Abstracts of Papers

Monday, September 6

Morning Session:  Opening Ceremony (Chairman - J.T. Hougen)

A1. Research in High Resolution Infrared Spectroscopy:
    An Overview
    K. Narahari Rao

    Investigations in diatomic emission spectra, conventional polyatomic absorption studies, with special reference to carbon-13 species and ozone will be used as examples to discuss the technological and spectroscopic developments in this rapidly expanding area. Obligations of professionals in molecular structural studies in disseminating the results of basic research will be considered in view of the implication of these results to studies of the earth's atmosphere, astrophysical problems and molecular laser emissions.

A2. Selective Infrared Laser Photophysics and Photochemistry of Molecules
    V.S. Letochov

A3. Laser Spectroscopy
    L. Henry

    The laser spectroscopy for absorption studies is at present in a period of rapid development and must be compared with others methods. The apparatus function of classical spectrometers is limited by the optical path difference (in grating or Fourier Transform spectroscopy ...) or equivalent optical
path difference (in Fabry-Perrot or Connes interferometers ...) created by the analysis element. The apparatus function width can be of the same size as the Doppler-Fizeau width of a gas spectral line if the analysing element is able to create a path difference \(10^6\) times the wavelength of the spectral line as a consequence for the medium infrared the spectrometers are rather big apparatus.

The laser spectroscopy gives easily the Doppler-Fizeau profile of lines but frequency calibration and intensities measurements are not obtained very easily at present. A critical comparison of the different method in absorption spectroscopy will be developed.

If a laser gives, in one mode, a sufficient power non linear absorption (and fluorescence) occurs and opens a very fructuous way to obtain spectra with a resolving power far over the Doppler-Fizeau width with a very high calibration precision. A review of recent result in this field will be given for the infrared part of the spectrum.

Afternoon Session (Chairman - K. Narahari Rao)

B1. **Calculation of Vibrational Level Populations in Multiphoton Absorption Processes**

J.T. Hougen

A simple procedure has been developed for computing steady-state excited vibrational state populations for multiphoton absorption processes in many level systems. The procedure combines various techniques already in the literature, principally expansion of the density matrix as a Fouries series in the frequency of the monochromatic radiation field, and introduction of line-
widths and thermal relaxation by the addition of empirical terms to the density-matrix time-development equation. Numerical computations can be carried out quickly on idealized systems, using commercially available band matrix inversion routines. A sample calculation for a 10-level, 9-photon process will be presented.

82. Diode Laser Spectroscopy and Vibration-Rotation Assignments
R. S. McDowell, H. W. Galbrath, B. J. Krohn, C. D. Cantrell and E. D. Hinkley

The stretching fundamental $\nu_3$ of SF$_6$ at 948 cm$^{-1}$ has been studied using a tunable Pb$_{0.88}$Sn$_{0.12}$Te semiconductor diode laser (resolution $10^{-5}$ cm$^{-1}$) over the region 943.87 - 949.74 cm$^{-1}$, which includes all or portion of the manifolds $P(64)$ to $R(34)$. Each $J$ manifold (for $J > 1$) is split according to the various allowed octahedral sublevels. For $J > 23$, adjoining manifolds overlap, and the spectrum rapidly becomes more complex. Quantum numbers ($J$ values and octahedral symmetry types) have been assigned for all $P$- and $R$-branch transitions in the above spectral region that originate from the vibrational ground state (some 2000 transitions). Of special interest are the assignments near the CO$_2 P(14)$, $P(18)$, and $P(20)$ laser lines, since SF$_6$ is an important nonlinear adsorbed at 10.6 $\mu$m. The SF$_6$ transitions nearest these three laser frequencies are $R(28) A_2^0$, $P(33) A_2^1$, and an $F_2$ component of $P(59)$ or $P(60)$, respectively. The presence of a single non-degenerate SF$_6$ transition near CO$_2 P(14)$ helps to explain the observed nearly ideal pulse breakup in self-induced transparency at this frequency (2)
but not at $\text{CO}_2 P(20)$. From $\text{SF}_6$ spectra that were calibrated directly against the $\text{CO}_2$ laser lines by heterodyne methods, the molecular constants have been determined; some of these are (in cm$^{-1}$):

\begin{align*}
m &= 947.9675 \pm 0.0011 \text{ (band center)}, \\
n &= 0.055688 \pm 0.000016 \quad B + B_0 - 2(B_3), \\
p &= (-1.518 \pm 0.012) \times 10^{-5} \quad B_3 - B_0, \\
q &= (-2.460 \pm 0.007) \times 10^{-5} \text{ (primary splitting constant)}. \end{align*}

Tentative assignments will also be discussed for the complex Q-branch region, in which $\text{CO}_2 P(16)$ occurs. Similar but less extensive spectra have been obtained of the bending fundamental $\nu_4$ at 615 cm$^{-1}$; here the octahedral splitting of the $J$ manifolds is much smaller.


B3. **Fourier Infrared Spectroscopy of Transients**

A.W. Mantz

With the realization of simultaneous temporal and spectral multiplexing in the infrared using Fourier Transform Spectrometers, it is possible to study entirely new classes of problems which were not generally accessible to infrared techniques before. Now it is possible to simultaneously obtain high spectral resolution and realize spectral signal to noise normally associated with spectrally multiplexed systems on transient samples whose lifetimes...
are orders of magnitude shorter than the time required to collect one interferogram.

Results of time resolved spectral studies will be presented with a discussion of the gains in signal to noise one realizes over rapid scan devices. Interesting new applications will also be discussed.

B4. IUPAC Tables of Wavenumbers
A.R.H. Cole

The IUPAC "Tables of Wavenumbers for the Calibration of Infrared Spectrometers" were first published in 1961 and have been out of print for some years. The Commission on Molecular Structure and Spectroscopy commissioned the production of a revised edition of the Tables in 1974. The new edition follows the format of the first edition with Part I catering for high resolution spectrometers and Part II for lower resolution commercial instruments. Both Parts have been extended to cover the far infrared region.

The material in Part I has been completely rewritten. All data are accurate to ± 0.005 cm\(^{-1}\) or better and the highlights are the 2-0 and 1-0 carbon monoxide bands which are now known to an absolute accuracy of ± 0.0002 cm\(^{-1}\). New, high resolution diagrams accompany all tables of numerical data.

The new edition, to be published for IUPAC by Pergamon Press, will be issued in late 1976.

B5. Collision-Broadened Line Shape Measurements on Planetary Atmospheric Molecules
P. Varanasi

Collision-broadened line shape measurements relevant to the radiative atmosphere of the terre-
trial as well as of the outer planets, have been performed in our laboratory. Data on the shapes, widths and intensities are presented for the infrared lines of CO, CO₂, H₂O, HCl, CH₄, NH₃, C₂H₂ and C₂H₆. The broadening gases have been such dominant atmospheric constituents as N₂, CO₂, H₂ and He. From the data at temperatures between 150⁰K and 300⁰K, temperature-dependence of the important line shape parameters has been determined. Our results are compared with those based upon available theoretical models.

Collision-broadened line widths in CO-CO₂ and CO-O₂ collisions have been calculated by incorporating interactions due to octopoles and hexadecapoles and short range repulsive interactions into Anderson's theory. It is shown how these higher-order interactions can be manipulated to yield good agreement with experimental data. A critical evaluation of this totally empirical manipulation suggests that a thorough revision of the theory is required for all but simple dipole-dipole interactions. In the process of the evaluation, the values of the multipole moment are discussed.

86. Relaxation vibrationnelle de N₂O excite par N₂ active par spectroscopie d'émission a haute resolvance
A. Picard

L'étude à haute résolution des spectres de N₂O excité par N₂ activé permet de déterminer les populations des niveaux de vibration dont on observe la fluorescence. Le rythmement d'émission spontanée issu des niveaux excités de N₂O est analysé à l'aide d'un spectromètre interférentiel SISAM. L'étude des spectres ainsi obtenus permet d'identifier 14 transitions rovibrationnelles (correspondant à \( v_3 = +1 \)) qui
contribuent à l'émission et de déterminer les populations des niveaux mis en jeu à partir des intensités des raies observées. À partir des équations d'évolution qui régissent les transferts d'énergie par collisions intermoléculaires, nous avons élaboré un modèle analytique qui rend compte de l'évolution temporelle du nombre moyen de quantas de $\nu_3$ résultant de l'expérience.

Des valeurs moyennes des constantes intermoléculaires et intramoléculaires ont pu être déterminées pour les processus d'échanges d'énergie $N_2O-N_2$ et $N_2O$ (mode $\nu_3$) - $N_2O$ (modes $\nu_2$, $\nu_1$).

Le modèle proposé pour l'évolution des populations du niveau 001 permet de déterminer une valeur expérimentale de la constante de transfert de ce niveau vers les niveaux n.m.0.

Les constantes de transfert $K_{N_2O-N_2}$ calculées d'après la théorie de Sharma et Brau permettent de rendre compte de l'expérience de façon satisfaisante.

**B7. Intensity Distribution in Pure Rotational Raman Spectra of Linear Molecules in the Ground and Excited Vibrational States, Application to CO$_2$, N$_2O$ and C$_2$H$_2$**

H. Finsterhölzl, J.G. Hochenbleicher, K. Alcàmann and G. Strey

The pure rotational Raman spectra of CO$_2$, N$_2O$ and C$_2$H$_2$ have been recorded with argon laser excitation and a resolution of about 0.3 cm$^{-1}$.

J=1 transitions in the excited $\Pi$-states are clearly resolved up to about J=9. Formulae for the intensity distribution in rotational Raman spectra of linear molecules in the ground and vibrational $\Pi$-states have been derived including
the effect of l-type doubling. After a qualitative discussion these formulae are applied to a quantitative analysis of the spectra.

Tuesday, September 7

Morning Session: Laser Spectroscopy, Saturated Absorption
(Chairman - L. Henry)

Cl. Assignment of CH$_3$Br Transitions Pumped by CO$_2$ Laser

C. Betrencourt-Stirnemann and J.C. Deroche

35 far-infrared laser lines in CH$_3$Br illuminated by CO$_2$ laser were observed by T.Y. Chang and J.D. McGee (1). Assignments for these F.I.R. laser lines as well as for the CH$_3$Br transitions which are pumped are proposed here. Moreover, it was possible to determine in each case the isotopic species involved.

For the $\nu_6$ band, 11 coincidences were assigned to CH$_3^8^{18}$Br and 9 coincidences to CH$_3^7^{18}$Br. Although we observed only few coincidences for each isotope, the accuracy of the measurements and the high J and K quantum numbers values involved allowed us to determine molecular constants. We obtained in particular

\[
\begin{align*}
\nu &= 954.866 & \alpha_A^6 &= -29.54 \times 10^{-3} \\
\alpha_B^6 &= 1.137 \times 10^{-3} & \Delta \zeta &= 1.1566 \\
\nu &= 954.804 & \alpha_A^6 &= -29.59 \times 10^{-3} \\
\alpha_B^6 &= 1.135 \times 10^{-3} & \Delta \zeta &= 1.1561
\end{align*}
\]

(all values in cm$^{-1}$)
The others F.I.R. laser emissions were found to be due to $^{13}\text{CH}_3\text{Br}$ or highly excited vibrational states.


C2. **Vibrational Dependence of the Hyperfine Quadrupole Constant in NH$_3$ Observed by Saturated Absorption Spectroscopy**

M. Ouhayoun, J. Bordé and C. Bordé

The hyperfine structure of the $^Q(8,7)$ line of $^{14}\text{NH}_3$ (at 927.739 cm$^{-1}$) has been resolved by saturated absorption spectroscopy. The splitting of the $\Delta F = 0$ lines has been interpreted as a clear evidence of the vibrational dependence of the electric quadrupole interaction constant.

C3. **Transient Saturation in the ND$_3$ Inversion Spectrum**

S.N. Murzin and B.D. Osipov

The most interesting phenomena, which have been observed under saturation conditions in gas microwave spectroscopy, are the line saturation (1), the double resonance (2) and the variation of static dielectric permeability (3). The variation of static dielectric permeability of NH$_3$ under conditions of saturation of the inversion line $J=3$, $K=3$ is observed by a modulated technique (3).

This paper reports the dependence of the static dielectric permeability of ND$_3$ on gas pressure and the transient characteristics of the effect under saturation conditions of ND$_3$ $J=3,3$: $J=4,4$ lines by a pulse technique (4). It is shown that the relaxation time of the effect in this case is of the same order of magnitude as the rotational relaxation time in the gas.
C4. Double Resonance Study of Hyperfine Structure of the \( \text{CH}_3\text{I}^{127} \) Molecule

B.D. Osipov

On the base of double resonance phenomenon in molecular gas (1), a new high resolution method for radiofrequency range spectroscopy is developed. Pulse double resonance spectrometer of very high resolution is built. For decimetre wave range the doppler line-width \((\sim 2 \text{ kc})\) is nearly achieved. The spectrometer we used for study some transitions between n=5 levels of \( \text{CH}_3\text{I}^{127} \) molecule. The \( ^{127} \) quadrupole coupling dependence upon rotational states is investigated. A linear quadrupole effect for \( J=3, K=2 \) level is observed. Magnetic structure due protons is resolved. More precisely \( I,J \)-interaction constants (2) are determined, calculations of quadrupole energies being made up to 3-th order (3). Magnetic interaction of second order (Fermi type resonance for \( F_1=7/2 \) and \( 9/2; J=K=3 \) levels), is observed and the upper limit of hexadecapole interaction constant for \( ^{127} \) nucleus estimated.

C5. **Laser-Microwave Double Resonance and Double Photon Spectroscopy in Some Linear Molecules**

H. Jones and F. Kohler

From observation of Laser-microwave double resonance and double photon transitions involving the 9.4 μm, R(20) CO₂ laser line it has been shown that the R(2) transition of the \( \nu_1 \) infrared band of FCN lies 104 ± 15 MHz lower in frequency than this laser line i.e. \( \text{R}(2) = 1079.5871 \pm 0.0005 \text{ cm}^{-1} \). Refined measurements using a Lamb-dip technique will be discussed. Details of Laser-mm-wave double resonance experiments in D-C=C-F employing the 9.4 μm R(14) CO₂ laser line will be presented.

C6. **Laser-Infrared Double Resonance Experiments in Some Symmetric-Top Molecule**

F. Kohler and H. Jones

From the observation of double resonance effects on the microwave spectrum two coincidences between 9.4 μm CO₂ laser lines and infrared transitions of the \( \nu_6 \rightarrow (\nu_6 + \nu_1) \) band of CF₃Br have been determined: R(30) laser line coincident with \( \text{Q}_{R_2}(7) \), \( F = 17/2 \leftrightarrow 17/2 \) transition, R(28) laser line coincident with all four \( \Delta F=0 \) hyperfine components of the \( \text{Q}_{O_8}(13) \) transition. In both cases other infrared transitions lay within the tuning range of the laser. The frequencies of these two laser lines allowed calculations of the band center frequency \( \nu_0 = 1083.530 \pm 0.001 \text{ cm}^{-1} \) and \( \alpha_A = 11.93 \pm 0.3 \text{ MHz} \), for the \( \nu_6 \rightarrow (\nu_6 + \nu_1) \) band. \( \alpha_B \) constants were determined for the vibrational states \( \nu_6, (\nu_6+\nu_1), \nu_1 \) and \( \nu_3 \). In CF₃I seven coincidences have been found and identified. Details and discussion of the assignment will be given.
C7. **Isotope Detection by High Resolution Laser Spectroscopy**
W. Radloff

C8. **Lamb-Dip Spectroscopy with the**
E. Meisel

C9. **Diode Laser Spectra of Matrix Isolated Molecules**
M. Dubs

**Afternoon Session: Submillimeter and Microwave Spectroscopy (Chairman - K. Yamada)**

D1. **Submillimeter Microwave Spectroscopy: Theory and Experiment**
A.F. Krupnov and A.V. Burenin

A further development of the submillimeter microwave spectroscopy with a scanning RAD spectrometer [1,2] in NIRFI, Gorky, U.S.S.R. is described. Digital control of the submillimeter frequency from the frequency synthesizer with the possibility of automatic scanning is carried out.

A new method proposed earlier [3] of obtaining the sub-Doppler lines in gas spectrometers with the spectral line signal reception by a sample parameter change under the action of radiation is considered.

Feynman quantization [4] in a curved space for the system with a finite number of the degrees of freedom described by the classical Lagrangian \[ L = \frac{1}{2} G_{ij}(x) \dot{x}^i \dot{x}^j - V(x) \] is considered. On this base there is developed a new and the most general method of obtaining the sum rules for coefficients in the rotational-vibrational Hamiltonian
operator.

Submillimeter rotational spectrum of OCS is investigated. Frequencies of some hundreds of lines, belonging to 61 spectroscopically different species of OCS are measured with an accuracy up to $10^{-8}$. There are investigated the transitions of $16_012C_{32}S$ (93.7\%) in the states $(00^00), (011c,d_0), (10^00), (02^00), (022c,d_0), (111c,d_0), (031c,d_0), (0330), (20^00), (12^00), (12^2c,d_0), (04^00), (04^2c,d_0), (04^40),(00^0I); 16_012C_{34}S (4.16\%) in the states $(00^00), (011c,d_0), (10^00), (02^00), (022c,d_0), (111c,d_0), (031c,d_0), (0330); 16_013C_{32}S (1.05\%) and 16_012C_{33}S (0.75\%) in the states $(00^00), (011c,d_0), (10^00), (02^00), (022c,d_0); 18_012C_{32}S (0.192\%), 16_013C_{34}S (0.047\%), 17_012C_{32}S (0.035\%) and 16_012C_{36}S (0.013\%) in the states $(00^00), (011c,d_0); 18_012C_{34}S (0.0085\%) and 16_013C_{33}S (0.0084\%) in the state $(00^00)$. The results of the spectra treatment are given.

02. **Accurate Measurement of the Formic Acid Submillimeter Laser CW Lines**

J. Bellet, O. Dangoisse, A. Deldalle and JP Splingard

An optically pumped Formic Acid laser has been built. The CO$_2$ laser power is focused into the semi-confocal Fabry Perot cavity through the concave mirror coupling hole. The submillimeter radiation is coupled out through the same hole and directed to a point contact diode. The detection of frequency beats between the harmonics of a millimeter source and the laser lines makes possible accurate measurements of the submillimeter frequencies. Between 400 and 1000 GHz 9 CW lines have been observed and measured with an uncertainty of 0.5 to 1 MHz.

03. **High Resolution Rotational Spectra of Methyl Halides Using a Molecular Beam Spectrometer**

D. Boucher, J. Burie, J. Demaison, A. Dubrulle and G. Journal

A molecular beam - absorption spectrometer has been developed in our laboratory. High resolution is obtained by using a molecular beam which travels perpendicularly to the direction of propagation of radiation. This allows a reduction of the Doppler broadening by a factor of about 60. The smallest detectable power absorption is \( \frac{P}{P_{\text{max}}} \approx 10^{-5} \) (\( P \approx 10^{-7} \) W).

The hyperfine structure of the ground state rotational transitions of methyl halides is investigated between 70 GHz and 240 GHz with this spectrometer. Combining these measurements with the results of conventional spectroscopy allows us to determine with great accuracy the \( B \) rotational constant, the quadratic and sextic centrifugal distortion constants, the two spin - rotation constants of the
halogens and the quadrupole coupling constant. Moreover, it is found necessary to take into account the interaction of centrifugal distortion with quadrupole coupling.

**D4. Microwave Studies of Rotational Isomerism in Allylamine: The N-cis, Lone Electron Pair-Gauche Isomer**

I. Botskor and H.D. Rudolph

The fourth distinct rotational isomer of allylamine, the N-cis Lep-gauche form, has been identified. The isomer has two equivalent forms which are symmetrical with respect to the heavy atom plane. The possibility low barrier restricting torsion around the CN axis causes tunneling between the two minima, and the rotational spectrum is perturbed deviating from a ARR. The preliminary results allow the determination of the "average"\(^a\) rotational constants of the ground state from the measured a-type lines (which generally are not split): \(A = 16\ 170 \pm 120\); \(B = 5\ 796.0\) and \(C = 4\ 459.4\) (in MHz). The possibility of determining the "potential surface" which restricts torsion among the isomeric forms connected through two degrees of freedom will be discussed.

\(^a\) Though strictly, each well has a distinct set of rotational constants.

**D5. Vibration-Rotation Interaction in the Alkali Hydroxides**

E.P. Pearson and B.P. Winnewisser

Gas phase microwave and millimeter wave spectra and matrix isolation infrared spectra of the alkali hydroxides have now been studied with sufficient
completeness to suggest trends and general conclusions. Although this group of molecules displays a unique pattern of vibrational satellites in the pure rotational spectrum, it is concluded that the alkali hydroxides are reasonably well-behaved linear molecules.

Our analysis of the rotational spectrum of KOH and KOD yields a large, positive value of $x_{\ell \ell}$ for each species, indicating that the energy of successive $\ell$ sublevels of a given bending state increase with $\ell$. The similarity of the alkali hydroxides suggests that this is a general pattern for these molecules. Since just the opposite behaviour is expected for a quasilinear molecule, this result supports the model of a true linear species with a single minimum in the bending potential function for the alkali hydroxides.

We have examined the term $\alpha_2$ in the expansion of the rotational constant $B_\nu$ for KOH and KOD following the procedure employed by Lide and Matsumura in the analysis of CsOH and RbOH. The results for KOH confirm the observation that the unusual values for $\alpha_2$ are related to the combined effects of large amplitude motion and anharmonicity.

The alkali hydroxides may be viewed through analogy with the alkali fluorides. The alkali-hydroxyl bonds are very similar to the ionic alkali-fluorine bonds. Because the OH ion is highly polar, bending of the hydroxides tends to weaken the metal-hydroxyl bond. The mnemonic picture explaining the sign of $\alpha_2$ is then one of lengthening of the M-O bond with excitation of the bending mode.
D6. On the $\mathcal{L}$-defect

L. Nemes

The inertia defect $\Delta$ is a very useful measure of planarity and as such has found widespread application. Less exploited is the more elusive quantity, the so-called $\mathcal{L}$-defect, defined, e.g., by the following formula:

$$
\Delta \mathcal{L} = \mathcal{L}'_{\text{ccc}} \cdot (\mathcal{L}_2 - \mathcal{L}_1) / (A+B)
$$

In the present paper an attempt is made to test this planarity constraint on a number of simple planar molecules, thoroughly analysed in the literature, to see how and to what extent can it be utilized in planarity problems.

Some empirically obtained ideas will be presented concerning the yet unexamined vibrational sources of the $\mathcal{L}$-defect.


Thursday, September 9

Morning Parallel Session: Spherical Top Molecules

(Chairman - M.R. Aliev)

El. New Application of Group Theory in the Study of Spherical Top Molecules

J. Moret-Bailly

It will be shown that to write down the hamiltonian of a molecule which possesses symmetries, the introduction of group theory is needed. The computation are easier if all used quantities are tensors relative to the group because it allows an
easy construction of operators, wave functions and matrix elements by the use of coupling coefficients and Wigner-Eckart theorem.

In the case of spherical top molecules, the rotation group is, in first approximation, the symmetry group of the molecule. A great care must be taken to correlate the standard components of the spherical tensors to the cubic ones (in $T_d$ or $O_h$).

A new classical application of this method is the study of fundamental threefold degenerate bands of spherical top molecules (CH$_4$, CD$_4$, SiH$_4$, SF$_6$, ...) for which a precise use of group theory gives an almost diagonal hamiltonian matrix.

For a long time, the study of other bands was very difficult. New group techniques allow to compute more easily the vibration-rotation spectra of fundamental, overtone or combination bands in which appear twofold degenerate oscillators.

A precise group treatment of hyperfine structures simplifies and generalizes much the old theories.

E2. Recent Developments in High-Resolution Spectroscopy of Spherical-Top Molecules

K. Fox

Recent experimental measurements and theoretical developments for tetrahedral $XY_4$ and octahedral $XY_6$ molecules like CH$_4$ and SF$_6$, respectively, will be discussed. In particular, two general problems will be addressed: absolute intensities and corresponding transition moments, and isotope shifts.

The theoretical expression which relates the total strength of a vibration-rotation band of a tetrahedral or octahedral molecule to an individual
line strength and to an appropriate transition
electric-dipole moment has been re-examined.\textsuperscript{1}
Values of these transition moments have been in-
ferred from experimental band and line strengths.
For the few molecules where direct comparisons can
be made, the agreement between the values of tran-
sition moments obtained by the two methods is sa-
tisfactory. Remarkable symmetries in the results
are found for a variety of spherical-top molecules,
which suggests that transition electric-dipole mo-
ments may be transferable from molecule to molecule
for similar vibrations.

Isotope shifts for cleanly resolved absorption
lines of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in the 6000 cm\textsuperscript{-1} region
have recently been measured at high spectral reso-
lution.\textsuperscript{2} Such data make it possible to specify iso-
tope shifts, if not the isotope shift, definitively.
Shifts measured in this way are independent, to an
excellent approximation, of effects of temperature
and pressure. The theory of isotope shifts, especially
their dependence on rotational J- and fine-structure
quantum numbers, will be considered for spherical-top
molecules.

Related application such as the abundance of
$\text{CH}_4$, $\text{GeH}_4$, and $\text{SiH}_4$ in the atmosphere of Jupiter
will be discussed briefly.\textsuperscript{3}

\textsuperscript{1} K. Fox and W. B. Person, J. Chem. Phys., to be published 15 June (1976)
\textsuperscript{2} K. Fox, G. W. Halsey, and D. E. Jennings, in Proceedings of the Symposium on Molecular Structure and Spectro-
scopy, Ohio State University, 14-18 June (1976), Abstract RM9
\textsuperscript{3} K. Fox, in Molecular Spectroscopy: Modern Research, ed. K. Narahari Rao and C. W. Mathews (Academic, New
E3. Relations entre les différents schémas de couplage rotation-vibration dans l'étude des bandes des molécules du type XY\(_4\)

J.P. Champion

En première approximation, il est souvent possible d'étudier la structure fine des sous-niveaux vibrationnels des molécules toupie-sphérique, dans le groupe o (3), en introduisant un moment angulaire vibrationnel J coupé avec le moment angulaire rotationnel \( J \) du rotateur sphérique.

L'écriture de l'hamiltonien relatif à un sous-niveau vibrationnel donné, est conditionnée par les deux principales exigences suivantes:

I Construire des fonctions de base aussi proches que possible des fonctions propres.

II Considérer tous les opérateurs correspondant à toutes les interactions éventuelles.

Un schéma de couplage donné, ne satisfait qu'exceptionnellement ces deux exigences. Ainsi l'étude d'un sous-niveau vibrationel F\(_2\) avec J=1 (ex. 2Y\(_3\) de CH\(_4\) et CD\(_4\); Fox 1962) exclut à priori toute interaction avec d'autre sous-niveaux. Inversement, l'étude des sous-niveaux E et F\(_2\) à partir de J=2 peut conduire à des fonctions de base très éloignées des fonctions propres (ex. Y\(_2\) et Y\(_4\) de CH\(_4\); Berger 1975).

Dans ce travail, nous proposons un formalisme qui réalise simultanément les deux conditions précédentes:

a) En considérant des valeurs de \( J \) pouvant dépasser deux, il est possible d'étudier toutes les interactions possibles entre divers sous-niveaux.
b) Des relations théoriques simples entre les paramètres spectraux introduits dans les différents schémas de couplage permettent de passer aisément d'un couplage à un autre.

c) Enfin nous donnons l'expression des éléments matriciels de combinaisons d'opérateur couplés suivant un schéma A dans des fonctions de base couplées suivant un autre schéma B.


E4. Etude des bandes harmoniques $2\gamma_3$ et $2\gamma_4$ des molécules $XY_4$. Application à $2\gamma_4$ de CH$_4$ et $2\gamma_3$ de SiH$_4$.

G. Pierre

Les bandes harmoniques du type $2\gamma_3$ ou $2\gamma_4$ des molécules à symétrie tétraédrique ont été étudiées par FOX (1962); celui-ci a montré que suivant l'importance relative des termes de l'hamiltonien, on était conduit à considérer, pour le sous-niveau $\ell = 2$, les deux schémas de couplage suivants:

1. Les fonctions rovibrationnelles sont construites par couplage d'une fonction rotationnelle $\psi^J$ et d'une fonction vibrationnelle $\psi^2$, ces fonctions sont proches des fonctions propres de la bande $2\gamma_4$ de CH$_4$.

2. L'autre schéma correspond à un découplage des deux sous-niveaux E et F$_2$. Le sous-niveau F$_2$ est construit sur les fonctions de base ($\psi^J \times \psi^1$)$^R$. Les bandes correspondant à ce type de couplage ont
l'allure des fondamentales triplement dégénérées (2\(\nu_3\) de CH\(_4\)).

Dans le présent travail, nous montrons les résultats obtenus sur les bandes 2\(\nu_4\) de CH\(_4\) et 2\(\nu_3\) de SiH\(_4\) étudiées à l'aide du premier schéma de couplage. Celui-ci permet de construire simplement tous les opérateurs du sous-niveau \(l = 2\), mais dans des fonctions de base éloignées des fonctions propres, si les sous-niveaux vibrationnels E et F\(_2\) interagissent faiblement.

Ces deux bandes sont d'allure très différentes, en effet:

Les fonctions propres de la bande 2\(\nu_4\) de CH\(_4\) sont proches des fonctions \((\gamma^3 \times \gamma^2)^R\) et le niveau excité se décompose en cinq branches pour chaque valeur de J.

La bande 2\(\nu_3\) de SiH\(_4\) présente deux niveaux E et F\(_2\) nettement séparés pour les faibles valeurs de J, mais l'interaction devient importante quand J augmente (J > 10). Cette bande a donc été étudiée à l'aide du même schéma de couplage.

E5. Doubly Degenerate Vibrational Levels for Spherical Tops: A General Study Using the O(3) Tensor Formalism

F. Michelot

Although the vibrational wave functions for a doubly degenerate level of a spherical top molecule do not form the basis for an irreducible representation of the rotation group, we show that it is possible to define vibration-rotation basis functions as irreducible tensors of this group. We consider successively the fundamental \(\gamma_2(E)\) and the sublevel \(l = 2\) of the first overtone of a triply degenerate fundamental; from this we show that the method can
be easily generalized. Considering then vibration-rotation operators of the Hamiltonian we give the method allowing the computation of their matrix elements.

E6. The Microwave Distortion Moment Spectra of a Series of Tetrahedral Molecules

M.C.L. Gerry, I. Ozier, R.H. Kagann and R.M. Lees

A review will be presented of our recent results in the distortion moment spectroscopy of tetrahedral molecules in their ground vibronic states. The spectra have been obtained using a 1 kHz Stark modulated spectrometer modified to have a sensitivity of \( \sim 1 \times 10^{-11} \text{ cm}^{-1} \). Our early studies of \(^{12}\text{CH}_4\) have now been extended to \(^{13}\text{CH}_4\) and \(^{28}\text{SiH}_4\). For \(^{13}\text{CH}_4\) we have measured seven Q-branch transitions, from which we have derived values for the six distortion constants which characterize the tensor part of the rotational Hamiltonian up to the eighth degree in the angular momentum. The values are compared with their counterparts for \(^{12}\text{CH}_4\), and the differences are discussed in relation to theoretical predictions. For \(^{28}\text{SiH}_4\) we have measured twelve transitions and have derived values for the same tensor distortion constants. In addition, using the Stark effect, we have measured the distortion dipole moment of silane. Comparison will be made of our values with infrared and microwave-infrared double resonance measurements. The implications for future studies, including high resolution infrared, will be discussed.

Morning Parallel Session: Fourier Transform Spectroscopy
(Chairman - A. Mantz)

EE1. High Resolution Fourier Spectra of Five Isotopic Species of N₂O. Potential Energy Function
C. Amiot

The spectra of the following isotopic species of the nitrous oxide molecule: ¹⁴N₂¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁵N₂¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N₂¹⁸O have been systematically recorded with the third generation Fourier Transform Interferometer. The width of the unapodized apparatus function is equal to 2.5 \(10^{-3}\) cm\(^{-1}\) and it is possible to record more than 10 spectral elements in 10 hours. The spectral range 3000 cm\(^{-1}\) -6500 cm\(^{-1}\) was first studied; an automatic line assignment computer program was written (1). With the new instrumental improvements (2) the InSb spectral region from 1750 cm\(^{-1}\) to 3000 cm\(^{-1}\) was recorded. All our results permit us to assign 350 vibration-rotation bands composed of 35000 lines (1)(2)(3)(4).

We have calculated a set of coefficients for the development of the potential energy function to the fourth order of approximation (5)(6). The spectral positions of the vibrational levels below 6500 cm\(^{-1}\) have been obtained for the twelve stable isotopic species of the molecule. 50% of the levels positions are reproduced with an accuracy better than 20 \(10^{-3}\) cm\(^{-1}\); the maximum deviation is equal to 0.3 cm\(^{-1}\).

(5) C. Amiot, Ph.D. Thesis C.N.R.S. No.12433 Paris 1976
The Fourier-transform Spectrometer for 0.6-100
with Resolution 0.01-0.005 cm⁻¹

A.A. Balashov, V.S. Bukreev, V.A. Vagin, N.A.
Kultepin, J.N. Nesteruk, G.N. Zhizhin

The device intends for IR absorption and
radiation vibration-rotation band fine structure
studies of gases and for absorption and luminis­
cence band fine structure studies of crystals at
cryogenic temperature. The vacuum optical-mecha­
nical arrangement is realized to work in spectral
region of strong atmospheric absorption. Wave­
length range is 0.6-100μ, resolving power better
than 0.01 cm⁻¹ being reached all over the diapason.
The principal optical system of the device is the
Michelson interferometer. The mirrors of the inter­
erferometer are the cat's-eye retroreflectors. The
digital device of the interferogram is made on the
basis of the frequency stabilized He-Ne laser. For
accurate determining of the movable mirror position
the laser beam passes the same optical way as the
infrared radiation. The movable mirror passes an
advance choosed step the digital device put into
operation the measuring part of the interferometer.
The value of the signal is measured at a settled
point and is converted in a digital form to obtain
a paper tape output. The tape may be used to put
the digital values of the interferogram into a
digital computer. At the present time the device is
supplied with quartz beamsplitter and operates in
interval 0.6-3.5 μ. The beamsplitter maximum effici­
cy is at 1.7 μ. The detector is a cryogenic PbS
photoresistor. To measure the apparatus function
of the device the He-Ne laser radiation was recor­
ded. The absorption spectra of methane in 1.7
spectral region were also obtained.
Infrared Luminiscence Studies of Dy\textsuperscript{2+}-doped CaF\textsubscript{2} at Helium Temperature on High Resolution Fourier Spectrometer

A.A. Balashov, V.S. Bukreev, V.A. Vagin, E.B. Perminov, G.N. Zhizhin

The spectrum of luminiscence of Dy\textsuperscript{2+}-doped CaF\textsubscript{2} crystal has an anomalous narrow band (\(\nu = 4239.7 \text{ cm}^{-1}\)) for solids. There are an approximate data for its width only, but no reliable ones are present on the sharp of the band. We have measured the luminiscence spectrum of the crystal at 77\textdegree K and 4.2\textdegree K utilizing fourier-transform spectrometer UFTS-01. The excitation of the luminiscence have been realized with iodine cycle heating lamp (100 wt). Longwave range of the lamp was cut with cold mirror to reduce the scattered light. Data obtained gave possibility to measure with high reliability contour and bandwidth at 77\textdegree K (\(\Delta \nu = 0.2 \text{ cm}^{-1}\); apparatus function width \(\approx 0.07 \text{ cm}^{-1}\)). We could also estimate the width of the band in question was less than 0.04 \text{ cm}^{-1} at 4.2\textdegree K. It be possible to narrow the apparatus function after output data volume will be expanded. It 1 come true, when up-dating of output system will be done.

EE4. Scanning Fabry-Perot Interferometers SI-1 and SKI-1 for the 5 - 30\textmu m Region

V.A. Asoikin, V.G. Koloshnikov

The characteristics of the Fabry-Perot interferometer SI-1 and the compound Fabry-Perot interferometer SKI-1 are examined. The interferometers are operating in the 5 - 30\textmu m region. Mechanical scanning systems with directional friction driving are used in both interferometers. The instruments are equiped also with piezoscanning system. The
temperature dependence of the distance between mirrors is compensated. Combined mechanical and piezo-electrical adjusting systems are used. The diameters of mirrors are about 60 mm. The interferometer SI-1 makes it possible to achieve a sharpness coefficient in the 10-20 range and the compound interferometer SKI-1 in the 1 - 100 range. Resolution of both interferometers varies in the 5 - 2 \times 10^{-3} \text{ cm}^{-1} range because of the distance variation between mirrors. It is shown that both interferometers can be used in the IR as well as in the visible region of the spectrum.

EE5. Rotational Analysis of the 5350 \( \bar{R} \) Band of Iodine by Means of Fourier Transform Spectroscopy

S. Gerstenkorn and P. Luc

We have recorded the 5350 \( \bar{R} \) (0,30) band of iodine spectrum with high resolution by means of Fourier transform spectroscopy. The rotational lines in the P and R branches were measured to about \( J=160 \), with reference to uranium standards emitted by a hollow-cathode. The difference between two sets of measurements were less than 0.001 cm\(^{-1}\), and the standard deviation between the observed frequencies and those calculated with the spectroscopic constants \( B_v \), \( D_v \) and \( H_v \) is 0.0007 cm\(^{-1}\). The precision reached is an order of magnitude greater than in previously published data, and the constants \( H_v \) of the iodine absorption spectrum have been determined for the first time. This work shows that the use of Fourier transform spectroscopy is particularly advisable for molecular absorption studies in the visible region, where, although the multiplex gain is lost, the throughput gain remains and this enables the performance to approach that achieved in the infrared.
EE6. Generalizing of instrument profile in Fourier spectroscopy and application on high resolution
G. Fanske

A well interpretable form of a generalized instrument profile has been found. It may be applied on some problems in Fourier spectroscopy. The most important application seems to be in high resolution spectroscopy, particularly for vibration-rotation structure of bands in the mid-IR, rotation spectra and profiles of lines, too. The experimental expense and data files will be reduced considerably in these cases.

Indeed, an additional software package will be need for deconvolution of the more complicated instrument profile. Two consequences of the new method are a filter effect in resolution region and an improvement in signal to noise relation for high resolution.

Afternoon Session: Theory and Analysis of the High Resolution Infrared Spectra (Chairman - J. Bordé)

Fl. Six Years to Know Something About Six Atoms Molecules. Study of Six Isotopic Species of Ethylene
D. Van Lerberghe

F2. Forbidden Rotational Spectra of Nonplanar Molecules in Degenerate Electronic States
M.R. Aliev

The possibility of electric dipole moments in orbitally degenerate E states of D$_{3h}$ molecules in weak Jahn-Teller (JT) limit was first considered by
Child and Longuet-Higgins (1). Recently Bersuker et al. (2) discussed static JT limit for Td molecules. We have considered this problem in a general way. Starting from weak or strong coupling cases we perform contact transformations on vibronic Hamiltonian similar to that used in vibration-rotation problem. However, zero-order approximation in strong vibronic case is different. Coherent states are used as a natural bases in the strong JT limit. Explicit expressions for the vibronic dipole moments are derived for Exe and Etx coupling cases including several modes of vibrations. A rough estimate of the JT dipole is given for the ground vibronic state of CH₄. Some aspects of vibrational transitions in degenerate electronic states are also discussed.


**F3. Spectres haute resolution infrarouge et micrownde de la bande \( \nu_2 \) de l'ozone**

A. Barbe, C. Secroun, P. Jouve, B. Duterage,
N. Monnanteuil, J.C. Depennet, J. Bellet et P. Pinson

La bande d'absorption à 0.6 μ de l'ozone présente un très haut intérêt du fait de sa situation dans la fenêtre atmosphérique à 10 μ et de sa très forte absorption. Nous l'avons enregistrée entre 1000 cm⁻¹ et 1070 cm⁻¹ avec une résolution de 0.012 cm⁻¹; plus de 1000 transitions de la bande \( \nu_2 \) ont été pointées.

D'autre part, 40 transitions microwndes des états excités \( \nu_1 \) et \( \nu_3 = 1 \) ont été mesurées.
entre 15 et 80 GHz.

Les données ont été traitées à l'aide d'un Hamiltonian de type Watson. Les deux niveaux \( v_1 \) et \( v_3 = 1 \) ont été calculés simultanément en faisant intervenir des termes de couplage tenant compte de la résonance de Coriolis. Les résultats ont permis d'interpréter toutes les transitions microondes observées correspondant à \( J \leq 30 \) et \( K \leq 5 \) et en infrarouge à \( J \leq 55 \), \( K \leq 18 \).

Nous donnons sous forme de tableaux les interprétations, les fréquences observées avec une précision de \( 10^{-3} \) cm\(^{-1} \) et les fréquences et intensités calculées avec les coefficients de mixage mettant en évidence plusieurs résonances localisées.

F4. Accidental and Essential Resonances in the Spectrum of CH\(_3\)F Near 2500 cm\(^{-1}\)

M. Betrencourt and M. Morillon-Chapey

The analysis of Fourier Transform spectrum (limit of resolution 0.007 cm\(^{-1}\)) of combination bands \( v_2 + v_3 \) (\( A_1 \) species) and \( v_3 + v_5 \) (\( E \) species) has allowed the study of X-Y Coriolis resonance between the states \( v_2 = 1 \) and \( v_5 = 1 \). The vibrational levels \( v_2 \) = \( v_3 \) = 1 and \( v_3 = v_5 = 1 \) are 15 cm\(^{-1}\) apart and the interaction is very strong. The combination of the Coriolis resonance and the essential interaction of 1-type (2,2) in \( v_3 + v_5 \) gives rise to a "giant" 1-type doubling: for \( J = 25 \) the shift between the levels is about 17 cm\(^{-1}\).

A second essential interaction exists in the perpendicular band: the rotational 1-type (2,-1) resonance, the effect of which is small, but the addition of this interaction and the Coriolis one causes chain of resonances between rovibrational
levels and gives rise to a doubling of $^{3}P_{3}(J)$
transition in the perpendicular band.

Molecular parameters and coupling constants
have been derived:

$$\begin{align*}
\nu_2^+ & \nu_3 & \nu_3^+ & \nu_5 \\
\nu_0 & 2499.791 & 2513.798 \\
\alpha^A & -0.0136 & 0.0551 \\
\alpha^B & 0.01496 & 0.00910 \\
\Lambda^5 & -1.2550 \\
\Omega_B \zeta^x_{2,5} & = 0.5010
\end{align*}$$

All values in cm$^{-1}$

F5. Centrifugal Distortion Coefficients of Ozone $^{16}O_3$

M.Y. Chan and M. Parker

Theoretical expressions for the sextic centrifugal distortion constants of non-linear triatomic molecules, as given by Sumberg and Parker$^1$, have been evaluated for the ozone molecule. For our calculation we used the harmonic frequencies and cubic anharmonic potential constants as determined by Barbe, Secroun and Jouve$^2$. The calculated distortion constants were compared to a complete set of measured distortion constants recently determined by Maki$^3$ from high-resolution spectra obtained at the National Bureau of Standards (USA). Our comparison takes into account the procedure of reducing the general triatomic vibration-rotation Hamiltonian to the particular Watson-type Hamiltonian$^4$ used by Maki. Even though the measured constants range over four orders of magnitude, we find that the theory reproduces the relative magnitudes and the algebraic signs of the constants quite well. Absolute quantitative agree-
ment is better than order-of-magnitude, with a consistent tendency for the calculated values to run larger than the measured values.

1. D.A. Sumberg and P.M. Parker, J. Mol. Spectrosc. 48, 459 (1973)

F6. A Model for the Interpretation of UV, IR and Microwave Spectra of the OH Radical

J.L. Destombes, Mme C. Marliere and G. Journal

A fitting procedure was carried out to give a theoretical interpretation of the whole observed spectrum (MW, IR, and UV). As in the first approximation (i.e. "unique perturber approximation") only the $A^2 \Sigma^+$ state interacts with the $x^2 \Pi$ state, the calculated transition frequencies are obtained by direct diagonalization of the molecular hamiltonian in the $A^2 \Sigma^+ \times x^2 \Pi$ subspace. The effects of the all other excited $2 \Sigma$ states and vibrational states can be taken into account by means of perturbation theory with third order perturbation terms.

In the present investigation the following experimental data have been used:

- 0,0 band of the $A^2 \Sigma^+ \rightarrow x^2 \Pi$ transition (190 lines $J \leq 51/2$)
- Rotational spectrum of the $x^2 \Pi$, $v = 0$ state (48 lines $J \leq 51/2$)
- Hyperfine structure of the $A$ doubling spectrum in $2 \Pi 3/2$ and $2 \Pi 1/2$, $v = 0$ states (52 lines $J \leq 15/2$)
It is then possible to fit the experimental spectra with RMS errors of 16 kHz for MW, 0.005 cm\(^{-1}\) for IR and 0.026 cm\(^{-1}\).

Friday, September 10

Morning Session: Molecules

(Chairman - G. Strey)

G1. The Vibration-Rotation Interactions Among the Three Bending Modes of HNCO and HNCS Studied by Microwave and Millimeterwave Spectra

K. Yamada, M. Winnewisser, L.B. Szalanski and M.C.L. Gerry

The isocyanic acid HNCO and isothiocyanic acid HNCS are known to be quasilinear molecules which exhibit anomalous rotational and vibrational spectra. The quasilinearity of these molecules is believed to originate from the large amplitude HNC bending motion. Therefore precise information about the vibrational excited states of this bending mode is necessary in order to enhance the understanding of the dynamics of these molecules.

In the present study, the microwave and millimeter wave spectra of NHCO and HNCS have been measured in their three bending excited states: \(\nu_a, \nu_b, \text{ and } \nu_c\), where \(\nu_a, \nu_b, \text{ and } \nu_c\) indicate the lowest, medium and highest bending mode, respectively.

For HNCO, a number of \(a\)-type rotational transitions, \(\Delta K_a = 0\), were assigned, up to \(J = 10\leftrightarrow 9\) (220 GHz), to the \(K_a = 0, 1, 2\), and 3 branches of these three vibrational states, except the \(K_a = 1\) lines for \(\nu_c\), which have not yet
been identified. The spectrum indicates the
presence of a large a-type Coriolis resonance
and many local accidental resonances. Some of
these resonances yield some information for
assigning the out-of-plane bending mode by using
the selection rules of the rovibrational inter­
actions.

For HNCS, in addition to the a-type $K_a=0$
and 1 transitions from excited vibrational states,
$\nu_a$, $\nu_b$, and $\nu_c$, we have assigned the b-type
transitions, $K_a = 0\leftrightarrow 1$ arising from the $\nu_a$
vibrational state.

Examples of the vibrational assignment dedu­
ced from the results of the rovibrational analysis
of the studied interactions will be presented.

G2. **Millimeter Wave Spectrum of Hydrogen Isocyanide, HNC, and its Astrophysical Implications**

R.A. Creswell, E.F. Pearson, M. Winnewisser and
G. Winnewisser

Many compounds of general formula R-N-C have
been well characterized and studied spectroscopi­
cally. However, the parent molecule HNC has pro­
ved to be somewhat elusive. Evidence for its
existence was obtained in 1963 by Milligan and Ja­
cox from matrix isolation infrared absorption
studies. Recently Arrington and Ogryzlo observed
a resolvable I.R. emission feature at 2.74 microns
in reactions of active nitrogen with HCN, C$_2$H$_2$
which they assigned to HNC. An unidentified inter­
stellar emission line at 90.7 GHz reported by
Snyder and Buhl in 1971 was postulated to be due
to the $J = 1 - 0$ transition of HNC. Our laboratory
measurements on HNC unequivocally confirm this
assignment.
We have employed a harmonic generator millimeter wave spectrometer with a dedicated computer signal processing system to observe this new molecular species. The absorption cell was 2.5 m long, 10 cm diameter glass pipe attached to a fast pumping system. Production of HNC was obtained by mixing discharged nitrogen with CH₃I at the inlet port to the cell.

We have studied several isotopic species of HNC from which we derive the following structure: \( r(\text{H-N}) = 0.987(3) \) Å and \( r(\text{N-C}) = 1.171(4) \) Å. The interstellar emission features of the isoelectronic molecules HNC, HCN and HCO⁺ as observed in the various molecular clouds will be discussed.

G3. "Inverse" Eigenvalue Problem for the One-Dimensional Schrödinger Equation With a Singularity, Application to Quasilinear Molecules HCNO and DCNO
I. Boháček, V. Danielis, O. Papoušek and V. Špirko

Numerical methods of the integration of the one-dimensional Schrödinger equation with a singularity in the potential energy term are discussed. Results are used in a least squares determination of the potential function parameters from the experimental bending-rotation spectra of the quasilinear molecules HCNO and DCNO.

G4. The Pure Rotational Spectrum of \( ^{18}\text{H}_2\text{O} \) and \( ^{17}\text{H}_2\text{O} \) in the Far Infrared
F. Winther

Between 530 and 50 cm⁻¹, 125 rotational lines of \( ^{18}\text{H}_2\text{O} \) and 50 lines of \( ^{17}\text{H}_2\text{O} \) have been detected in
the spectrum of natural water. Several spectra at different pressures up to 18 Torr were run with a 3 m cell at room temperature. The instrument used was a Beckman/RIIC FS-720 interferometer with a maximum resolution of 0.08 cm\(^{-1}\) over the whole range.

To obtain a set of energy levels for the ground state of \(H_2^{18}O\), calculated values of the \(1^{0}l\), \(2^{10}\), \(2^{20}\), and \(3^{13}\) states plus the combination differences \(7^{43}1^{-41}\) and \(10^{110}-8^{10}\) (from 1)) were used. For the \(H_2^{17}O\) ground state, several combination differences from 1), 2), and 3) had to be used because of the lower number of lines observed.

The results are in good agreement with the levels of Toth and Margolis 4) \((H_2^{18}O)\) and De Lucia et al. 5) \((H_2^{17}O)\) but extend to higher energies. Some observed lines are given below:

<table>
<thead>
<tr>
<th>(J'K_aK_c)</th>
<th>(J''K_aK_c)</th>
<th>(H_2^{18}O) obs. cm(^{-1})</th>
<th>(H_2^{17}O) obs. cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 3 4</td>
<td>5 2 3</td>
<td>200.210</td>
<td>201.276</td>
</tr>
<tr>
<td>4 4 1</td>
<td>3 3 0</td>
<td>200.337</td>
<td>201.443</td>
</tr>
<tr>
<td>4 4 0</td>
<td>3 3 1</td>
<td>200.578</td>
<td>201.683</td>
</tr>
<tr>
<td>5 3 2</td>
<td>4 2 3</td>
<td>207.113</td>
<td>207.743</td>
</tr>
<tr>
<td>7 3 5</td>
<td>6 2 4</td>
<td>211.519</td>
<td></td>
</tr>
<tr>
<td>11 0 11</td>
<td>10 1 10</td>
<td>211.668</td>
<td>212.108</td>
</tr>
<tr>
<td>10 1 9</td>
<td>9 2 8</td>
<td>211.813</td>
<td></td>
</tr>
</tbody>
</table>

G. Analysis of the "K-structure" of the Torsional Fundamental of Acetaldehyde

H. Hollenstein and F. Hinther

The far-infrared spectrum of acetaldehyde, measured with a Beckman R11372C interferometer (resolution 0.3 cm$^{-1}$) shows a prominent doublet near 147 cm$^{-1}$ accompanied by extended subband structures on both high and low frequency sides. The present investigation is concerned with the analysis of these subband patterns. A model based mainly on the conventional semi-rigid approach was developed, which allowed a unique identification of approximately 30 subbands with distinct 0-subbranches. Four molecular parameters were adjusted by a least squares fit. The frequencies of the pure torsional transitions 0,0A$\leftrightarrow$1,0A and 0,0E$\leftrightarrow$1,0E were found to be 143.88 and 142.64 cm$^{-1}$, respectively. The results will be compared with parameters from microwave spectroscopy.

G6. Rotational Analysis of the Far-Infrared Spectrum of cis-HNSO

J. Hink, K. Göl and L. Henne

Far-infrared spectra of cis-HNSO has been recorded in the range 10-60 cm$^{-1}$ using a Beckman FS-720 interferometer. A double-path absorption cell has been adopted to the interferometer operating at a path length 0.5 m. The resolution achieved was about 0.1 cm$^{-1}$.

Using Kirchhoff's 1 microwave data and the centrifugal distortion coefficients of SO$_2$, the structure of the far-infrared spectrum was predicted. On this basis the rotational assignment was
performed and a bootstrap procedure was applied to reduce rotational data to molecular constants. Johns and Olson's least-square procedure was used in these calculations.


G7. Rotational-Vibrational Infrared and Raman Spectra of Dimethylmercury

J. Mink, G. Kemény and R. Kremó

The infrared vapour phase spectrum of (CH₃)₂Hg and (CD₃)₂Hg was recorded with medium resolution, the rotational structure of v₇ and v₉ was obtained using a DIGILAB FTS-14 spectrometer.

Using Rao, Stoicheff and Turner's rotational constants obtained from the pure rotational Raman spectra of these samples a rotational analysis was performed for v₇ and v₉ bands and the Coriolis constants (ξ₇ and ξ₉) were obtained. The force field calculation was revised on the basis of infrared and Raman vapour phase vibrational frequencies.

**Afternoon Session: Potential Functions of Polyatomic Molecules, Miscellaneous (Chairman - J. Morst-Dailly)**


N. Hussan and I. Jobard

By drawing constant energy contours diagrams we examine the behaviour of the force field of the carbon dioxide molecule recently determined by A. Chedin and Z. Cihla using the available vibrational data. Contour maps are also drawn for a potential energy function of CO₂ iterated with pure vibrational data. Several series expansions of the potential energy function of CO₂ have been determined up to different orders of approximation. Comparisons are made and the improvement brought by the introduction of rotational data is shown. In each case, the potential expansion is considered in terms of \( \sum_{e} \) or \( \sum_{r} \).


V. Špirko

The inaccuracy of the standard polynomial approximation of the potential energy function, \( V \), and of the elements of the inverse moment of inertia tensor, \( C^{-1} \), is discussed. An algorithm allowing the "exact" determination of rotational energy levels of any molecule is proposed, and its applicability is demonstrated by numerical calculations.
H3. Calculation of Rotational Frequencies of Small Linear Radicals From Ab Initio CI-data: HCN (for comparison); HCN, HCC⁺, HCC⁺, HNN⁺

P. Henning, W.P. Kraemer, G.H. Diercksen

Within the last years more than 40 different molecules in interstellar gas clouds have been identified from their radiofrequency spectra. Some further lines were tentatively assigned to rotational transitions of radicals which, under laboratory conditions, are too unstable to be measured at that time. The present work allows a positive identification of some astronomically observed lines and predicts other lines for the different isotopic species of the molecules above, which makes possible an economic search for those lines both in radioastronomy and laboratory. Extensive ab initio SCF- and CI-calculations using an "improved double-zeta plus polarisation" basis set - (1lslp/5s4pld) on C, N, O and (6slp/3slp) on H - have been carried out to determine the potential energy for 28 nuclear configurations of each molecule. From those points on the potential hypersurface the equilibrium structure and the force constants up to fourth order have been computed iteratively in a combined Newton-Raphson scheme together with a linear least squares fit.

From the \( r_e \) values one gets immediately \( B_e \) values for all isotopic species of the molecule. Using usual formula obtained by a conventional perturbation calculation up to second order one find spectroscopic constants \( \omega_i, x_{ij}, \alpha_i \) depending on the force constants.

Comparison with experimental data for HCN shows that the lower rotational frequencies are exact within about 0.2 \%, while the vibrational
frequencies have a systematic deviation of about 10%.

Several of the predicted rotational lines for different isotopic species of the above molecules have been found recently in interstellar space and in laboratory within the error limits of our calculations.

H4. The Many-Body Diagrammatic Perturbation Theory of Rotation-Vibration Spectra

V. Kvasnička

A many-body diagrammatic perturbation theory of rotation-vibration spectra (1,2) is presented. This approach is based on the following two techniques:

(i) The second-quantization formalism, where a rotating-vibrating molecule can be formally treated as a system of interacting "particles" called vibrons (an analogy of phonons in solid-state physics), obeying the Bose-Einstein statistics.

(ii) The many-body diagrammatic theory of model hamiltonians (3,4).

The rotation-vibration excitation energies are then determined as the eigenvalues of some finite-dimensional model eigenproblem. An illustrative example of a diatomic molecule is presented.

1. V. Kvasnička, Mol.Phys., sent for publication, April 1976
2. V. Kvasnička, in Advances of Chemical Physics, invited review article, March 1976
Broadening of Vibrational Lines in Liquids Caused by Short Range Interactions

K. Sarka and S.A. Kirillov

Contribution of short range repulsion interactions to broadening of vibrational lines of tetrahedral molecules in liquids is studied. The short range intermolecular energy is described as sum of pairwise interatomic energies of Born-Mayer type: $E(r) = V_{\exp(-\alpha r)}$, where $r$ is distance between interacting atoms. The part of intermolecular energy which depends on normal coordinate of studied molecule $Q_j$ is separated and matrix element of transition $v_j \rightarrow v_j - 1$ is calculated. The probability of transition $v_j \rightarrow v_j - 1$ per unit time is calculated using the perturbation formula. Results are applied to $A_1$ and $E$ vibrations of $XY_4$ tetrahedral molecule and very simple expressions for contribution of short-range forces to line-broadening of these vibrations are obtained, e.g. for $E$ vibration this contribution $\delta \omega$ can be calculated from the following expression:

$$\delta \omega = \text{const. } \varphi(\omega) \int_0^\infty \exp(-2\alpha r)(\alpha + 1/r)^2 \Phi(r) dr$$

where $\varphi(\omega)$ is normalized spectral density, which is also discussed and $\Phi(r)$ is molecular radial distribution function. Calculated results are compared with experimental data on $CCl_4$ vibrations.
Higher-Order Vibrational-Rotational Perturbation Theory

J.K.G. Watson

Investigation of Isotopic Dependence of Parameters in Polyatomic Molecules

A.D. Bykov, Yu.S. Makushkin and O.N. Ulenikov

A method is developed allowing to make simultaneous transformations of the quantum-chemical Hamiltonians of various isotopic modifications of polyatomic molecule into internal coordinates.

The obtained Hamiltonians are used to determine the relations among different molecular and spectroscopic constants of isotopic modifications. Equations for calculating harmonic frequencies, force constants, Coriolis constants, matrix elements of the inverse moments of inertia etc. for arbitrary isotopic substitutions in polyatomic molecules are obtained. Application of the obtained results to determine the relations among spectroscopic anharmonic, vibration-rotation constants, \( \mathcal{C} \) - and other constants is shown on the basis of symmetric isotopic substitutions in \( X_2Y \) molecules (both linear and nonlinear).

Effective Hamiltonians Having Applications in the Theory of Vibrational-Rotational Spectra

Yu.S. Makushkin and Vl.G. Tyuterev

A common practice in the molecular spectroscopy is to introduce effective Hamiltonians \( \mathcal{H}^{\text{eff}} \) (instead of the full electronic-nuclear energy operator) which describe a part of the spectrum we are interested in (for instance \( \mathcal{H}^{\text{vib.-rot.}}, \mathcal{H}^{(\text{e})\text{rot.}}, \ldots \)). Various
methods exist for deriving $H^{\text{eff}}$ using different mathematical technique. Various formulations lead in general to different $H^{\text{eff}}$ and prove to be convenient for solving different problems.

The formulation of Generalized Contact Transformations will be presented from which a number of other methods mentioned above may be obtained as partial cases (1). The method to be reported has been applied for derivation of centrifugal distortional Hamiltonian both for degenerate and nondegenerate vibrational states. The derivation of $H_{\text{rot}}$ is shown to be equivalent to the transformation to new variables in $H_{\text{vib.-rot}}$, so that $H_{\text{vib.-rot}}$ takes the form of $H_{\text{rot}}$. The problem of ambiguity of constants will be discussed. A special attention has been paid to accidental resonance for the treatment of which the Fock representation proves to have some advantages (2).

Application also has been made for derivation of effective inversional Hamiltonian $H_{\text{vib, J,k}}^{\text{inv}}$ for NH$_3$.

In turn method may be employed for partial or full diagonalization of $H^{\text{eff}}$. The treatment of centrifugal distortional effects for trigonally and tetragonally symmetric molecules (diagonalization of $H_{\text{rot}}$) and automatic analytical calculations of vib. rot. energies for diatomics (diagonalization of $H_{\text{vib.-rot}}$) will be presented.

1. Vl.G. Tyuterev, Effective Hamiltonians, in the book "Intramolecular interactions and infrared spectra of atmospheric gases", Tomsk, 1975, p. 3-46
Stark Spectroscopy of the \( \nu_4 \) Vibration-Rotation Band of Methyl Isocyanide Using CO\(_2\) and N\(_2\)O Lasers

M. Römhold

The fundamental \( \nu_4 \) vibration-rotation band of methyl isocyanide has been studied by using CO\(_2\) and N\(_2\)O lasers and electric field tuning of molecular absorption lines. Many resonances corresponding to P, Q or R transitions with low J and K values have been observed. Accurate values of rotational constants and dipole moments of upper and lower state are obtained.

Absorption Spectra and Energy Level Scheme of Uranium (+3)

J. Drozdzynski

Rovibrational Analysis of the Principal Isotopic Species of Carbonyl Sulphide

A. Fayt and R. Vandenhaute

The previous rovibrational analysis of OCS were based only on the vibrational energies and the rotational constants. We propose a least-squares analysis on all the microwave and infrared measurements: we select experimental frequencies for a few J values and we use them directly as experimental data. This analysis has been applied to the principal isotopic species of Carbonyl Sulphide (\( 16_0\)\( 12\)\( C^{32}S \), \( 18_0\)\( 12\)\( C^{32}S \) and \( 16_0\)\( 13\)\( C^{32}S \)), and yields more precise parameters than previously. Finally we propose a molecular geometry for OCS.

Frequency Measurements of Hyper-fine Structure Lines for Inversion Transition of the Ammonia Molecule for the States \( J=K=2-8 \)

J. Galica, S. Gierszal, E. Miś-Kuźmińska, W. Prussak