ from the microwave data.

The present paper reports an exemplification of these aspects on 1,1-difluoroethylene: Rotational and distortion constants have been obtained for all 18 excited states, including 8 fundamental levels, up to 1300 cm$^{-1}$. Work to determine $\nu^0$-values by FTIR and laser/microwave double resonance experiments will be carried out this summer, and the hoped-for results will be included along with a forcefield calculation for this compound.

Similar work on furazan and trifluoroethylene will be discussed and current work on cis-1,2-difluoroethylene will be described.
Microwave Studies of 3-Aminopropionitrile and 1-Amino-3-Butyne.

Ole-Anders Braathen, Karl-Magnus Marstokk and Harald Møllendal.

Department of Chemistry, The University of Oslo, P.O.Box 1033, Blindern, Oslo 3, Norway.

Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding and Centrifugal Distortion of both molecules have been determined and will be presented.
Microwave spectrum of 3-Fluor-Propyne

-Structure, dipole moment, centrifugal distortion analysis and assignment of vibrational satellites-

H.-N. Hübenermann, H.-D. Rudolph, J. Botskor
Abteilung Physikalische Chemie, Universität Ulm, FRG

From the rotational constants of H₂FCCH, H₂FCCH, H₀FCCH, H₀FCCH, H₂FCCH, H₂FCCH and H₂FCCH substitution parameters are determined as: rₐCH(methyl) = 1.09 Å, rₐCH(methyl) = 1.05 Å, rₐC₆H₄ = 1.20 Å, rₐC₆H₄ = 1.45 Å, rₐHz = 1.08 Å, <HC-C = 110.4°, <HC-C = 109.3°, <CCC = 178.9° and <HC-C = 179.6°. The CCC-chain is bent away from the fluorine atom. From the rotational constants and the center of mass condition we obtained: rₐCF = 1.39 Å, <CCF = 111.0°. All angles are exact to ±0.5° (ten times standard error due to errors in the rotational constants).

The values for the constants in the vibrational ground state of the normal isotope are: A = 35.639.02 MHz, B = 4.608.83 MHz, C = 4.183.53 MHz, ΔJ = 2.63 kHz, ΔJK = -70.2 kHz, ΔK = 1.35 kHz, ΔJ = 0.565 kHz and ΔK = 17.2 kHz.

Using Stark measurements we determined the dipole moment to be μ = 1.733 ± 0.015 D with the components μₐ = 1.027 ± 0.011 D and μ₉ = 1.395 ± 0.012 D. The direction of the vector μ coincides within 4° with the CF-bond.

We were further able to assign the vibrational satellites of three excited states and to make a complete centrifugal distortion analysis of these states. They were ν₄₀, the symmetric valence vibration (1220 cm⁻¹), ν₄₅, the asymmetric valence vibration (320 cm⁻¹) and ν₂, the C-C-F-deformation vibration (540 cm⁻¹). The frequencies of these vibrational transitions from microwave intensity measurements are in concordance with the IR- and Raman-spectra.

The Y₆ Band of Isotopic Species of CF₂Cl₂ fromIR-MW Double Resonance

G. Taubmann, H. Jones
First Observation of Magnetic Hyperfine Structure in the Infrared Spectrum of Ammonia

J. Bordé, Ch. Salomon, Ch. Chardonnet, Ch. Bréant, A. Van Lerberghe and Ch. J. Bordé
Laboratoire de Physique des Lasers, Université Paris-Nord, CNRS
LA 282, Av.J.B. Clément 93430 Villetaneuse FRANCE

The as R(2,0) line of the \( \nu_2 \) band of \( ^{15}\text{NH}_3 \) has been recorded with a 2.2kHz linewidth (HWHM) with the saturation spectrometer of Villetaneuse [1]. The spectrum exhibits a nicely resolved magnetic hyperfine structure which extends over \( \sim 50 \) kHz. The theoretical fit of this structure takes into account the \( N \) spin-rotation, \( H \) spin-rotation, \( H \) spin-\( H \) spin and \( H \) spin-\( N \) spin interactions [2]. For these operators, the values of the coupling constants and their vibrational dependence will be discussed.


Sub-Doppler laser-Stark spectroscopy of the 6 micron $^{14}$NH$_3$ bands

W. H. Weber
Research Staff, Ford Motor Company
Dearborn, MI 48121 USA

Stark-tuned saturation spectroscopy has become a widely applicable technique for high resolution infrared studies of molecules with a permanent dipole moment. This paper describes recent results on the $v_4$ and $2v_2$ bands of $^{14}$NH$_3$ obtained using this technique with an isotopic CO laser and an intracavity Stark cell. Over 1500 Lamb dips have been identified, associated with about 200 NH$_3$ lines. Approximately 50 of these have not been previously assigned, including 29 that are perturbation induced $v_4$ transitions following the selection rules $\Delta K = \pm 2$, $\Delta \Lambda = \mp 1$, $a \leftrightarrow s$. The data were analyzed to determine values for the ground state dipole moment in a number of rotational states and to determine the relative frequencies between the NH$_3$ lines and the CO laser lines. In favorable cases these relative frequencies could be established with an accuracy of 5-10 MHz, which is comparable to that obtainable with heterodyne methods.

A detailed study of the nuclear quadrupole hyperfine structure on several lines was also made. These experiments were done using a second, external Stark cell, which was double-passed to produce Lamb dips, while the intracavity cell was used to Lamb-dip stabilize the laser. This external cavity method reduces the detection sensitivity. However, it avoids many of the problems that plague the intracavity measurements, such as frequency drift or pulling of the free-running laser and excessive power broadening in the laser cavity. The result is a resolution of a few hundred kHz and a long term frequency stability of a few tens of kHz, which allows the use of signal averaging to look at very weak lines. The quadrupole coupling coefficient is measured in several excited vibrational states with much greater precision than had been done previously.

Internal Coordinate Formulation for the Vibration-Rotation Hamiltonian of the $X_3$ Molecule

V. Spirko, P.R. Bunker, P. Jensen

The vibration-rotation Hamiltonian for an equilateral $X_3$ molecule is completed in terms of the geometrically defined bond stretching coordinates, $\Delta r_i$, and expanded in the form of a power series of the variables $y_i = 1 - \exp\left\{-a \Delta r_i^2\right\}$. The reason for the use of the variables $y_i$ is twofold: Stretching potentials exhibit much stronger convergence in $y_i$'s than in $\Delta r_i$'s, and, the vibrational terms expressed in $y_i$'s may be advantageously treated in the Morse oscillator basis set.

Using the Carney and Porter ab initio data


vibrational spectra of $N_3^+$ are calculated (variationally using a symmetry adapted Morse oscillator basis set). The results indicate that a quartic form of the potential function in the $y_i$'s is adequate in this case, and that satisfactory results may be obtained with a relatively small basis set.

Measurements of $K=3$ Splittings in Pure Inversion Spectrum of Ammonia $^{14}ND_3$ and $^{15}ND_3$ in the $v(2) = 1$ State

A. Guarnieri
The infrared spectrum of ND$_3$ has been recorded in the ranges 8-200 cm$^{-1}$ and 500-1300 cm$^{-1}$ with a resolution of about 0.005 cm$^{-1}$. These spectral regions cover the rotation-inversion spectrum of the molecule in the ground state, and the $\nu_2$ and $\nu_4$ vibrational bands.

A simultaneous analysis of the ground state transitions, the combination differences derived from the $\nu_2$ and $\nu_4$ bands, and the pure inversion (1, 2) and inversion-rotation measurements (3) gave very precise values for the ground state parameters.

The effective spectroscopic parameters and the interaction constants between $\nu_2=1$ and $\nu_4=1$ vibrational states obtained from the analysis reproduced the observed transitions wavenumbers within their experimental uncertainty.

Dipole Moment of \( \text{AsH}_3 \) by Laser-Stark Spectroscopy.

G. Di Lonardo, A. Trombetti
Istituto di Chimica Fisica e Spettroscopia - Università di Bologna

From the intracavity laser Stark resonances of the \( R(3,3) \) and \( P(4,3) \) transitions of the \( \nu_2 \) band of \( \text{AsH}_3 \), we have obtained the electric dipole moment of this molecule in the ground and \( \nu_2 = 1 \) states. The very high resolution provided by the saturation technique allows the observation of the nuclear quadrupole structure of these transitions and of the doublet structure of \( K=3 \) levels of \( \text{AsH}_3 \). The dipole moments derived from these data are:

\[ \mu \text{ (ground state)} = 0.2150(7) \text{ D} \]

\[ \mu \text{ (} \nu_2 = 1 \text{ state)} = 0.2165(7) \text{ D} \]

**L B7. Quasi-Symmetric Top Molecules**

M. Kreglewski
High resolution vibration-rotation spectra, taken on Kauppinen's interferometer at Oulu, will be reported for the fundamental vibrations of cis and trans HONO, H O¹⁵NO, and DONO below 12000 cm⁻¹. The details of the vibration-rotation analysis of these bands will be presented.
High precision infrared spectroscopy with a diode laser driven by a step by step T.F. interferometer.

A. Valentin\(^x\), L. Henry\(^x\), Ch. Nicolas\(^x\), J. Chazelas\(^x\)

A. Mantz\(^{xx}\)

The step by step T.F. interferometer of the Laboratoire de Spectromenie Moléculaire has special devices to drive one arm of the Michelson interferometer and the apparatus can stay at rest indefinitely on a chosen fringe of a stabilized helium neon laser.

This peculiar advantage is used to transfer the stability and the precision of the He-Ne laser to a diode. The diode sweeps the gain profile of one of his modes by steps fixed by the fringes given by a helium-neon laser. The locking of the diode on one of the fringes of its own emission gives in the Michelson interferometer, is made quite easy using the built-in facility for controlling the polarization current of the Laser Analytics system: a line, Doppler-Fizeau width limited, at 4.5 \(\mu\)m, can be analyzed in 40 steps, each step being determined with a precision of 8 \(10^6\) \(\text{cm}^{-1}\) or better.

Illustration and previous experimental results will be discussed.

\(^x\) Laboratoire de Spectromenie Moléculaire, Université Pierre et Marie Curie, Tour 13, 4 Place Jussieu, 75230 Paris Cedex 05, France

\(^{xx}\) Laser Analytics, Inc., 25 Wiggins Avenue, Bedford, Massachusetts 01730, U.S.A.

---

**B9. Spectroscopic Analysis by Infrared Diode Laser of a New Experimental Source of Radicals**

P. Chollet, G. Guelachvili, M. Morillon-Chapey
The work was done on diode laser spectrometer (DLS) with rapid periodic frequency tuning. The longterm stability has been improved to $10^{-4}$ cm$^{-1}$/h by stabilizing of scanning frequency cycles through the absorption line of reference gas. Laser frequency fluctuations in the case of rapid tuning were investigated. It was shown that resolution of such DLS (better than $10^{-4}$ cm$^{-1}$) is sufficient for high resolution spectroscopy. Precision of frequency scale calibration is about $5\times10^{-4}$ cm$^{-1}$.

Doppler limited spectra of fundamental and hot bands and overtones of several polyatomic molecules were investigated. Particularly spectrum of transverse $\sqrt{14}$ band of bensene and spectroscopic constants of this molecule are obtained.

Effects of collisional broadening in spectrum with high density of spectral lines were investigated. Correlation procedure is used to get an average value of linewidths from experimental spectrum. The beginning of interference phenomena of spectral lines was observed. This effect allowed us to distinguish several broadening mechanisms. Effects corresponding to structure or vibration resonance, quantum effects in relative movement of molecules are assumed to explain experimental results.

The use of all information contained in the spectrum under study enables to get considerable improvement in diode laser gas analyzer detectivity. In this case the high sensitivity was obtained that allows us to detect the resonance absorption of $10^{-7} - 10^{-6}$ parts of the incident power during the time of 0.5 s. As an example, detection of Freon-12 in atmosphere ($3\times10^{-8}$ %) is shown.
Infrared Spectrum of the $\nu_4$-Parallel-Band of Acetonitrile between 890 and 960 cm$^{-1}$

P. Wallraff, Koichi Yamada, R. Schieder and G. Winnewisser

I. Physikalisches Institut, Universität zu Köln

The $\nu_4$-vibration-rotation spectrum of acetonitrile (CH$_3$CN) has been measured using a newly constructed diode laser spectrometer. The essential difference between this new spectrometer and the commercially available one lies in the current control unit of the laser diode. In the new system the laser current is controlled digitally by a microprocessor. Several functions are programmed for a rapid saw-tooth sweep to observe the spectrum in video by a CRT-display and for a modulated slow sweep to detect the signal by a lock-in-amplifier.

The spectrum was observed in the range between 890 to 960 cm$^{-1}$ with the Doppler-limited resolution. We have assigned the P-, Q-, and R-branch of the $\nu_4$ fundamental band, a parallel band of C-C stretching vibration, up to $K = 8$. A small anomaly has been found in high $K$-lines which may be explained by an anharmonic resonance with $v_8 = 3^3$ state.

Details of the spectrometer and the analysis of this band will be presented.
POSTER SESSION

P 81. Diode Laser Spectroscopy of the Discharge Products of Vinylcyanide

W. Klebsch, Koichi Yamada and G. Winnewisser
I. Physikalisches Institut, Universität zu Köln, 5 Köln 41

The unstable radical CCCN has been found both in interstellar space (IRC+10216) and in laboratory by observing a few millimeter wave rotational transitions. In the present work we describe the tentative detection of this molecule by a diode laser spectrometer, in the region of CN stretching vibration near 2260 cm⁻¹.

To generate this molecule we use a dc-discharge-tube, 1.90 m in length, with White's type mirrors mounted inside for multiple reflections of the diode laser beam. The absorption path length in normal use is 36 m. By flowing vinylcyanide and nitrogen with a mixing ratio of one to one a dynamical equilibrium pressure of about 200 Pascal in the cell could be maintained. In a glow discharge at 7 kV and 5 mA (ballast resistance: 100 kΩ) we observed known absorption lines of HCCCN near 2260 cm⁻¹. After a slight increase of the voltage the discharge current "jumps" to 18 mA; the spectra then contain additional new lines (total 50) which cannot be assigned so far to known molecules. We assign these new absorption lines tentatively to the free radical CCCN. The assignment of presently 8 lines indicates the expected P- and R-branch behavior of a linear molecule. The distances between the lines seem to be very close to the expected B⁺⁺ B⁻⁻ of CCCN.

P 82. The ν₃ Band Region of Isotopic Species of CS₂ from Diode Laser Spectroscopy

J. Lindenmayer, H. Jones
Spectra of \( \text{C}_3\text{O}_2 \) near 540 cm\(^{-1} \) have been recorded with a BOMEM interferometer at an apodized resolution of 0.004 cm\(^{-1} \). After deconvolution an effective line width of \( \sim 0.0018 \) cm\(^{-1} \) has been attained enabling significant progress to be made in the analysis. In addition to confirming an earlier analysis of the \( \nu_6 \) fundamental (1), many of the combination levels involving one quantum of \( \nu_6 \) and up to 3 quanta of the low lying bending vibration \( \nu_7 \) have also been identified and analysed. The combination states of \( \nu_6 \) with various quanta of \( \nu_7 \) have been analysed using an extended version of the semirigid bender model (2), and aspects of this analysis will be discussed.


P B4. Calculation of the Franck-Condon Factors for XY$_3$
Pyramidal Molecules

V. Špirko, V. Danielis

Pyramidal AH$_3$ molecules exhibit long progressions in the inversion mode (V$_2$) in their vibronic spectra (the reason for this is that the molecules are essentially planar in their excited states). Though the extended progression of V$_2$ appears to fully characterize the spectrum, attempts to explain this structure in terms of the Franck-Condon factors calculated over one-dimensional vibrational wavefunctions have not been very successful. Apparently the interaction of the inversion motion with other vibrations is to be respected. In the present contribution the role of this interaction is studied for the band system (A - X) of ammonia using a simple modification of the nonrigid inverctor Hamiltonian [V. Špirko, J. Mol. Spectrosc. 101, 30 (1983)]

P B5. Ab Initio Rotation-Vibration Energies of PH$_3$

S. Civiš, P. Čársky, V. Špirko

75 points on the potential energy surface of the ground electronic state of the phosphine molecule have been calculated ab initio using the many-body perturbation theory (with energies up to 12000 cm$^{-1}$ above equilibrium). A polynomial potential function has been fitted to these points using the inverse reduced potential for the out-of-plane motion and the standard polynomial for the remaining vibration motions. Using the nonrigid inverctor Hamiltonian with this polynomial function (quartic in the in-plane coordinates but duodenary in the out-of-plane coordinate!) the rotation-vibration energies have been calculated and found in a reasonable agreement with experiment. The results are believed to be helpful in the determination of a realistic experimental potential function of the phosphine molecule.
The $\nu_1$ and $\nu_3$ fundamental bands of $^{14}\text{NH}_3$ have been measured under nearly Doppler-limited resolution using the techniques of Fourier transform, coherent anti-Stokes Raman, and difference-frequency laser spectroscopy. The effective values of the band origins, rotational and centrifugal distortion constants, and parameters of the vibrational-rotational interactions have been obtained by analysing these bands as essentially regular parallel and perpendicular bands, with the "off-diagonal" local resonance interactions excluded from the fit. The "diagonal" $\ell$-type resonance effects have been included into the analysis of the $\nu_3$ band for the $+\ell$, $K = 1$ and $-\ell$, $K = 2$ levels.
The \( \nu_1 \) and \( \nu_5 \) fundamental bands of D\(_2\)CO and Improved Ground State Constants

H.-J. Clar, K. Yamada, F. W. Birss, G. Winnewisser
I. Physikalisches Institut, Universität zu Köln, 5 Köln 41, Deutschland

and

H. Gush
Dept. of Physics, University of British Columbia, Vancouver, Canada

The symmetric and antisymmetric C–D stretching vibrations of D\(_2\)CO, the \( \nu_1 \) and \( \nu_5 \) fundamental bands, have been measured with high resolution spectrometers. The region near the origin of the \( \nu_1 \) band, 2026 - 2087 cm\(^{-1}\), has been recorded by a tunable diode laser spectrometer with Doppler limited resolution and with an accuracy of about 0.001 cm\(^{-1}\). The measurements were extended to the region between 2000 and 2300 cm\(^{-1}\) using a BOMEM Fourier transform spectrometer at the University of British Columbia. The limit of instrumental resolution was 0.004 cm\(^{-1}\).

About 600 lines were assigned to the \( \nu_1 \) fundamental band and more than 1000 to the \( \nu_5 \) band. The band origins were found at \( \nu_1 = 2060.917 \) cm\(^{-1}\) and \( \nu_5 = 2162.922 \) cm\(^{-1}\). From the assigned transitions in the \( \nu_1 \) and \( \nu_5 \) bands infrared combination differences for the ground state have been performed. By fitting the 1230 combination differences simultaneously with the published microwave data, we have achieved a complete set of very accurate molecular parameters for the ground vibrational state of D\(_2\)CO.

Both excited states \( \nu_1 = 1 \) and \( \nu_5 = 1 \) were found to be strongly perturbed by other states due to Fermi and Coriolis interactions. Thus only rough estimations for the rotational constants of these states can be given. Possible interactions will be discussed.
Recently we have measured the pressure broadening and shift of several transitions of the $v_2 (1 \pm 0)$ band (1) and $v_2 (2 \pm 1)$ band (2) of ammonia around 10 \( \mu \text{m} \). The experimental data have been compared with the calculated ones by using the Anderson theory. The agreement is quite satisfactory both for the width and for the shift. Now we have measured both width and shift versus the pressure of a few transitions of the $v_2 (2 \pm 1)$ band, which fall around 16 \( \mu \text{m} \). These transitions, identified as $2aQ(J,k)$ (3), have a broadening similar to the $2sQ(J,k)$ ones at 10 \( \mu \text{m} \) and so smaller than that of the transitions, whose initial state is in the vibrational ground state. However, we have measured red shifts of the same order of magnitude as the blue shifts of the $2sQ$ transitions. Both these experimental results have been explained within the frame of the impact approximation of the Anderson theory.

(+ Present address: IFAM (C.N.R.), Via del Giardino n. 3, 56100 Pisa (Italy).
On the Hamiltonian of the Molecules Connecting Large-Amplitude Vibrations.

A. D. Bykov, O. N. Ulenikov

The Institute of Atmospheric Optics, Siberian Branch USSR Acad. Sci., Tomsk, 634055, USSR

From the analysis of an approach, Ref. (1), which transforms the Hamiltonian

\[ H = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + V(x_{\alpha}) \]

of molecules (Hamiltonian in Cartesian coordinates) to the Hamiltonian depending on rotation and vibration coordinates, it is shown that when obtaining the Watson Hamiltonian, the requirement for smallness of introduced vibrational coordinates is not used in any steps. As a consequence, independent of existence of large amplitude vibrations in a molecule, the "kinetic" part of the Hamiltonian can always be represented in the Watson form which is considerably simpler that the complex Hamiltonian of Hougen-Bunker-Johns or its analog in the molecules with internal rotations or inversion. It is essential that the vibrations of large amplitude can be more than one in number. It is shown that anharmonic constants of H\textsubscript{2}O - type molecules are not independent. When solving the problem of their determination from the experimental data this circumstance should be taken into account.

References

On Classification of Molecules with Berry Pseudorotation

A.V. Burenin

A traditional scheme of the classification of molecular states is based on the CNPI group (see, for example, /1/). It is assumed, that the CNPI group includes all the symmetry elements necessary to characterize the problem on the stationary states of the molecule in the given electron state. It is shown in this report that this requirement is very rigid and can be fulfilled not in all cases. In particular, it cannot be fulfilled for the molecules with the Berry pseudorotation /2/. An attempt to write the symmetry elements corresponding to the Berry pseudorotation in the form of the elements of the CNPI group leads to an incorrect classification of the molecular states. It is demonstrated that the molecules with the Berry pseudorotation can be considered within the framework of the classification of the molecular states developed recently by the author (see, for example, /3/).

P 813. Peculiarities of H-propanol conformational structure
A.A. Abdurakhmanov*, G.I. Ismailzadeh
Physical Institute, Azerb. SSR Acad. of Sci., Baku, USSR

H-propanol molecule, \( \text{CH}_3\text{CH}_2^\text{H} \text{CH}_2^\text{H} \text{OH} \), with 2 degrees of internal rotation freedom for asymmetrical OH and CH\(_2\)OH fragments about CO and CC axes, respectively, was studied at the Institute by MW gas spectroscopy. It was established that H-propanol existed in at least 5 rotational isomer forms, three of them being conformationally "forbidden" ones as not corresponding to the permitted "chess-board" configurations of asymmetric atomic groups in respect to the molecule framework. To prove mentioned abnormalities both quantitatively and qualitatively as well as to study in detail intramolecular interactions which stabilize energetically "disadvantageous" conformers we have investigated \( \text{CH}_3\text{CH}_2^\text{D} \text{CH}_2^\text{D} \text{OD} \) molecule. The molecule MW spectrum was studied and compared with the analogous one of the original molecule that unambiguously supported the existence of H-propanol in at least 5 energetically non-equivalent rotational isomer forms with the following \( \Psi \) and \( \Phi \) structural parameters: 1) 0° and 0°; 2) 30° and -10°; 3) 80° and 20°; 4) -10° and 116°; 5) 80° and 116°. The second, the third and the fifth conformers were energetically "disadvantageous". The conformers' MW spectra studies showed the existence of intramolecular orientational interactions (predicted by one of the authors*) between the lone electron pairs of oxygen atom and the nearest CH-bonds of methyl (and methylene) groups. Conformer structural parameters were refined, intramolecular interaction contribution into dipole moment values was determined, stabilizing potentials, energy differences between conformers and their relative stabilities were estimated.
Spectroscopy of the Gasdynamically Cooled SF$_6$ by the Third Harmonic Generation Method

E. Khokhlov

High-Resolution Coherent Stokes Raman Spectroscopy of $^{32}$SF$_6$ and $^{34}$SF$_6$

D.N. Kozlov, M.R. Malikov, V.V. Smirnov, S.Yu. Volkov
General Physics Institute, Moscow, USSR

We present coherent Stokes Raman spectra near 774 cm$^{-1}$ with resolved rotational structures of the totally symmetric $\nu_1$ fundamental Q-branch of SF$_6$ molecules with different sulphur isotopes. Our high-resolution CARS/CSRS spectrometer is based on two cw narrow band ($\sim 10^{-4}$ cm$^{-1}$) tunable dye lasers which are pulse amplified by two dye amplifiers. The amplifiers are pumped by 10 Hz frequency-doubled Nd$^{3+}$:YAG-laser. Resulting parameters of tunable pulsed byharmonic pumping are: $P_1 \approx 1$ MW, $P_2 \approx 100$ kW, $\tau_p = 10$ ns, $\Delta \nu = 3 \cdot 10^{-3}$ cm$^{-1}$. Absolute Raman frequency calibration with a precision of 0.001 cm$^{-1}$ is produced by a wavemeter using Fizeau-type interferometers.

The spectroscopic possibilities of our spectrometer are well demonstrated by rotationally resolved CSRS spectra of the $\nu_1$ Q-branch of $^{32}$SF$_6$ and $^{34}$SF$_6$ molecules. The spectra were recorded in cooled low pressure gases (0.1 - 1 torr) at temperatures 150-180 K. The rotational lines positions in the Q-branch can be described with high accuracy by those of rigid rotor: $\nu_J = \nu_1 - \Delta J (J+1)$, and no centrifugal distortion or octahedral splitting is observed in the experiment up to $J = 70$. As a result an analysis of spectral data has allowed us to determine for the first time the rotation-vibration parameter $\alpha_1 (^{34}$SF$_6$) = (1.0859 ± 0.0003) \times 10^{-4}$ cm$^{-1}$ and the isotopic shift $\nu_1 (^{34}$SF$_6$) - $\nu_1 (^{32}$SF$_6$) = 0.0626 ± 0.0014 cm$^{-1}$.
Diode Laser Spectroscopy of Transient Molecular Processes

V. M. Krivtson, Yu. A. Kuritsyn, G. N. Makarov, and A. Puretski
Institute of Spectroscopy, USSR Academy of Sciences,
Troitzk, Moscow Region, USSR 142092

The possibility of the study of transient molecular processes by pulsed diode lasers will be discussed. The results of two papers in which Pb$_{1-x}$Sn$_x$Se diode lasers have been used for monitoring and spectroscopy of molecular events with time resolution of 100 ns and spectral resolution of $10^{-3}$ cm$^{-1}$ will be presented.

A pulsed diode laser was used to investigate the multiphoton induced depletion of rotational sublevels of the ground vibrational state of the SF$_6$ molecules cool in a pulsed free jet. The fraction of molecules excited by a pumping pulse from individual rotational sublevels was measured and its dependence on the exciting pulse frequency and energy density was investigated.

A method of double optical-IR resonance has been used for study of the spectral properties of the highly excited ($v=18-19$) vibrational-rotational states in CrO$_2$Cl$_2$. The molecules were prepared in high vibrational states by electronic excitation with Nd:YAG laser followed by nonradiative electronic-vibrational energy conversion. The induced IR absorption and its time evolution have been measured. The spectral FWHM at 100-ns delay with respect to exciting pulse was 15 cm$^{-1}$. 
Ethyl alcohol $\text{CH}_3\text{CH}_2\text{OH}$ is one of the molecules that has been studied in detail by various spectroscopic methods. The most valuable information on its conformational, structural and electrical features, its internal energetics had been obtained by MW-spectroscopy of 14 isotopical species of this molecule. It has been unambiguously established previously that ethanol molecule existed only in two isomeric trans ($\Psi = 0^\circ$) and gauche ($\Psi = 120^\circ$) forms. However, one of the authors* has assumed that some specific orientational interactions in hydrocarbons and their substitutes were to be realized, and so we revised our previously studied MW-spectra to prove by the experimental data the possibility of not only theoretically permitted chess-board type conformers but some "forbidden" ones. The analysis of the authors' investigations and of some other published data gave us the explanation of the excited state spectra and allowed by some new facts to conclude that the ethanol molecule had not only two but at least 5 rotational isomers. The most interesting of those conformations are the ones connected with the hydroxyl rotation at azimuthal rotation angles of $\Psi = 30^\circ$ and $\Psi = 80^\circ$ about the axis which formed with C-O bond rotational cone topping in C atom centre. Our computer programs permitted to identify rotational transitions in the MW-spectra and to get spectroscopic constants, structural parameters and stabilizing potentials. It has been proved that in the ethanol molecule specific interactions lead to the existence of energetically "disadvantageous" conformers.
New Representations on Conformational Properties of Iso-propanol Molecule
A.A. Abdurakhmanov
Physical Institute, Azerb.SSR Acad.of Sci., Baku, USSR

Studies on isopropanol, \((\text{CH}_3)_2\text{CH}^\bullet\text{OH}\), MW-spectra demonstrated the molecule existence in two energetically non-equivalent trans \((\Psi=0^\circ)\) and gauche \((\Psi=120^\circ)\) conformers. Saturated isopropanol spectrum also gave two spectra which we attributed to \(v=0\) and \(v=1\) states of coiled conformer. Further detailed investigations to experimentally prove the rotational "multiisomerism" in isopropanol led to another three spectra identification. Analysis of rotational constants, \(\Delta\) parameters, dipole moments, Stark effect, transition intensities and their correlation to the analogous parameters of trans \(0^\circ\) and gauche \(120^\circ\) conformers showed these spectra to be non-associated with their excited states. Meanwhile they were identified by some peculiar features with coiled conformers which in total with trans- and gauche ones composed a multiisomer series of \(\Psi=0^\circ, 30^\circ, 90^\circ, 120^\circ,\) and \(150^\circ\) parameters for OH hydroxyl asimuthal rotation angle about the axis which formed with C-O bond rotational cone topping in the C atom centre. The existence of isopropanol molecule in some coiled isomers with uncommon \(\Psi=30^\circ, 90^\circ, 150^\circ\) parameters was a contradiction to the established conformational representations of only "chess-board" forms \(\Psi=0^\circ\) and \(120^\circ\) in single-bond molecules. The realization of energetically "disadvantageous" conformers was proved to be due to the possibility (predicted by the author) of existence in the isopropanol molecule of specific orientational interactions between the lone electron pairs of oxygen atom and the nearest CH-bonds of both methyl groups. Rotational constants and probable structural parameters were established, the contribution of stabilizing potential in "forbidden" conformers was estimated.
Interpretation of Nitric Acid Molecular Spectrum and Determination of Its Derivatives of Dipole Moment

O.K. Voitsekhovskaya, F.V. Konusov, V.N. Cherepanov
The Institute of Atmospheric Optics, Siberian Branch
USSR Acad. Sci., Tomsk, 634055, USSR

This paper presents the formulas obtained for the intensities of spectral vibration-rotation lines of \( C_9 \) symmetry plane molecule taking into account intramolecular interactions. This has made it possible for the authors, using the literature data on the parameters of the Hamiltonian \([1]\) and one of the components of dipole moment \( \mu_{(2)} \) \([2]\), to identify the experimental spectrum \([3]\) and to determine the both components of the dipole moment \( \mu_{a(2)} = 0.18 \) D and \( \mu_{b(2)} = 0.38 \) D by the least-square method.

References

Determination of Higher Derivatives of Dipole Method of Triatomic Molecules
O.K. Voitsekhovskaya, O.N. Sulakshina
Institute of Atmospheric Optics SB USSR Acad. Sci., Tomsk, 634055, USSR

A series of parameters of dipole momentum function of molecules of asymmetric top was calculated in this paper. The data on the intensity of vibration bands and vibration-rotation lines were used as initial information.

The analytical expressions connecting the transition momenta with the molecular constants served as an operational apparatus for determining the values of derivatives. The relationships for matrix elements lacking in the literature were written by the authors using the perturbation theory of the second order for the wave function. For the bands, participating in the resonance, the coefficients of mixing were estimated and the "undistorted" values of transition moments were calculated.
Investigation of Probabilities of Vibration-Rotation Transitions of Diatomic Stable Radicals
O.K. Voitsekhovskaya, O.N. Sulakshina
Institute of Atmospheric Optics SB USSR Acad. Sci., Tomsk, 634055, USSR

The analytical relations for the probabilities of rotational transitions of diatomic molecules in state $^2\Pi$, both of the main bands and satellite bands with $\Delta V = 1,2$ are obtained in this paper. It is shown that for calculation of transition probabilities of the main bands $^2\Pi_{\frac{1}{2}} - ^2\Pi_{\frac{3}{2}}$, $^2\Pi_{\frac{3}{2}} - ^2\Pi_{\frac{5}{2}}$ one can use the relations valid for the molecules in the state $^1\Sigma$, if the vibration dependence of eigenvectors of the matrix of an effective Hamiltonian for the state $^2\Pi$ is unessential. The spin-orbital interaction mainly exists in rotational intensities for satellite bands. On the basis of the relations suggested an algorithm of calculation of spectral line parameters was developed, and the numerical results were obtained for the NO molecule.
"Current Research in Millimeter-wave and infrared molecular spectroscopy at the Laboratoire de Spectroscopie Hertzienne of Lille".

J. DEMAISON

The present status in several projects currently developed at Lille will be discussed.

The millimeter-wave spectroscopy of ions and other transient species in a RF plasma has been continued (CH, ¹³CN, HCS⁺).

The millimeter-wave spectra of other molecules of potential interest to radioastronomers have also been measured. They include molecules with internal rotation. Our measurements have allowed us to certain improved centrifugal distortion constants and internal rotation parameters.

Studies of the line broadening parameters of constituents of the earth atmosphere has been begun. Results concerning CO, O₃ and H₂O will be reported.

Doppler-free two-photon spectroscopy is performed with a CO₂ waveguide laser. The absorption cell is set inside the cavity of the laser. Spectra of SF₆ and SiF₄ have been obtained with several CO₂ emission lines. The resolution of 50 kHz FWHM has been achieved. Assignments of SF₆ spectra performed by C.W. Patterson from Los Alamos Lab have allowed us to obtain an accurate determination of the 2V₃ parameters.

Some Further Microwave Pressure Line Shift Studies

High-resolution IR-CARS Spectrometer and Spectroscopy of the Interacting $\nu_1$ and $\nu_3$ Vibrations of Tetrahedral Molecules

D.N. Kozlov, V.V. Smirnov, S.Yu. Volkov
General Physics Institute, Moscow, USSR

A number of problems of molecular spectroscopy requires simultaneous recording of both Raman and IR spectra of object under study. The authors have built up a high-resolution ($\sim 10^{-3}$ cm$^{-1}$) computer-controlled spectrometer which provides an opportunity to obtain simultaneously IR and Raman spectra in the spectral range of 1900-5000 cm$^{-1}$. The basis of the spectrometer is two cw narrow band laser sources, the frequency of one of them ($\omega_1$) being fixed while the frequency of the other ($\omega_2$) being tunable. Raman spectra are obtained by means of CARS, where signal power at frequency $\omega_3 = 2\omega_1 - \omega_2$ versus $\omega_2$ is recorded. At the same time the radiation of these two pumping lasers is converted in an appropriate nonlinear crystal into IR-radiation at frequency $\omega_{IR} = \omega_1 - \omega_2$. This tunable light source is used to record absorption spectra. Absolute frequency calibration with the accuracy of 0.001 cm$^{-1}$ is carried out by a wavemeter in which Fizeau-type interferometers are employed.

Our spectrometer has been used to obtain rotationally resolved Q-branches of IR spectra of the $\nu_3$ and of CARS spectra of the $\nu_1$ fundamentals in $^{28}$SiH$_4$ and $^{74}$GeH$_4$ molecules. In these molecules the $\nu_1$ and $\nu_3$ vibrational states are quasi-degenerate. Theoretical analysis of the experimental data has been carried out taking into account rovibrational Coriolis-type interaction of these states. Spectral lines have been assigned and parameters of the effective Hamiltonian for $\left\{\nu_1, \nu_3\right\}$ group have been determined.
With a high power intracavity Ar\(^+\) laser (500 W) Raman spectra of very weak transitions are observed, e.g. the v=0 \(\rightarrow\) v=2 transition of N\(_2\) being a thousand times weaker than the v=0 \(\rightarrow\) v=1 transition.

From the overtone and combination tone transitions in the Raman spectra of molecules like C\(_2\)H\(_4\) and SF\(_6\) (cross-)anharmonicity constants \(X_{ik}\) can be extracted. Knowledge of this is of importance in the field of IR multiphoton excitation.

From the measured overtone intensities the anharmonicity shifts and the spectral structures information is obtained about higher derivatives of the polarisability tensor, Fermi resonances, Coriolis interactions, etc.
High Resolution Raman Spectroscopy of Gases with a Fourier Transform Spectrometer

Alfons Weber
Molecular Spectroscopy Division
National Bureau of Standards
Washington, D.C. 20234

Donald E. Jennings
NASA-Goddard Space Flight Center
Greenbelt, MD

James W. Brault
Kitt Peak National Observatory
Tucson, AZ

High Resolution Raman spectra of gases have been recorded using a Fourier transform spectrometer. An argon-ion laser and multiple-pass Raman cell [1] were set up at the McMath FTS of the National Solar Observatory at Kitt Peak. The FTS was operated in the conventional manner, except that a photomultiplier was used as a detector. The Raman cell was placed both inside and outside the laser cavity, and both laser polarizations were used. Spectra were recorded both with and without Rayleigh blocking filters. The technique produced spectra of pure-rotational and rotation-vibration bands of H₂, D₂, N₂, O₂, C₂H₂, and CO₂. The technique has advantages over conventional laser Raman methods using grating spectrographs or spectrometers because of the high throughput, wide spectral coverage, and high calibration accuracy of the FTS. In addition, the large dynamic range of the McMath FTS allows the Rayleigh line to be recorded without filtering.

The spectrum of D₂ was used to measure the frequencies of seven pure-rotation transitions and nine rotation-vibration transitions. Signal-to-noise in the lines was as high as 150 after eight hours of integration, producing accuracies of a few milliwavenumbers. A rotation-vibration analysis of D₂ will be presented.

L C6. Discussion About the Accuracy and the Resolution of the Fourier Transform Spectrometer

J. Kauppinen

L C7. Analysis of Rovibrational Transitions $^{13}\text{C}_0^{16}0^{18} \rightarrow \text{OV}_2V_3\rightarrow \text{OV}_2(V_3-1) (V_2=0,1)$ Observed in High Resolution Emission Spectra in the 4,5$\mu$m Region.

BAILLY D. and ROSSETTI C.

Laboratoire d'Infrarouge, Associé au CNRS, Université Paris-Sud, Bât. 350, 91405 ORSAY CEDEX, FRANCE

As a part of a more extensive work on CO$_2$ isotopic species in emission studied by Fourier Transform Spectroscopy (Resolution : $5.4 \times 10^{-3}$ cm$^{-1}$), spectroscopic constants and band centers are given for Σ-Σ ($l=0$) and Π-Π vibrational ($l=1$) transitions of $^{13}\text{C}_0^{16}0^{18}$ located in the spectral range : 2 300 - 2 050 cm$^{-1}$.

These constants reproduce about 700 experimental wavenumbers with a RMS of the order of $3 \times 10^{-5}$ cm$^{-1}$ for the best vibrational transition, less than $1 \times 10^{-4}$ cm$^{-1}$ for most of the others.

From experimental wavenumbers belonging to the first Σ-Σ transitions, molecular parameters have been determined : the validity of such parameters will be discussed in relation with previous results concerning $^{12}\text{C}_0^{16}0^{18}$, the other non symmetric molecule we have studied.
A Combined Rotational-Zeeman and Cotton-Mouton effect investigation of the electromagnetic tensor properties of simple hydrocarbons

H. Häußler, H. Kling, and W. Hüttner
Universität Ulm, Abteilung Chemische Physik, FRG

We have carried out high resolution measurements of the second order rotational Zeeman effect on a series of saturated and unsaturated hydrocarbons. The resulting molecular susceptibility anisotropies $\Delta \xi$ were then least squares analysed in terms of three cylindric (C-H, C=C, C=O), and two asymmetric (C=C) additive bond anisotropy parameters.

In order to be able to include non-polar molecules, and to collect information on the optical polarizability anisotropies $\Delta \alpha$ for a similar least squares procedure in terms of bond polarizabilities, we have also measured the temperature dependence of the magnetic field induced birefringence (Cotton-Mouton effect) of a number of gases under low pressure (yielding $\Delta \xi \cdot \Delta \alpha$).

The analyses show that both bond additivity schemes can be applied with moderate accuracy. There are, however, serious exceptions (for example, ethane) which can be easily recognized by applying symmetry arguments to the data of related molecules. Deviations from the bond additivity approximation can be quantitatively explained by mutual interactions of induced bond dipoles if bond tensor deformations are taken into account in terms of hyperpolarizabilities.1)

Our results can be used to predict $\Delta \xi$ and $\Delta \alpha$ of the monomeric hydrocarbon skeletons in polymers and gels which in turn are of value in perceiving chain conformations from magneto-optical measurements.

1) D. Haase, private communication
Afternoon Session (Chairman - A.R.W. McKellar)

LC9. The Theoretical Study of the Pentade of Interacting Vibrational States in the Methane Molecule
V.I. Perevalov, D.A. Sadovskii, Vl.G. Tyuterev, B.T. Zhilinskii
Institute of Atmospheric Optics SB USSR Acad. Sci., Tomsk, 634055, USSR
*Moscow State University, Moscow, USSR

The effective Hamiltonian in terms of the irreducible tensor operator for the pentade of interacting states 1000, 0101, 0200, 0010 and 0002 of tetrahedral XY₄ molecules is derived by the contact transformation and the comparison is made with the recent fits performed by Poussique et al. and Lolck et al. for CH₄ pentade. The results of the calculation of spectroscopic parameters of the types q²J², q²J³, q³ and q⁴ based on molecular force field are discussed.
Numerical Contact Transformation of Anharmonic Force Fields

D.H. Whiffen

Either perturbation theory or unitary contact transformations can be used to obtain closed form expressions for spectroscopy parameters such as $x$, $y$, $\alpha$, $q$, $D$, etc. from anharmonic force fields. The derived expressions are not wholly applicable when the existence of close resonances, especially Fermi resonances, makes the order of magnitude classification unrealistic.

With modern computers closed forms are no longer essential and the problem can be solved by setting up an appropriate matrix, and diagonalizing [1]. The need for realistic truncation of the potentially infinite matrices leads to large matrices which are time consuming to solve for their eigenvalues. Chedin [2], has introduced numerical contact transformation as an alternative solution to this problem.

Such a programme has been written in Newcastle upon Tyne for linear triatomic molecules and compared with the earlier method [1]. The numerical results are very close for vibrational energies and rotational constants, but differ slightly for centrifugal distortion. The relative errors, timings, ease of extension to larger problems etc. will be discussed.


Relating Alternative Formulations of Asymmetric-Rotator Hamiltonians
Written as Power Series in Angular Momentum

Paul M. Parker
Department of Physics, Michigan State University, East Lansing, USA

Effective rotational Hamiltonians, written as power series in the body-fixed Cartesian angular momentum components \( P_\alpha \) (\( \alpha = a, b, c \)), have been used extensively in the analysis of high-resolution pure rotation and vibration-rotation spectra. For asymmetric rotators, in addition to the Watson standard form, two somewhat different cylindrical-tensor forms are widely used.\(^1\) Empirical constants are usually reported in one of the latter forms whereas the standard form relates more directly to model Hamiltonians and reduction-invariant combinations of empirical constants. When higher power angular-momentum terms are included in the Hamiltonian, the relations between the coefficients of the various forms become quite involved, especially if they are not to be reduction-specific. Since coefficients of octic, dextic and even higher powers of angular momentum are now regularly reported, it appears desirable to relate the various Hamiltonian forms in use in a comprehensive and practical way. The results of such an attempt will be described.

Pure Rotational Spectrum of Hydrogen Sulphide Molecule.
New Measurements and Analysis
G.DiLonardo, O.L.Polyansky, M.Yu.Tretyakov

The results of the new measurements and analysis of the pure rotational spectrum of the hydrogen sulphide molecule are presented. 120 FIR rotational lines between 26 cm\(^{-1}\) and 83 cm\(^{-1}\) were measured by the Fourier spectrometer (Bologna, Italy). 50 submillimeter rotational lines were measured by the RAD spectrometer (Gorky USSR). The data include lines with rotational quantum number up to \(J=13\) and with absorption coefficient down to \(\tilde{\gamma} = 6 \times 10^{-8}\) cm\(^{-1}\).

The analysis include frequencies of both newly obtained lines and known microwave (39) lines \([1]\) of \(\text{H}_2\text{S}\) pure rotational spectrum.

The data up to \(J=11\) were fitted within the experimental errors to the Watson's rotational Hamiltonian \([2]\) (standard deviation \(\tilde{\gamma} = 1\)) using 24 parameters up to \(J^8\). The attempt to fit data for \(J=12\) and \(J=13\) lines to this model resulted in worsening of the fit (standard deviation \(\tilde{\gamma} = 3\)).

The use of the one-dimensional approximation of the Watson's Hamiltonian \([3]\) permitted to fit the data up to \(J=13\) with standard deviation \(\tilde{\gamma} = 0.9\) in the model with the same number of parameters (24) and the same order of the terms \((J^8)\) as in the previous case. Parameters of the approximation are the usual Watson's parameters rearranged according to the formulas of the Padé approximants \([4]\).

3. O.L.Polyansky, L.G.Staruchina, to be published.
Ground state constants of quasi-spherical symmetric molecules. 
Application to $\text{PH}_3$ and $\text{POF}_3$.

G. TARRAGO and M. DANG-NHU,
Laboratoire d'Infrarouge,
Bât. 350. Campus d'Orsay,
F - 91405 ORSAY Cedex. France

The molecules $\text{PH}_3$ as well as $\text{POF}_3$ are quasi-spherical symmetric tops characterized by close values of the rotational inertial constants $A$ and $B$: the ratio $|A - B|/B$ is only 12% for $\text{PH}_3$ and 5% for $\text{POF}_3$. In such a case, the non diagonal contributions in $K$ ($\Delta K = \pm 3, \pm 6$) to the ground state energies may become large enough to require diagonalization of Hamiltonian matrices. This model is necessary to account for present microwave data, with their high sensitivity and accuracy. Such an approach insures an adequate convergence of the spectroscopic constants involved in energy calculation and reduces significantly their number. The results thus obtained for $\text{PH}_3$ and $\text{POF}_3$ will be presented.
POSTER SESSION

P C1.  High-Resolution CARS Spectroscopy on Small Molecules
       D. Illig

P C2.  A New Continuous Wave CARS Spectrometer for Doppler
       Limited High Resolution Gas Spectroscopy
       H. Frunder

P C3.  A generalization of Watson's centrifugal distortion terms for asymmetric internal rotor
       L. Sztraka

Dept. of Physical Chemistry, Polytechnical University of Budapest, Hungary

Derivation of the first and second order centrifugal distortion terms for methanol-like asymmetric internal rotors is presented. The method is a generalization of Watson's one completed by taking into account the periodic properties of internal rotor angular momenta averages. 11 first and 16 second order determinable coefficients have been obtained. The results have been tested by fitting the microwave data of methanol and methyl-amine.
Investigation of the Selective Multiple Quantum Excitation in Molecules Varying the Light Polarization

H.-H. Ritze, V. Stert, H. Albrecht, W. Radloff

We have measured the absorbed energy per SF$_6$-molecule irradiated by an intense CO$_2$-laser radiation. In general, the multiple photon absorption coefficient is different for linearly and circularly polarized light. There are excitation frequencies where circularly polarized light leads to a stronger absorption, at other frequencies the molecules are more effectively excited by linearly polarized light. This behaviour can be understood using some simple models. Interpreting the polarization dependence we can get information about the role of the rotational compensation of anharmonicity.

The experiments were carried out firstly in a gas cell at room temperature and secondly in a cooled molecular beam. In the second case the excitation channels are reduced because of the lower line-density and the influence of "pure" multiphoton resonances without population of the intermediate levels can be detected.
A photometric ellipsometer is used in combination with a Fourier-transform-spectrometer to measure the ellipsometric parameters \( \Psi \) and \( \Delta \), with
\[
\tan \Psi \cdot e^{i \Delta} = \frac{r_L}{r_P}.
\]
and \( r_P \) and \( r_L \) are the reflection coefficients for the perpendicular and parallel direction respectively. For \( \Psi \) and \( \Delta \) the dielectric function \( \hat{\varepsilon} \) or the optical constants \((n, k)\) are calculated by use of the well known relation of the metal optics, if the surface is clean and isotropic
\[
\hat{\varepsilon} = \varepsilon_1 + i \varepsilon_2 = (n^2 - k^2) + i 2nk.
\]
The problems of anisotropic materials and surface layers will be discussed also. For the ATR-configuration, \( n \) and \( k \) can be calculated directly without the knowledge of penetration depth. Experimental results are presented.
The Herzberg and $E^1\Pi - A^1\Pi$ Systems in the Spectra of five CO Isotopic Molecules.

R. Kępa and M. Rytel
Pedagogical College, Rzeszów, Poland.

In the emission spectrum of the carbon monoxide molecule, 36 bands of the Herzberg system and 11 bands of the $E^1\Pi - A^1\Pi$ system have been obtained. The bands have been photographed at about 0.7 Å/mm reciprocal dispersion in five isotopic molecules; $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{14}\text{C}^{16}\text{O}$, and $^{13}\text{C}^{18}\text{O}$. After a complete rotational analysis of bands, the following preliminary molecular constants have been calculated: (1) the rotational constants $B_v$, $D_v$, $Y_{01}$, $Y_{11}$, and $Y_{21}$ for $E^1\Pi$, $C^1\Sigma^+$ and $A^1\Pi$ states, (2) the band origins $c_{0v}$ for the $E - A$ and $C - A$ transitions, (3) the distances between the $v=0$ levels in the $E$, $C$ and $A$ states, (4) the vibrational constants $Y_{10}$, $Y_{20}$ and $Y_{30}$ for this states. In the $E^1\Pi$ state a large (as for so heavy molecule) $\Lambda$-doubling has been observed. The parameters of this effect and their isotopic dependence have been calculated and theoretically considered.
Optimization of the Effective Rotational Pade Hamiltonian Operator of the Molecule

Burenin A.V.

The effective rotational Hamiltonian operator in the form of the Pade approximant was successfully used recently in a number of papers (see, for example, /1, 2/) for treatment of data on the frequencies of the rotational transitions of nonrigid molecules. One of the main problems associated with an application of effective Hamiltonian operators, is the problem of an unambiguous determination of the parameters of these operators from the experimental data. The problem was not considered in the first papers on the use of the effective Pade Hamiltonian operator (among them /1, 2/). This resulted in a large number of excess model parameters in fitting of experimental data in these papers. The problem of an unambiguous determination of model parameters of the Pade Hamiltonian operator was first investigated in /3, 4/. The results of these papers enabled one to transform the Pade Hamiltonian operator to the form with a smaller number of independent parameters. The given form is better than the traditional representation of the Hamiltonian operator as a Taylor series even in the region of application of the Taylor series. In the present paper we give the solution of the problem on optimization of the form of the Pade Hamiltonian operator, which enabled us to reduce the number of the model parameters necessary for treatment of experimental data compared with /3, 4/.

One-Dimensional Approximation of the Effective Rotational Hamiltonian. Ground State of Water Molecule

O.L. Polyansky and L.G. Starukhina

Institute of Applied Physics, Academy of Sciences of the USSR, Gorky, USSR

Convergent sequences (for any rotational quantum numbers J and K) of the one-dimensional approximations of the effective rotational Hamiltonian for asymmetric tops /1/ were constructed.

The approximation is the rearrangement of usual perturbation terms according to various approximant formulas (Pade /2/ or Borel /4/ approximants, for example).

Joint retreatment of all available data on the ground state of water molecule based on the obtained expressions was carried out. The difference between observed and calculated levels up to J = 35 and K = 20 did not exceed 3 cm\(^{-1}\) in the model of 30 (terms up to \(J_{10}\) were used) usual Watson's parameters rearranged into one-dimensional approximation expressions. The standard deviation \(\sigma\) for 23 MW and about 400 IR line frequencies was equal to 3.

Use of the Borel method /4/ for the preliminary fitting of the water ground state levels /3/ permitted to obtain similar results in the model of 24 parameters up to \(J^8\) (the maximum difference between observed and calculated levels was \(E_{\text{obs}} - E_{\text{cal}} = 6\) cm\(^{-1}\) for the level \(20_{20,0}^1\)).

The $v_1$ band of CD$_3$I

M. Koivusaari, R. Anttila, and G. Guelachvili

The infrared band $v_1$ of CD$_3$I has been recorded at an instrumental resolution of 0.0054 cm$^{-1}$ with the aid of the Fourier spectrometer at Laboratoire d'Infrarouge in Orsay. The absorption path length was 52 m and two pressures, 0.07 Torr and 0.9 Torr, were used.

More than 2000 lines were assigned to the $v_1$ band. The highest $K$ and $J$ values were 15 and 93, respectively. The ground state combination differences from $v_1$, $v_4$, [1] and $2v_5^0$, all based on the same spectra, were treated together. When fixing $B_0 = 0.2014825$ cm$^{-1}$ [2] the fit of 1526 differences led to $D_{0}^J = 1.2428(4) \times 10^{-7}$ cm$^{-1}$, $D_{0}^{JK} = 1.600(2) \times 10^{-6}$ cm$^{-1}$ and $H_{0}^{JJJ} = -2.1(5) \times 10^{-14}$ cm$^{-1}$.

The first lines $R_K(J=K)$ and $P_K(J=K+1)$ in the sub bands of $v_1$ appeared as doublets, when $K \leq 8$. This splitting can be explained as the hyperfine structure caused by the quadrupole interaction of the iodine nucleus.

There are several local perturbation in $v_1$. When the apparently perturbed lines were omitted a fit of 900 lines ($K \leq 11$) gave the results: $v_0 = 2155.4284(1)$ cm$^{-1}$, $\alpha_1^B = 0.11811(8) \times 10^{-3}$ cm$^{-1}$ and $\alpha_1^A = 21.212(5) \times 10^{-3}$ cm$^{-1}$. The crossings in the sub bands $K = 4-7$ evidently are due to a Coriolis type interaction with $3v_3 + v_6^{\pm 1}$ and that in the sub band $K = 11$ is caused by $v_3 + v_5^{\pm 1} + v_6^{\pm 1}$. The fits to analyze the resonances quantitatively are in progress.


M. Koivusaari*, R. Anttila* and G. Guelachvili**

*Department of Physics, University of Oulu
Oulu, Finland
**Laboratoire d'Infrarouge, Université de Paris-Sud
Orsay, France
Our Stark cell has been placed inside the CO₂ laser cavity to improve the sensitivity of our Stark measurements and to easily saturate any transition except some slightly allowed ones. The Stark field is uniform within 10⁻⁴ and can reach 100 kV/cm. The Stark spectra of deuterated cyanoacetylene DCCCN have been recorded for many P lines of the 9.4 μm band of the CO₂ laser, and a few thousand lines have been measured, most of them with a Lmdip. They correspond to the 2 ν₅ band and to the associated hot bands from ν₇, ν₅, ν₆, 2 ν₇, ν₆ + ν₇, ... levels. Many assignments have been obtained in the firsts of them, including numerous zero field forbidden transitions ΔJ = 0, ± 2, ± 3, and also some high J transitions (J = 15). A band by band analysis has been applied to our data, with a perfect agreement between observed and calculated values in spite of the complexity of the upper state levels. Indeed most of them are combinations of the degenerate vibrations ν₅, ν₆ and ν₇, with strong l-type and vibrational l-type resonances between the sublevels. The analysis of those levels will be discussed, including the electrical parameters of DCCCN.

On the other hand, classical spectra of HCCCN and DCCCN in the range 200 - 300 cm⁻¹ have been recorded at the Wuppertal University, leading to complementary informations about the lowest degenerate vibrational states.
The vibration-rotation spectrum has been recorded, between 930 and 960 cm\(^{-1}\), using a Fourier Transform Spectrometer with a resolution of 0.0015 cm\(^{-1}\). On this spectrum the K-structure of the \(v_3\) and \(v_3 + v_7 - v_7\) bands is well resolved.

Lines belonging to the fundamental band have been observed until \(J = 70\), and the analysis of the structure enabled us to determine nine spectroscopic constants yielding a standard deviation comparable to the experimental precision.

For the \(v_3 + v_7 - v_7\) band it has been possible to identify lines until \(J = 50\). Five constants were calculated for this band.

Other hot bands arise in the recorded spectral range but they are too weak to be analysed.
The F.T. Infrared Spectrum of Silane in the 1000 cm\(^{-1}\) region: Experimental Results and Analysis

G. PIERRE, A. VALENTIN, L. HENRY

The infrared spectrum of silane in natural abundance has been recorded between 840 to 1040 cm\(^{-1}\) with very high resolution (FWHM = 0.003 cm\(^{-1}\)) by the Fourier Transform Spectrometer of the Laboratoire de Spectrométrie Moléculaire de PARIS. The line positions have an accuracy of 2 \times 10^{-4} \text{ cm}^{-1}.

The analysis of the spectrum gives:

- 4 scalar parameters of the ground state developed through the sixth order.
- 30 parameters of the dyad \(v_2/v_4\) developed through the fifth order.

These parameters reproduce the experimental spectrum with a standard deviation of 3 \times 10^{-4} \text{ cm}^{-1}.

The three isotopic species of the silane have been studied.

The microwaves transitions of dyad-dyad (\(v_i - v_j\) with \(i\) and \(j = 2\) or 4) have been calculated with a good accuracy. Some of these transitions have been observed by the professor BAUDER and coworkers of the E.T.H. of ZURICH.

The difference band triad \((2v_2/v_2 + v_4/2v_4) - \text{dyad} (v_2/v_4)\) predicted by extrapolation will be presented.
Simultaneous Analysis of two Vibrational Polyads in XY₄ Spherical Top Molecules: ¹²CD₄ diad + pentad

G. POUSSIGUE, E. PASCAUD, J.E. LOLCK*
Laboratoire d'Infrarouge, Bât. 350, Campus d'Orsay,
F-91405 ORSAY Cedex, France.
*Kemisk Institut, Division of Chemical Physics, Langølandsvej 140,
DK-8000 Aarhus C (DENMARK).

The vibrational polyads, which appear in light spherical top molecules of XY₄ type, can be analyzed and fitted separately. But in fact they involve common Hamiltonian parameters.

A first approach of the rovibrational analysis performed these last years, as well on ¹²CH₄ as on ¹²CD₄, was to treat successively the polyads with increasing vibrational energies i.e.: the ground state, then the diad (ν₂ = 1, ν₄ = 1), then the pentad (ν₄ = 2, ν₂ = ν₄ = 1, ν₂ = 2, ν₃ = 1, ν₁ = 1) ... and, at each new analysis, the values of the parameters derived from lower polyads are used.

Now we are able to treat simultaneously two polyads in order to have a better determination of the common parameters, and to avoid at least partially some strong correlations.

A computer program has been written in this aim and it is now applied to the special case of ¹²CD₄ diad and pentad. All assigned rovibrational levels up to J' = 20 are fitted simultaneously and 79 parameters are adjusted. Only the well determined ground state parameters remain fixed. The comparison with the separated treatment will be discussed.
Millimeterwave Spectrum and Internal Rotation of 1-Silylpropyne, CH₃C≡CSiH₃

Jun Nakagawa*, Manfred Bester, Koichi Yamada and Gisbert Winnewisser
Erstes Physikalisches Institut, Universität zu Köln, 5000 Köln 41, Federal Republic of Germany

The rotational transitions of CH₃C≡CSiH₃ have been observed in the millimeterwave region using a computer-controlled source-frequency modulation spectrometer with a 1.1 m long free space absorption cell. The observed spectrum clearly shows the effect of internal rotation with a small potential barrier and has been analyzed by calculating the torsion-rotation energies on the basis of torsional wavefunctions obtained by diagonalizing the torsional part of the Hamiltonian. The least squares analysis has yielded the rotational constant B = 2068.2817(4) MHz and a few centrifugal distortion constants. The barrier height to the internal rotation has been determined to be 3.77(70) cm⁻¹ from the contour map of the standard deviation. Also the A rotational constant of the silyl group around the symmetry axis has been estimated by fixing the A constant of the methyl group to the value of A(CH₃C≡CH).

* On leave from the Department of Chemistry, Faculty of Science, Hiroshima University.
The $v_9$ Band of $H_2CN_2$ (Diazirine) by Doppler-Limited Fourier-Transform Infrared Spectroscopy.

A. Gambi, and M. Pedrali, Dipartimento di Spettroscopia, Elettrochimica e Chimica Fisica, Università di Venezia, I-30123 VENEZIA (Italy).

M. Winnewisser, Physikalisch-Chemisches Institut der Justus-Liebig Universität Giessen, D-6300 GIESSEN (West Germany).

G. Guelachvili, Laboratoire d'Infrarouge, Université de Paris-Sud, Associé au C.N.R.S., F-91405 ORSAY Cedex (France).

The rovibrational analysis of the $v_3$ fundamental (A-type band, $A_1$ species, CH$_2$ deformation) and of the $v_7$ fundamental (B-type band, $B_1$ species, CN asymmetric stretching) have been carried out previously on the medium resolution infrared spectra of diazirine (1,2), developing methods for the assignment of this kind of very asymmetric rotor ($\kappa=-0.427$). With the intention of extending these assignment methods and of providing complete, reliable molecular constants for diazirine, the high resolution Fourier-transform infrared spectrum of diazirine was recorded between 1000 and 2750 cm$^{-1}$ at the Laboratoire d'Infrarouge in Orsay, with a resolution of 0.0054 cm$^{-1}$.

We will report here the rovibrational analysis of the $v_9$ fundamental vibrational band of diazirine. This band at 1124.914 cm$^{-1}$, of symmetry species $B_2$ in the molecular point group $C_{2v}$ to which the diazirine molecule belongs, is a C-type band and can be approximatively described as a CH$_2$ rocking vibration. Due to the high resolution achieved in the spectrum, it was possible to assign several Q-branch transitions in addition to P- and R-branch transitions.

A reliable set of rotational and centrifugal distorsion constants for the state $v_9=1$ together with a discussion of the features of this C-type band will be given.


The infrared spectra of $^{13}$C isotopically enriched diazirine was recorded in Giessen at a medium resolution of about 0.08 cm$^{-1}$ with a Digilab FTS 20 between 450 and 3800 cm$^{-1}$, whereas the high resolution spectrum (about 0.005 cm$^{-1}$) was measured in Orsay between 1250 and 2000 cm$^{-1}$. We report here the rovibrational analysis of the A-type parallel band $v_3$ (CH$_2$ deformation) at 1458 cm$^{-1}$. A preliminary assignment of the strongest rovibrational transitions was made for the P and R branches in the spectrum at medium resolution. Since in this spectrum the Q branches could not be resolved and some transitions were blended with lines arising from the main isotopic species, which was present at about 11% relative abundance, the molecular parameters obtained in this spectrum were used in order to assign the high resolution spectrum. In this spectrum many Q branch transitions with $K_a+K_c=J$ and $K_a+K_c=J+1$ were resolved and could be assigned. Using Watson's A-reduced Hamiltonian, rotational and centrifugal distortion constants were determined for the $v_3=1$ state.
Band Contour Analysis of the \( v_3 \) Band in \( ^{15}\text{N}-\text{Labeled} \) Diazirine, \( \text{H}_2\text{CN}_2 \)

by

J. Vogt and A. Gambi
Physikalisch-Chemisches Institut
Justus-Liebig-Universität Giessen
Heinrich-Buff-Ring 58
D-6300 Giessen
West-Germany

Within the framework of research concerning the molecular constants of diazomethane and its structural isomers by means of microwave, millimeter wave and Fourier transform infrared spectroscopy, various isotopically enriched samples of diazirine have been studied at high resolution. The infrared spectrum of \( ^{15}\text{N}-\text{labeled} \) diazirine was recorded with a Digilab FTS 20 at a resolution of 0.08 cm\(^{-1}\). Since no high resolution data were available and the measured spectrum is only partly resolved, band contour analysis based on limited explicit assignments was used in order to determine rotational and centrifugal distortion constants. In this paper we report the analysis of the \( \Lambda \)-type parallel band \( v_3 \) (CH\(_2\) deformation) at 1452 cm\(^{-1}\).
Local Perturbations in the \( v_4 \) Vibration-Rotation Band of \( H_3^{74}Ge^{35}Cl \).

C. di Lauro, F. Lattanzi, and H. Buerger

Universities of Napoli (Italy), Calabria (Italy), and Wuppertal (West Germany).

Local perturbations are found to affect the position of lines for certain limited ranges of \( J \)-values in all \( k \cdot l \) branches of \( v_4 \).

The perturbation patterns are very complex and should be caused by a system of perturbers involving several vibrational levels. However, the examination of details of the perturbation features observed on the \( R_0 \) and \( R_{\alpha} \)-branches, compared to the observations on the neighbouring branches, suggests that the main perturber is \( 3v_3 + v_5 \), coupled to \( v_4 \) by anharmonic interaction. The large difference between the values of \( B \) in the two vibrational states accounts for the occurrence of crossing in the \( J \)-structure.

A complex system of perturber levels is considered and will be tested by computer calculations.
Diode Laser Spectroscopy of Line Broadening in Polyatomic Molecules: Correlation Technique

E.V. Stepanov

Institute of General Physics of Ac. of Sc., Moscow, USSR

Correlation processing of diode laser spectrum makes it possible to investigate collision broadening of lines of polyatomic molecules. It is possible to obtain rather long intervals of full resolution molecular absorption spectrum due to wide region of continuous frequency tuning (0.5 - 3 cm\(^{-1}\)) and narrow laser line (of about 10\(^{-6}\) cm\(^{-1}\)). In the case of polyatomic molecules such as SF\(_6\), CF\(_2\)Cl\(_2\) several hundreds of lines are located in the one cm\(^{-1}\) spectral region of IR rotation-vibrational transitions. These lines are particularly overlapped and this makes it difficult to analyse line broadening by usual methods. But the large number of lines in the detected region permits us to apply correlation technique for this purpose.

Averaged coefficients of line broadening in SF\(_6\) and CF\(_2\)Cl\(_2\) were measured by using correlation technique. Various gases such as He, Ne, Ar, Kr, Xe, CO, N\(_2\), H\(_2\), isotope modification \(^{34}\)SF\(_6\) were used as foreign broadening gases. Their pressures were changed from 0 to 100 Torr. 10\(^{-\mu}\) transitions were under investigation.

In most cases the broadening coefficients decreased with increase of pressure. The decrease takes place when the linewidths become comparable with average value of the fine splitting in the spectra (~10\(^{-2}\) cm\(^{-1}\)). Thus the effect may be connected with interference of spectral lines. The switching off of some collisional-relaxation mechanisms is the result of this interference of spectral lines. The dependence of the cross-sections of collisional relaxation processes on the mass and structure of broadening molecules and on the presence of resonant relaxation channels was investigated.
The Torsional Hot Band of $\nu_g$ of Ethane, $\nu_g + \nu_4 = \nu_4$

G. Halsey

Theoretical Models of Intramolecular Interactions
Consideration in Line Intensities
O.K. Voitsekhovskaya, Yu.S. Makushkin, O.N. Sulakshina, V.N. Cherepanov
The Institute of Atmospheric Optics SB USSR Acad.Sci., Tomsk, 634055, USSR

In this paper the models of registration of intramolecular interactions when calculating the line intensities are based on the theory of effective rotational Hamiltonians, being at present the most efficient theory in theoretical spectroscopy. In this case, the authors use both projection formulations of the perturbation theory and the methods of generalized contact transformations.

The relations of the parameters of vibration-rotation interaction with molecular constants for a series of bands with $\sum_{\ell} |\nu'_{\ell} - \nu_{\ell}| \leq 3$ of diatomic linear molecules and asymmetric top molecules were determined.

The developed methods of calculation of line intensities enable one to take into account together with usual vibration-rotation interactions the spin-orbital interaction in the molecules of NO($s = 1/2$) type, spin-spin interaction in O$_2$(s=1), spin-rotational interaction in NO$_2$(s=1/2) in the molecules with electron spin different from zero. The last interactions are the reasons of qualitative variation of the molecular spectrum behavior. They result in line splitting and, therefore, it is necessary to take them into account for reliable interpretation of superfine structure of experimental spectra and for prediction of new lines.
Rotational Analysis of the $3p^2F_2 - 3s^2A_1$ Electronic Transition of the ND$_4$ Molecule

James K. G. Watson

The 14828 cm$^{-1}$ band of ND$_4^+$, originally observed in emission and more recently in absorption, is assigned to the 0-0 band of the transition $3p^2F_2 - 3s^2A_1$ of the odd electron outside the ND$_4^+$ core. The most prominent features of the rotational structure are two P-branch heads separated by about 6 cm$^{-1}$, each of which is split into subsidiary heads by the tetrahedral fine structure. The main doubling is due to spin-orbit coupling, while the tetrahedral splitting is produced by Jahn-Teller effects. A detailed fit of the high-resolution absorption spectrum will be described, and the Jahn-Teller constants will be compared with ab initio predictions.
Use of the Irreducible Tensor Sets for Analysis of Vibration-Rotation Spectra of Molecules

A.E. Cheglokov, V.N. Saveliev, and O.N. Ulenikov
The Institute of Atmospheric Optics, Siberian Branch USSR Acad. Sci., Tomsk, 634055, USSR

In the framework of formalism of irreducible tensor sets the formulas are obtained determining the matrix elements of the Hamiltonian and the reduced dipole moment of an arbitrary molecule as functions of spectroscopic constants, "6r" and "9r" - symbols and isoscalar factors of molecular group symmetry. The results obtained are of general character and allow consideration of different types of intramolecular effects and interactions, including various types of splittings and resonance interactions. Transition from the molecules of one symmetry to the other one is realized by simple change of "6r" - "9r" - symbols and isoscalar factors.

The formulas for the elements of reduction matrixes and isoscalar factor K for the molecules of symmetry Td were obtained in analytical form. The isoscalar factors were determined in analytical form for a series of another cubic groups, including the groups C3v and D3h.

The formulas were obtained for describing the rotational structure and line intensities of the molecules of C3v and D3h symmetry for any vibration-rotation bands taking into account resonance interactions and inversion. The formulas are obtained describing k and lk-doubling not only for lower but for higher values of quantum number k. For the molecules of NH3 type from general formulas the physically-validated analog of Pade-operator was obtained, allowing description of inversion spectra with experimental accuracy (i.e., ~1 kHz).
D4. Spectral features of multiphoton absorption in SF$_6$ supersonic molecular beams

W. Radloff and V. Stert

Central Institute of Optics and Spectroscopy, Academy of Sciences of the GDR

To study the multiphoton excitation of molecules at a low density of populated energetic states and without disturbances by collisions we have investigated molecules cooled in free jet expansions from a pulsed supersonic nozzle. If the molecules beams are seeded in noble gases the internal temperatures have been diminished further. For the excitation of the molecules a TEA CO$_2$ laser is used. We have investigated the dependence of the multiphoton absorption of SF$_6$ on the wavelength, the fluence and the polarization state of the laser field. The interpretation of the experiments gets some insight into the spectral characteristics of the multiphoton transitions between the low lying vibrational states. The results are compared with related investigations of the multiphoton excitation of SF$_6$ in a cell at room temperature.
Results from High Resolution Spectroscopy for the Use in Infrared Photochemistry

H. Hollenstein, M. Quack and H.J. Thöne
Laboratorium für Physikalische Chemie der ETH
ETH-Zentrum
CH-8092 Zürich, Switzerland

Infrared Photochemistry depends heavily upon the use of intense infrared absorption bands in polyatomic molecules. A systematic understanding of group contributions to band intensities in well defined spectral ranges such as the range of the CO$_2$-laser is urgently needed in view of an almost complete lack of quantitative experimental data for the band strengths of all but the simplest polyatomic molecules.

In our contribution a model will be presented which allows the quantitative understanding and prediction of band intensities originating from the CF chromophore in organic molecules. An important step in the analysis of band intensity data is the proper assignment of vibrational bands and the origin of their intensity. This is possible only by using high resolution spectra allowing a rotational analysis even for heavier molecules, as will be illustrated in detail for the example of t-butyl fluoride. High resolution spectra from our BOMEM DA 002 interferometric spectrometer will be presented and analyzed. The detailed understanding of the nature of the strong absorption bands for this and related molecules allows us to make tentative predictions for the vibrational absorption of the CF-chromophore in various molecular environments.
Ground state quadrupole spectra of CH$_3$I and CH$_3$Br have been measured in the region 80-500 MHz with the precision about 100 Hz by using the RF-MW double resonance spectrometer. In particular, the values of quadrupole coupling constants and the centrifugal distortion parameters in quadrupole coupling have been determined (in KHz):

<table>
<thead>
<tr>
<th></th>
<th>$\text{eqQ}_0$</th>
<th>$\chi_J$</th>
<th>$\chi_K$</th>
<th>$\chi_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{CH}_3\text{I}$</td>
<td>-1934130.22(39)</td>
<td>-1.546(22)</td>
<td>-33.61(51)</td>
<td>22.46(11)</td>
</tr>
<tr>
<td>$^{13}\text{CH}_3\text{I}$</td>
<td>-1934232.71(34)</td>
<td>-1.443(89)</td>
<td>-31.63(24)</td>
<td>21.36(10)</td>
</tr>
<tr>
<td>CH$_3^{79}\text{Br}$</td>
<td>577130.0(19)</td>
<td>1.04(24)</td>
<td>7.9(27)</td>
<td>-5.9(11)</td>
</tr>
<tr>
<td>CH$_3^{81}\text{Br}$</td>
<td>482130.8(17)</td>
<td>0.46(20)</td>
<td>10.1(26)</td>
<td>-6.3(11)</td>
</tr>
</tbody>
</table>

The comparison with theory is made by using isotopic relations for $\chi$-constants. It has been shown that certain combinations of the $\chi$-constants are invariant in isotopic substitution. In particular case of CH$_3X$ molecules we have the following invariants (in KHz:)

- $\chi_J+\chi_K+2\chi_d = 9.76(4)$ for $^{12}\text{CH}_3\text{I}$ and $9.63(8)$ for $^{13}\text{CH}_3\text{I}$
- $(\chi_J/B_0^2)10^{15}=27.5(4)$ for $^{12}\text{CH}_3\text{I}$ and $28.4(17)$ for $^{13}\text{CH}_3\text{I}$
- $((\chi_J+\chi_K+2\chi_d)/\text{eqQ}_0)10^6 = -4.99(42)$ for CH$_3^{79}\text{Br}$ and $-4.37(48)$ for CH$_3^{81}\text{Br}$ which confirm the correctness of the results.

The procedure of calculation of the $\chi$-constants using the GF-matrix formalism will also be presented in this report.
Far-infrared spectroscopy on short lived species

J.P. Bekooy, W.Leo Meerts and A. Dymanus

Results will be presented obtained with an absorption spectrometer employing a tunable source of radiation in the sub-mm region. This narrow-band radiation is generated in Schottky barrier diodes from frequency mixing of klystrons with lines from an HCN laser. Side bands cover the frequency range of 700 to 1200 GHz using fundamental (typically 50 µW FIR power) and second harmonic (1 µW FIR) of the klystron frequencies. An increase of FIR power level by an order of magnitude has been achieved by improved coupling of radiation with diode. Sensitivity obtained corresponds to $y_{\text{min}} \sim 10^{-7}$ cm$^{-1}$ for an absorption path length of 1 m. The absorption cell consists of a hollow cathode discharge tube with temperature controlled cooling. Either source frequency or discharge current modulation has been applied. The spectrometer offers possibilities to observe rotational spectra of transient species like small molecular ions.
Quasi-Symmetric Top Molecule Approach to the Rotational-Vibrational Problem of CH$_3$XY Molecules: Application to CH$_3$OD

Jacek Koput
Department of Chemistry, A. Mickiewicz University, Poznań, Poland

The skeletal bending-torsion-rotation Hamiltonian which has been used previously to calculate vibration-rotation energy levels of CH$_3$XY molecules is extended here to account for a tilt of the CH$_3$ group symmetry axis. This extended five-dimensional Hamiltonian has been used to study the COD bending-torsion-rotation energy levels of [D] methanol, CH$_3$OD. The "effective" COD bending potential function has been chosen as a simple quadratic-quartic function. The 58 J = 1 → 0 and 2 → 1 rotational-torsional transitions (microwave, submillimeter wave and far infrared experimental data) has been fitted and the barrier to linearity of the COD skeleton has been found to be about 6700 cm$^{-1}$. The "effective" barrier to internal rotation has been found to be 366 cm$^{-1}$. 
The models of Hamiltonians of centrifugal distortions for the asymmetric top molecules, containing the $J^2$, $J_z^2$ operators in the closed form are discussed. New models provide a consistent description of asymptotic behavior and of the isotopic dependence of high-excited energies of $X_2Y$ molecules. The models are used for the description of vibration-rotation spectrum of $H_2O$ type molecules.
On Determining the Structural Parameters and the Potential Function of the H₂O Molecule

V.N.Bryukhanov, Yu.S.Makushkin, O.V.Naumenko, O.N.Ulenikov

Institute of Atmospheric Optics SB USSR Acad.Sci., Tomsk, 634055, USSR

The structural constants (ζ and α), harmonic frequencies (ω), sin j, the anharmonic constants of H₂O molecule were obtained based on the method suggested in [1] and the system for the analytical calculations [2-3]. (This system enables one to receive, using the computer, the analytical expressions for spectroscopic constants as the functions of the fundamental parameters of the molecule). The parameters obtained reproduce the anharmonic Xij, resonance rotational A, B, C and the centrifugal constants Δk, Δjk, Δj, δk of the H₂O molecule for all known vibrational states. The parameters of the other isotopic modifications were obtained using the isotopic relations [4], that enables one to describe satisfactorily more than 200 spectroscopic constants of the D₂O, HDO, H₂¹⁷O and H₂¹⁸O molecules.

References

V.N. Bryukhanov, and Yu.S. Makushkin

Institute of Atmospheric Optics SB USSR Acad. Sci., Tomsk, 634055, USSR

The analytical expressions for spectroscopic constants of asymmetric top molecules, linear molecules, symmetric top molecules, spherical top molecules were obtained based on the special system for analytical calculations using computer developed by the authors[1]. Their efficiency was shown for the calculation of high-excited vibration-rotation energy states and the determination of molecular parameters.

References

The Photo-Acoustic Spectrometers With the Visible and IR Pulsed Lasers

B.G.Ageev, Yu.N.Ponomarev, B.A.Tikhomirov

Institute of Atmospheric Optics SB USSR Acad.Sci., Tomsk, 634055, USSR

The paper describes the photo-acoustic spectrometers developed for investigating the nonlinear molecular absorption spectra in the gas phase. Characteristics of the developed spectrometers for 0.53; 0.69; 1.06 and 10.6 μm are presented. The measurement procedure for high intensities of excited radiation, the problems on data processing and the sources and the values of the measurement errors of photo-acoustic spectrometers have been considered.

The results of investigating the nonlinear spectroscopic effects in low-absorbing atmospheric gases in the visible and IR were presented. The comparison has been made between the possibilities of the nonlinear photo-acoustic spectroscopy method and the method of nonlinear spectroscopy with the multipass cells.
The Investigation of Nonlinear Spectroscopic Effects in Gases Using a Photo-Acoustic Method

B.G. Ageev, V.E. Zuev, Yu.N. Ponomarev, B.A. Tikhomirov

Institute of Atmospheric Optics SB USSR Acad. Sci., Tomsk, 634055, USSR

The paper discusses the application of the photo-acoustic method for investigating the nonlinear absorption spectra of the molecules in the gas phase. The connection between the acoustic signal and the parameters of the investigated medium and optical pulse characteristics was theoretically and experimentally investigated.

The dependence of the energy absorbed in H₂O and CO₂ molecular transitions (in binary mixtures with molecular and atomic gases and the air) on the radiation intensity and polarization was investigated. It was experimentally shown, that the value of energy absorbed in rotation-vibration transitions of the H₂O dipole molecule, essentially depends on the type of the radiation polarization. The experimental results are discussed.
Line Shape Spectroscopy in the Visible and Near Infrared  
V.A. Kapitanov, V.P. Kochanov, Yu.S. Makushkin,  
V.I. Serdyukov, A.M. Solodov, L.N. Sinitsa, I.S. Tyryshkin  
Institute of Atmospheric Optics SB USSR Acad. Sci.,  
Tomsk, 634055, USSR  

The complex investigations of H₂O vapor absorption  
spectra in the range of 0.59, 1.06, 1.2 μm and those  
of CO₂ in the 1.06 μm range have been carried out using  
the technique of intracavity and optoacoustic spectroscopy as well as by direct spectrophotometric long multipass cell measurements. A large number of weak vibration-rotation H₂O lines was recorded with the resolution of 0.001 cm⁻¹ and their absolute intensities (≈10⁻²³–10⁻²⁶ cm/mol) were determined with the uncertainty of 10%. Usage of the narrow-band optoacoustic and cell spectrometers as well as the wide-band intracavity ones, for which simple procedure of obtaining the collision widths was developed, enabled us to investigate carefully the line shapes of a number of H₂O and CO₂ lines and to determine the collision broadening coefficients.
Theory and New Technical Realization of Spectrometers Using a Coherent Spontaneous Radiation

L.I. Gershtein, M.L. Gershtein, A.V. Maslovsky, V.L. Vaks

The relation between an absorption and a coherent spontaneous radiation (CSR) in the spectrometer cell is considered. A simple relation between the electromagnetic wave power, that produces polarization in the gas, the absorption coefficient and the CSR power is stated. It has been shown that the limiting sensitivities of the spectrometer under consideration and the Stark spectrometer are practically the same.

A new technical realization of the CSR spectrometer is suggested /1/, which enables one to realize the absorption coefficient sensitivity close to the limiting one (not less than $10^{-9}$ cm$^{-1}$) in the millimetre and submillimetre wave ranges (which is impossible at present for the Stark spectrometer).

The CSR spectrometer was checked experimentally at the frequency 85 GHz.

We describe an experimental device for the observation of transient molecular species. A plasma is created by a R.F. discharge in a multiple pass cell. The cell is optically linked up both to a diode laser spectrometer and to a Fourier transform interferometer. The laser allows the observation of the plasma on length greater than 100 metres.

The absorption of the laser beam is used to check the global efficiency of the apparatus through the optimisation of several parameters of the R.F. excitation. When the radical production is optimal, the emission Fourier spectrum is recorded to obtain the whole spectral range of interest, with the possibility of monitoring in real time the creation parameters (flow rate, pressure, mixture, R.F. power) by the diode laser spectrometer.

This device has been applied first to the study of a SiH₄ plasma and more especially to detect the $^{28}$SiH radical in the 1 - 0 and 2 - 1 vibration-rotation bands of the fundamental electronic state. 142 lines have been identified with a good signal to noise ratio.

Other radicals have been observed by F.T.S.; in particular from a mixture $N_2 + H_2$ plasma, we observed NH molecule in the 3000 cm⁻¹ region.