

Poster Abstract Booklet

“Jewels in Spectroscopy”

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on the Occasion of his Retirement

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The spectroscopy of nitric acid hydrates crystals

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The relevance of nitric acid hydrates in stratospheric processes has prompted a large number of investigations on the structure and physicochemical properties of these species. We are carrying out in our lab a study on the spectroscopy of crystals of nitric acid and the mono-, di- and trihydrates, NAM, NAD and NAT, respectively, as a first step to addressing more elaborate systems, like binary or ternary mixtures of nitric acid with water, sulphuric acid or halogen compounds of atmospheric interest. Our work consists of a theoretical part, which deals with the determination of the crystalline structure of the species and the prediction of their infrared spectra, and of an experimental part, in which we record Reflection-Absorption infrared spectra of samples prepared under controlled conditions of low pressure and temperature.

The theoretical calculations are carried out with the recently developed program SIESTA (acronym for Spanish Initiative for Electronic Simulation of Thousands of Atoms), which allows the ab initio study of periodic systems of large size, by a method that scales linearly in time and computer memory requirements with the number of atoms in a simulation cell. After optimization of the geometry of the periodic structure, atomic forces are calculated, and ancillary programs can calculate the vibrational frequencies of the molecules within the cell, and provide a description of the Cartesian displacements of the atoms in every vibrational mode. From these, the dipole moment change in the vibration can be estimated, and hence the infrared intensity of each normal mode can be predicted.

The experimental work is performed on a cryostat cell built in our laboratory. The cell has a number of inlet devices to allow gases to be expanded within, and infrared radiation from a FTIR spectrometer to enter and exit. Films of the species under study are formed by condensing the appropriate gases or mixtures of them on a polished surface of gold or aluminium, whose temperature is controlled externally and can be varied between 80 and 325 K, thus allowing annealing to be performed. The thickness of the films can be monitored by varying the deposition conditions, and measured from interference fringes of a He-Ne laser. In our case, typical values were chosen between a few hundred nanometers and a few microns. The infrared beam of the spectrometer is focused onto the metal plate at an angle of incidence of 75°, and afterwards directed to a liquid nitrogen cooled MCT detector.

Examples of experimental and predicted spectra will be presented at the meeting, with a discussion on the proposed assignments.

Deuterium Fractionation and C/O Depletion in L134N

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ABSTRACT

A relation between the abundance ratio $R_D = [\text{DCO}^+]/[\text{HCO}^+]$ and the C and O depletion in molecular cloud is examined in a simple analytical chemical model, and applied to two positions of dark cloud L134N, the northeast position, L134N(NE), and the southern NH_3 core, L134N(NH_3 -S), where R_D 's are available. The depletion factor, f_D , which is defined such that a fraction $1/f_D$ of the initial O and C remains in the gas phase, is determined to be 1.9 and 8.1 for L134N(NE) and L134N(NH_3 -S), respectively. Highly fractionated NH_2D (Saito *et al.* 2000; Tiné *et al.* 2000) and even NHD_2 (Roueff *et al.* 2000) are recently detected only toward the strongly depleted NH_3 core. A simple relation between R_D and f_D is derived under a condition applicable to cores in relatively evolved stage. The depletion factor f_D and, accordingly, R_D are suggested to be an indicator of the evolution of dark cloud cores.

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MORPHOLOGY OF THE DIFFUSE CLOUDS TOWARD CYG OB2 N.5 AND N.12

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Following the discovery of H_3^+ by Oka and collaborators (1999, ApJ, 510, 251) in the diffuse gas in front of the star Cyg OB2 N.12 we mapped the region in $^{13}\text{CO}(1-0)$ with the Onsala radio telescope. A clumpy structure was discovered showing different condensations associated with distinct velocities. The main component was found to extend toward the star N.5. Thus, we enlarged the map in that direction. A new condensation was found with characteristics similar to those in front of the star N.12. The present observations are consistent with the C_2 absorption features of Gredel and Münch (1994, A&A, 285,640).

Adiabatic rapid passage and other nonlinear spectroscopic effects in the spectra of ammonia, ethylene, nitric oxide and methane at 5 and 10 μm .

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Recently there has been considerable interest in adiabatic passage effects in atomic and molecular gases subject to short laser pulses. We have carried out two series of experiments to investigate the use of Quantum Cascade (QC) lasers for producing adiabatic passage and a range of other nonlinear spectroscopic effects.

In the first experiments at Strathclyde University, the time of passage of the chirped QC laser pulse through a Doppler broadened line is sub-ns, very much faster than the relaxation times of low pressure molecular gases which are on the microsecond time scale. The frequency chirp is also much faster than in earlier experiments of Loy, greatly enhancing the chance of seeing rapid passage effects. Since the intensity of the pulse is at least 100 Wm^{-2} the combination of high intensity and a short interaction time, which is much faster than the relaxation processes, leads to the observation of strong adiabatic rapid passage signals and power dependent bleaching. We have observed these effects in several gases, in particular ethylene and ammonia. These effects persist even when the absorption lines are pressure broadened with up to 100 Torr of nitrogen. We have shown that these effects are present when any short, intense chirped pulse from a QC laser is used to probe the infrared spectrum of a molecule irrespective of the mode of operation of the spectrometer.

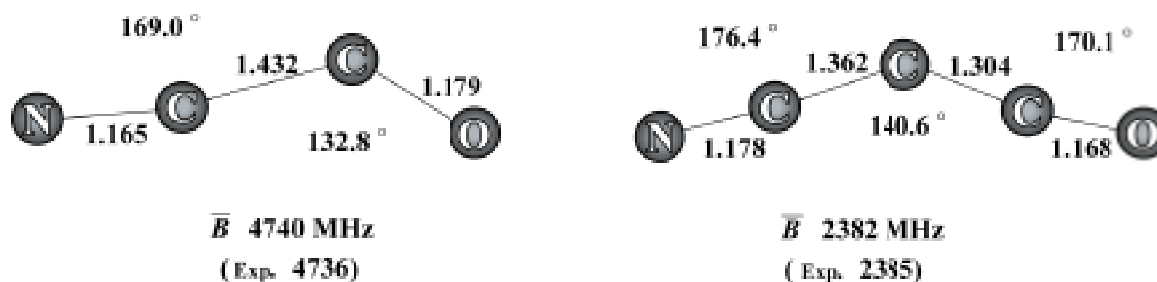
Following the experiments using a pulsed down-chirp quantum cascade laser spectrometer, we have extended the method at PNL by utilizing a novel system in which short red or blue frequency chirped pulses can be applied to specific molecular velocity classes across a Doppler broadened molecular absorption line by modulating the output of a CW QCL. The output from the high power CW QCL passes through an astigmatic Herriott cell with an effective path length of approximately 100 m. The molecules studied in this way have been nitric oxide and methane. We will describe a variety of nonlinear optical phenomena which can be explored in this way, including adiabatic following and the Autler-Townes effect. The relationship between this selective probing of specific velocity groups of the Doppler broadened lines and the adiabatic passage experiments involving all velocity components will be described.

Fourier-Transform Microwave Spectroscopy of NCCO and NCCCO

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Pure-rotational transitions of the NCCO and NCCCO radicals have been observed by Fourier-transform microwave spectroscopy. The radicals were produced in a supersonic jet by a pulsed electric discharge of 0.3% of pyruvitrile ($\text{CO}(\text{CN})(\text{CH}_3)$) in Ar for NCCO and a 0.3%/0.3% mixture of HC_3N and O_2 in Ar for NCCCO. Rotational transitions from $N = 1 - 0$ to $N = 3 - 2$ for NCCO, and those from $N = 2 - 1$ to $N = 6 - 5$ for NCCCO were observed. From the present observation, both of the radicals are found to have bent structures in the ground states, and the rotational, fine, and hyperfine constants have been precisely determined for the first time. The molecular structures obtained by *ab initio* calculations at RCCSD(T)/cc-pVTZ including the core correlation for NCCO and RCCSD(T)/cc-pVTZ for NCCCO are shown below. Quite good agreement was obtained between the rotational constants by the present experiments and those of the *ab initio* calculations: errors are only about 0.1% for both of the radicals. Discussions on the geometrical and electronic structures based on the determined molecular constants and results of the *ab initio* calculations are given. The present results are compared with those of the isoelectronic, HC_nO , and isovalent, NC_nS , carbon-chain series.



Molecular structures of *ab initio* calculations at the RCCSD(T)/cc-pVTZ level of theory. The core correlation was included for the calculation of NCCO.

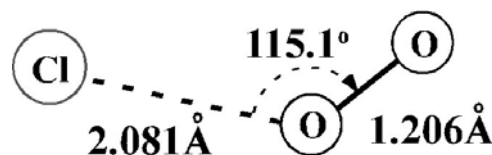
Fourier-Transform Microwave Spectroscopy and FTMW-millimeter-wave double resonance spectroscopy of XOO (X = Cl, Br) radicals

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CIOO is an important species for atmospheric chemistry because of its role in ozone destruction in the polar stratosphere. Many attempts to study this radical by high-resolution spectroscopy in the gas phase have been unsuccessful so far, presumably because of its kinetically unstableness due to the anomalously weak ClO bond which is almost equal to the hydrogen bond. Fourier transform microwave (FTMW) spectroscopy with a pulsed discharge nozzle has been successfully applied to open-shell radical complexes, which have similar experimental difficulties to CIOO. By using FTMW spectroscopy we are able to observe high-resolution spectra of CIOO in the gas phase for the first time. Finally, more than 200 *a*-type transitions (9GHz-39GHz) and 10 *b*-type transitions (80GHz) for the ^{35}Cl and ^{37}Cl isotopomers have been observed using FTMW and FTMW-millimeter-wave (MMW) double resonance spectroscopy, respectively. The rotational, centrifugal, spin rotation coupling, and hyperfine coupling constants have been determined by least squares fits. The hyperfine coupling constants indicate the species to have the $^2A''$ ground electronic state, similar to related radicals, XOO, XSO and XSS (X=H,F,Cl). The r_0 structure is determined to be $r_0(\text{OO}) = 1.226\text{\AA}$, and $r_0(\text{ClO}) = 2.075\text{\AA}$, $\theta_0(\text{ClOO}) = 116.4^\circ$. We have also performed extensive *ab initio* calculations, using CCSD(T), CASSCF and MRCI with aug-cc-pVXZ (X=D,T,Q,5). However many of them turned out to be inappropriate for CIOO, because it is indispensable to take account of static and dynamic electron correlations simultaneously. Only MRCI with a large basis set well reproduces the present experimental results. The r_e structure has been determined using the force field obtained by the *ab initio* calculations: $r_e(\text{OO}) = 1.206\text{\AA}$, and $r_e(\text{ClO}) = 2.081\text{\AA}$, $\theta_e(\text{ClOO}) = 115.1^\circ$.

We have also observed microwave spectra of BrOO. A detailed analysis similar to CIOO is now in progress. The nature of the anomalous XO bond for XOO becomes clear by the present experiments, *ab initio* calculations, and systematic comparisons to XSO and XSS radicals.



r_e structure of CIOO

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Heterogeneous chemistry on polar stratospheric clouds (PSCs) continues to be an area of intense research. Though much experimental work has been performed in an effort to better understand these types of reactions, there remains much to be learned. One important aspect that interests us concerns the role of water on the surface of ice. In particular, if these reactions are ionic, what role does the surface water play in hydrating the ions? Is there a limit to the number of ionic species that can be accommodated on the surface?

Experimentally we examine the interaction of reactive gases with the ice surface using infrared transmission spectroscopy and thin films of pure water ice as model PSCs. In this report we will present our most recent results concerning (a) the ionization of nitric acid on ice and (b) the isotope exchange of D_2O on ice.

Near-Infrared Spectroscopy of H_3^+ Above the Barrier to Linearity

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The first H_3^+ transitions above the barrier to linearity have been observed in absorption in the near infrared using a highly sensitive dual-beam, double-modulation technique with bidirectional optical multipassing. A total of twenty-two rovibrational transitions of H_3^+ have been detected and assigned to the fourth and fifth overtone and combination bands ($5\nu_2^1$, $5\nu_2^5$, $2\nu_1+2\nu_2^2$, $3\nu_1+\nu_2^1$, $\nu_1+4\nu_2^2$, $2\nu_1+3\nu_2^1$, and $6\nu_2^2$). These transitions, which are more than 4600 times weaker than the fundamental band, probe energy levels above $10,000\text{ cm}^{-1}$, the regime in which H_3^+ has enough energy to sample linear configurations. Experimentally determined energy levels above the barrier to linearity provide a critical test of *ab initio* calculations in this challenging regime. In this poster, we compare our results with several recent theoretical calculations.

Determination Dihedral Angles of Biphenyl Derivatives Adsorbed on Gold Nanoparticle Surfaces

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Self-assembled monolayers of aromatic compounds have a number of advantages due to their rigidity and conjugated nature. *p*-Biphenylthiolate (BPT) has been recently used for a negative resist of nanolithography or a molecular switch. For biphenyl-based thiols adsorbed on surfaces, the two phenyl rings have been assumed to be coplanar and their dihedral angles around the central bond have not been experimentally obtained until the present. We have studied the dihedral angle of BPT by means of surface-enhanced Raman scattering. The ν_{8a} band at $\sim 1597\text{ cm}^{-1}$ of BPT in its solid state was found to clearly split into the two features at ~ 1599 and $\sim 1587\text{ cm}^{-1}$ on Au nanoparticle surfaces. This result indicates that the orientation of the two phenyl rings should be quite different and do not lie coplanar on the nanoparticle surfaces. On the basis of the electromagnetic enhancement factor, the dihedral angle could be estimated to be $\sim 51^\circ$. Our Raman results on gold nanoparticle surfaces shall provide new evidence on the structure of self-assembled monolayers prepared by *p*-biphenylthiolates on Au surfaces.

Infrared Heterodyne Spectroscopy

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Of fundamental importance in the spectroscopy of dilute species is instrumental sensitivity. In laser absorption spectroscopy, extremely high sensitivity is in principle possible and is fundamentally limited only by shot noise---the statistical noise that arises from counting photons. Shot noise limited performance is very difficult to reach in practice due to large fluctuations in the intensity of lasers. This additional “noise” is roughly $1/f$ and can be lowered by encoding the experimental signal at high frequency via some sort of modulation technique. In order to completely escape this noise, however, modulation frequencies of greater than 1 MHz must be realized, which is not generally possible in experiment-based modulation schemes.

Heterodyne spectroscopy is a technique that relies on phase modulation of the laser with an electro-optic modulator. This technique is one of the few methods that can encode the signal at RF frequencies (>100 MHz) and has been applied to visible and near-IR lasers in the past with great success. In this poster we present the first use of heterodyne spectroscopy in the mid-IR and discuss the additional challenges when implementing it in the mid-IR. We demonstrate infrared heterodyne modulation with the study of molecular ion absorptions where we have detected absorptivities as low as $5 \times 10^{-9} \text{ cm}^{-1}$ @ 1 Hz bandwidth.

HIGH-RESOLUTION SPECTROSCOPY OF THE $B^4\Sigma_u^- \leftarrow X^4\Sigma_g^+$ TRANSITION OF C_2^+

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The first electronic spectrum of the molecular ion C_2^+ was recorded in 1984 by O'Keefe *et al.* in a beam of mass selected ions.¹ Three years later, Maier and coworkers did an extensive analysis on several bands of the $B \leftarrow X$ system.^{2 3 4} While their spectra showed several perturbations, the low resolution of their experiment hindered the analysis of the perturbation and the quartet spitting. In 1993, Zackrisson and Royen obtained a high resolution spectrum of the (0,1) band and determined the molecular constants and perturbation parameters.⁵

In the work that follows, velocity modulation with heterodyne detection has been used to record the (0,2), (1,3), and (6,9) bands of the $B \leftarrow X$ system of C_2^+ . The bands have been rotationally analyzed and their spectra show perturbations which are attributed to an interaction between the $B^4\Sigma_u^-$ and the $2^2\Pi_u$ states. As a result of the mixing between the $B^4\Sigma_u^-$ and the $2^2\Pi_u$ states, several forbidden transitions from the $X^4\Sigma_g^+$ state to the $2^2\Pi_u$ state have been observed. In addition to the forbidden transitions, weak lines from the satellite branches, for which $\Delta J \neq \Delta N$, are also observed. Molecular constants and perturbation parameters have been obtained.

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High Resolution Infrared Spectra of Helium Clusters Seeded with Single OCS, N₂O and CO Molecules

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Infrared spectra of He_N-OCS complexes with N up to about 20, He_N-N₂O complexes with N up to about 13, and He_N-CO complexes with N up to about 21 have been observed using a tunable diode laser spectrometer to probe pulsed supersonic expansions from moderately high pressure (<36 atm) cooled (>-150 °C) jet sources. Resolved rotation-vibration transitions for the He_N-OCS and He_N-N₂O complexes with smaller N (up to 8) have been assigned by confirming the observations of the corresponding pure rotational transitions in the microwave region. Resolved rotation-vibration transitions for He_N-CO have been assigned by the smooth vibrational shifts with the N growing. These are the largest van der Waals clusters for which high resolution spectra have been obtained with specific cluster size assignments. The results, when compared with the ones from observations in helium droplets, have interesting implications for the nature of superfluid-type behavior in these finite scale systems.

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Electronic Spectroscopy of Jet Cooled Thiophenoxy Radical

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Aromatic free radicals have their lowest electronic transition in visible region, and are one of the candidates for the carrier of DIBs. The benzyl type radical is one of the most fundamental aromatic free radicals and much attention has focused on radical derivatives. The thiophenoxy radical, C₆H₅S (ϕ -S), is an aromatic free radical with a benzyl type π -electronic structure. We have generated the thiophenoxy radical by ArF laser photolysis in supersonic free jet expansions, and observed laser induced fluorescence (LIF) of the green-blue band. We have measured the vibrationally and rotationally resolved LIF excitation spectra and the vibrationally resolved LIF dispersed spectra from single vibronic levels (SVL). On the basis of the precise vibrational analysis of the dispersed spectra, we propose new vibrational assignments to the excitation spectrum. The band types of the vibronic bands determined from the rotationally resolved excitation spectra make it possible us to determine a definite assignment of the D_2 $1^2A_2 - D_0$ 1^2B_1 , π^* π , electronic transition of the green-blue band of ϕ -S. Based on the results of the spectroscopic assignments, we will discuss the electronic and vibrational structure of ϕ -S both of the ground D_0 1^2B_2 and the second excited D_2 1^2A_2 states. We have also measured the time profiles of the SVL fluorescence of this radical under collision-free conditions, and determined extremely short fluorescence lifetimes for electronic transitions of the benzyl type. This unexpected finding was explicated as an intermediate case molecule behavior of ϕ -S. With the aid of computational calculations, we propose a sequential decomposition reaction process for the production of C₅H₅ and CS from ϕ -S (D_2 1^2A_2 D_1 1^2B_2 D_0 1^2B_1 decomposition) as the background decay channel of the intermediate case molecule scheme.

The C-H Stretch Spectrum of Ethylene in Liquid Helium Droplets

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In this poster we report our study of $^{12}\text{C}_2\text{H}_4$ monomer and its clusters in ^4He with the new, "second generation" helium droplet/infrared spectroscopy apparatus at UNC. The region containing the asymmetric C-H stretches of the monomer was scanned using a tunable, cw-OPO aligned collinearly with the droplet beam and detected with a quadrupole mass spectrometer. Rotationally resolved spectra were observed with line widths ranging from $0.03\text{--}0.6\text{ cm}^{-1}$, FWHM. In addition to the ν_{11} and ν_9 asymmetric C-H stretching fundamentals, the $\nu_2+\nu_{12}$ and $2\nu_{10}+\nu_{12}$ combination bands (which are anharmonically coupled to the ν_{11}) were observed and analyzed. Strong perturbations, apparently due to solvation, were observed in some of the high rotational states. Details of the new instrument and the analysis of the spectra will be presented.

Harnessing single molecule dynamics for nanotechnology

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Having found important applications in probing nanoscale biological dynamics and material heterogeneity, single molecule methods hold even greater promise as optical and electronic elements for nanoscale device applications. Crucial to future advances in molecular electronics, the harnessing of single molecule properties (quantized energy levels, unique behavior, incredibly small size ...) under ambient conditions remains a significant impediment to their use. Recently, we have utilized the properties of strongly fluorescent individual Ag nanoclusters (2~8 atoms in size, or "molecular silver") to not only yield photoactivated nanomaterials,¹ but also produce the first electroluminescent single molecule devices.² These room temperature nanoscale emissive sources exhibit discrete energy levels, polarity, and transistor behavior without complicated nanofabrication. Additionally, charge injection into discrete single nanocluster energy levels yields electroluminescent interconnects, simplifying measurement and information transfer.

¹ L. A. Peyser, A. E. Vinson, A. P. Bartko, and R. M. Dickson, *Science*, **291**, 103-106 (2001).

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Ion Sources Used at the Oka Ion Factory

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For many years, the spectroscopic study of ions of astrophysical significance has been the focus of much of Oka's research. These ions have been produced using three different sources. The positive column discharge tube, which has been the primary ion source in the Oka Ion Factory in recent years, can be used to create a plasma using either a DC or AC current. An AC discharge allows the use of velocity modulation for ion discrimination. In addition to the positive column discharge, the hollow cathode discharge has been used for carboion spectroscopy. In the hollow cathode, the plasma is contained in a metal tube which remains ionized by the photoelectric ejection of electrons from the metal. The high concentration of low temperature electrons result in a dominance of protonated ions. The newest source is a supersonic slit jet, which expands a high pressure gas into a low pressure chamber while passing a current through the slit to produce a plasma. The slit jet will produce rotationally cold ions in a nearly collisionless environment, thus more closely emulating the conditions in interstellar space. The details of these three ion sources will be discussed.

Indeterminacies in Molecular Spectroscopy

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An effective Hamiltonian $H(\mathbf{q}, \mathbf{p}; \mathbf{c})$ is in general a function of coordinates \mathbf{q} , momenta \mathbf{p} , and parameters or ‘constants’ \mathbf{c} . The latter are adjusted so that differences between eigenvalues of H/h fit the observed frequencies ν . However, the transformed Hamiltonian $\tilde{H}(\mathbf{q}, \mathbf{p}; \mathbf{c}, \mathbf{s}) = UHU^{-1}$, where $U(\mathbf{q}, \mathbf{p}; \mathbf{s})$ is a non-singular operator depending on parameters \mathbf{s} , has the same eigenvalues as H . If, in addition, \tilde{H} is identical in form to H with different values $\tilde{\mathbf{c}}(\mathbf{s})$ of the parameters,

$$\tilde{H}(\mathbf{q}, \mathbf{p}; \mathbf{c}, \mathbf{s}) \equiv H(\mathbf{q}, \mathbf{p}; \tilde{\mathbf{c}}(\mathbf{s})),$$

then the parameters $\tilde{\mathbf{c}}(\mathbf{s})$ and \mathbf{c} will give the same eigenvalues of H , and so are indistinguishable as far as the observed frequencies are concerned. There will therefore be a degree of indeterminacy in H for each parameter of \mathbf{s} , and the only determinable combinations of parameters are obtained by eliminating the \mathbf{s} parameters.

This argument was originally applied to centrifugal effects in asymmetric-top spectra¹, and has been widely used in various problems. A complication arises from the fact that the transformed Hamiltonian is usually an infinite series, which is necessarily truncated, and so the truncated \tilde{H} does not have exactly the same eigenvalues as H . Thus the truncated problem may seem to be determinate. However, the parameters determined $\tilde{\mathbf{c}}(\mathbf{s})$ contain an unknown contribution from the \mathbf{s} , and so are not reliable estimates of the true \mathbf{c} .

An application will be described to the diatomic vibration-rotation Hamiltonian, with Born-Oppenheimer-breakdown corrections,

$$H = \frac{1}{2\mu_C} p_r \left\{ 1 + \sum_i (m_e/M_i) Q^i(r) \right\} p_r + \frac{1}{2\mu_C r^2} \left\{ 1 + \sum_i (m_e/M_i) R^i(r) \right\} (J_x^2 + J_y^2) + V(r) + \sum_i (m_e/M_i) S^i(r),$$

where $\mu_C = M_A M_B / (M_A + M_B - C m_e)$ is a charge-modified reduced mass, and $Q^i(r)$, $R^i(r)$, and $S^i(r)$ are isotopically independent functions. It is shown that $Q^i(r)$ is completely indeterminate, and can be eliminated if $R^i(r)$ and $S^i(r)$ are replaced by

$$\tilde{R}^i(r) = R^i(r) - \frac{1}{r} \left\{ 2A_0^i + \int_{r_e^{\text{BO}}}^r Q^i(r') dr' \right\}, \quad \tilde{S}^i(r) = S^i(r) + \frac{1}{2} V'(r) \left\{ 2A_0^i + \int_{r_e^{\text{BO}}}^r Q^i(r') dr' \right\}.$$

The integration constant A_0^i is also an \mathbf{s} -type indeterminacy parameter, which has the effect that $R^i(r_e^{\text{BO}})$, which depends on the equilibrium dipole moment and g_J -factor, is indeterminate. Examples of fits of the extensive isotopic data for LiH with various degrees of truncation will be given.

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Time-resolved Fourier Transform infrared spectroscopy of Rydberg molecules

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A time-resolved Fourier transform spectroscopic method has been developed with a microcontroller SX and a high-resolution Bruker IFS 120 HR. During one cycle of the He-Ne laser fringe, 30 data points are recorded with a preset time interval of 2 or 3 μsec . This method is applied to infrared emission produced by a pulsed discharge in noble gases and hydrogen mixture. The discharge peak current was 0.5 A with 20 μsec duration. Pulsed afterglow was found to be an efficient source for ArH, He₂, etc. Spectral intensities of ArH and ArH⁺ showed different time profiles, depending on the production mechanism.

Several strong electronic bands of ArH were observed in the region of 2000-9000 cm^{-1} . We were able to assign the transitions of 5p - 6s band of ArH in 3700 cm^{-1} region for the first time, whereas the corresponding ArD band was analyzed by Dabrowski et al. (J. Chem. Phys. 104 (1996) 8245). The molecular constants of ArH have been derived in the present analysis. Moreover, many un-identified bands have been detected in afterglow plasma. Similarly, spectra of He₂ have been observed strongly in afterglow plasma, and it was found that emission intensities from some states became weak during discharge. Spectroscopic analysis has been carried out for newly observed infrared bands.

Rotationally Resolved Spectra of the $\lambda 4050$ Group of C_3 in Diffuse Interstellar Clouds and the Laboratory

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Recent detections of the smallest polyatomic carbon chain molecule, C_3 , have revealed an unexpectedly rich chemistry in the diffuse interstellar medium (ISM). C_3 now serves as a remote diagnostic of temperature and density in diffuse interstellar clouds. Among the few polyatomic species to be observed in the diffuse ISM, C_3 is also of fundamental interest to chemists as both the prototypical nonrigid system and the simplest cumulene. In order to survey the chemistry and physical conditions of various diffuse clouds, the rotationally resolved spectrum of the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ 000-000 transition of C_3 , centered at 4051.6 Å, has been observed along 10 translucent lines of sight. Analysis of these astronomical spectra has exposed an error in the laboratory assignment of the $R(0)$ transition. Cavity ringdown spectroscopy has been used to re-examine the 4051 Å band of C_3 yielding the first laboratory assignment of the $P(2)$ transition and confirming the incorrect previous laboratory assignment of the $R(0)$ transition. To interpret the astronomical spectra, a new method for the determination of column densities and analysis of excitation profiles involving the simulation and fitting of observed spectra has been developed. The populations of lower rotational levels ($J \leq 14$) in C_3 are best fit by thermal distributions that are consistent with the kinetic temperatures determined from the excitation profile of C_2 . Just as in the case of C_2 , higher rotational levels ($J > 14$) of C_3 show increased nonthermal population distributions in clouds which have been determined to have total gas densities below $\sim 500 \text{ cm}^{-3}$. These measurements provide a new challenge for comprehensive models of the excitation of C_3 in the diffuse ISM.