

A QUARTIC HAMILTONIAN APPLIED TO METHANE

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Electronic structure calculations can provide very accurate pictures of the potential energy surfaces of polyatomic systems. Thus, the possibility of combining the results of the theoretical methods with the ever increasing available spectroscopic data becomes more and more appealing. This represents both a way of obtaining improved surfaces and of checking the models adopted in the interpretation of the spectra.

As a development of a recent treatment by Halonen ¹, we have used a quartic Hamiltonian expressed in internal curvilinear coordinates, with a 9-dimensional basis of harmonic oscillator wavefunctions in symmetry coordinates, to fit the overtone vibrational spectra of all T_d symmetry isotopomers of methane simultaneously.

Near-resonant anharmonic interactions are treated at the first order, while weaker interactions are handled as second order perturbations. A set of optimized Born-Oppenheimer force constants is obtained, which reproduces the experimental data up to 9500 cm^{-1} with an R.M.S of 1.7 cm^{-1} and shows an excellent agreement with the results of *ab-initio* calculations ². A very efficient, seminumerical software package has been developed to treat the anharmonic problem of most kinds of non-linear molecules.

1. L. Halonen, J. Chem. Phys. 106 (1997) 831.

2. L. Lee, J. M. L. Martin and P. R. Taylor, J. Chem. Phys. 102 (1995) 254.

THREE BEAUTIFUL EXAMPLES OF FERMI RESONANCE: THE ν_9 , ν_{11} and ν_{12} BAND SYSTEMS of N_2O_4

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The spectra of 3 fundamental bands of N_2O_4 have been obtained using a supersonic slit jet system coupled to a Fourier transform spectrometer. Beam spectra of two of these bands have been previously investigated, both with an FT spectrometer^{a b} as well as with a diode laser spectrometer beam system^c. Substantial improvements have been made in the Brussels FT jet system since the previous study. This paper will illustrate some of the advantages of an FT system. The diode laser spectra obtained previously are of higher resolution than those from this study, but the diode laser spectra contained many gaps where either the diode did not operate or where atmospheric water vapor lines obscured portions of the band spectra. In addition, the intensities from the diode laser system were only qualitatively correct whereas with the FT system the entire band could be recorded and the intensities are far more quantitative. To obtain these spectra, a mixture of 40 % NO_2/N_2O_4 and 60 % argon was expanded through a 16 cm \times 15 μ m slit into a vacuum chamber evacuated by a 4000 m³/h Roots pumping system. The backing and background pressures were 800 and 0.1 hPa, respectively. Forty scans were averaged at an instrumental resolution of 0.005 cm⁻¹. Analysis of the spectra indicates that the beam temperature is close to 30 K.

The lowest frequency region, studied here for the first time, contains 2 *a*-type bands, nearly equal in intensity, centered at 747.85 and 755.37 cm⁻¹, which are due to a Fermi dyad arising from a resonance of the ν_{12} state with $\nu_6 + \nu_{10}$. The second region also contains 2 *a*-type bands, centered at 1261.07 and 1265.01 cm⁻¹, the higher frequency band having one third of the intensity of the lower. The stronger band is due to the fundamental, ν_{11} , and the weaker band is a combination band, $\nu_7 + \nu_8 + 2\nu_4$. In the previous studies, it was noted that ν_{11} was perturbed, but the "dark" state was not observed. In the ν_9 region around 5.7 μ m, two *b*-type bands have been observed, the fundamental centered at 1756.76 cm⁻¹ and a weaker band centered around 1733.9 cm⁻¹ due to $\nu_6 + \nu_{11}$. The intensity of the combination bands is almost entirely due to resonance mixing.

The transitions of all six bands observed have been fit to within the experimental uncertainty, and the Fermi interaction constants have been obtained.

^aF. Mélen, M. Carleer, and M. Herman, *Chem. Phys. Lett.* **199**, 124 (1992).

^bD. Luckhaus and M. Quack, *Chem. Phys. Lett.* **199**, 293 (1992).

^cJ. L. Domenech, A. M. Andrews, S.P. Belov, G. T. Fraser, and W. J. Lafferty, *J. Chem. Phys.* **100**, 6993 (1994).

A MODIFIED VIBRON MODEL OF MOLECULAR VIBRATIONS :
APPLICATION TO TRIATOMIC MOLECULES

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One of the most innovative advances in the theory of molecular vibrations of the past 15 years - the "vibron" model developed by Iachello *et al.*¹ - has not yet enjoyed broad popularity among spectroscopists apparently since, in its basic form, it does not provide sufficient precision for fitting observed energy levels. Improved precision has been attained by these authors by inclusion of higher order operators which, however, complicate the appealing simplicity of the basic model. Two different simple modifications of the vibron energy expressions are proposed which yield a substantial improvement of the precision while retaining the simplicity of the basic model. Application to a number of triatomic molecules will be reported.

¹ F. Iachello, *Chem.Phys.Lett.* 78, 581 (1981) ; F. Iachello and R. D. Levine, "Algebraic Theory of Molecules", Oxford University Press 1995.

SUBMILLIMETER-WAVE SPECTRAL LINES OF NEGATIVE IONS IDENTIFIED BY THEIR DOPPLER SHIFT

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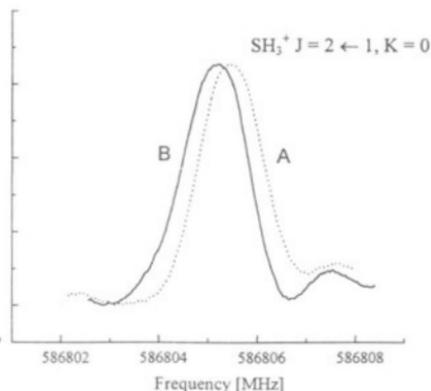
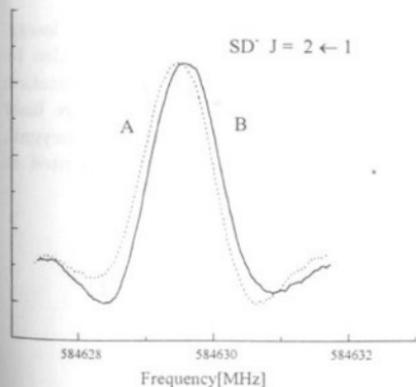
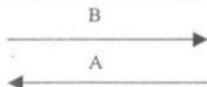
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For the first time submillimeter-wave transitions of an anion have been firmly identified. We observed one transition of SH^- ($J = 1 \leftarrow 0$, 564421.869 MHz) and two of SD^- ($J = 1 \leftarrow 0$, 292359.129 MHz; $J = 2 \leftarrow 1$, 584629.519 MHz) created in the positive column of an electric discharge set up in a mixture of H_2S and argon. By studying the Doppler shift brought about by the motion of charged species in the electric field of the discharge we were able to distinguish between positively and negatively charged ions and neutrals. We have hence shown that velocity modulation techniques commonly used for infrared spectroscopy could also be successfully applied for the study of ions in the submillimeter-wave region.

Direction of the beam



CAVITY ENHANCED POLARIZATION AND ABSORPTION SPECTROSCOPY

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As cavity ring down (CRD) spectroscopy has sufficiently matured by now, the implementation of this absorption detection method in a variety of existing spectroscopic techniques is to be expected.

Polarization dependent cavity ring down (PD-CRD) spectroscopy combines the advantages of magnetic rotation spectroscopy (MRS) and CRD spectroscopy. In this technique the *rate of polarization rotation* of the light is measured rather than the rate of absorption in CRD spectroscopy or the total polarization rotation in MRS. We demonstrated the PD-CRD technique in a study of the magneto-optical effects in molecular oxygen. In a magnetic field perpendicular to the axis of the ring down cavity (Voigt configuration), the absorption spectrum due to magnetic dichroism of the $b^1\Sigma_g^+(v=2) \leftarrow X^3\Sigma_g^-(v=0)$ transition of O_2 was measured. In a magnetic field parallel to the cavity axis (Faraday configuration), the dispersion spectrum due to magnetic circular birefringence was measured.

Polarized light can also be used in "conventional" CRD spectroscopy. The spectra of the $b^1\Sigma_g^+(v=0) \leftarrow X^3\Sigma_g^-(v=0)$ transition of O_2 were recorded by CRD spectroscopy with linearly and circularly polarized light in magnetic fields up to 20 Tesla. It was shown that the polarization state of the light is not (or hardly) affected by the mirrors of the cavity. Therefore, circularly polarized light can be used in the CRD setup to simplify the measured spectra.

The abovementioned CRD experiments have been performed with pulsed lasers. The high finesse optical stable cavity, which is used in these experiments, can also be used as a "multi-pass" absorption cell for narrow band cw absorption and polarization spectroscopy. Two diode lasers in different wavelength regions and a cw ring dye laser were used to show the applicability of the technique for sensitive detection of oxygen, water, and ammonia. This "cavity enhancement scheme" can also be implemented in magnetic rotation spectroscopy in order to measure the polarization rotation.

ROTATIONAL SPECTRA AND INTERNAL ROTATION OF DIENE-IRONTRICARBONYLS

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Carbonyls of transition metals play an important role as catalysts in many industrial processes. Diene-irontricarbonyls are used in many syntheses as a protecting or a stereo-directing group and thus the $\text{Fe}(\text{CO})_3$ -part can be considered as a functional group. Based on the structure of butadiene-1,3-irontricarbonyl, which has been studied before^{1,2}, following compounds were investigated by FT-MW-spectroscopy in a molecular beam:

1. isoprene-irontricarbonyl
2. 2,3-dimethylbutadiene-1,3-irontricarbonyl
3. *trans*-pentadiene-1,3-irontricarbonyl
4. *trans,trans*-hexadiene-2,4-irontricarbonyl

The most uncertain structural parameters were least-squares-fitted to the rotational constants and compared to the *ab initio*-calculated geometries. The fine structure of the rotational transitions allows to determine the torsional barrier for the molecules 1, 3, and 4.

1. S.G. Kukolich, M.A. Rohrig, G.L. Henderson, D.W. Wallace, and Qi-Qi Chen, *J. Chem. Phys.*, 97(2), 829-831, (1992).
2. S.G. Kukolich, M.A. Rohrig, D.W. Wallace, and G.L. Henderson, *J. Am. Chem. Soc.*, 115, 2021-2027, (1993).