

MO-POS-71

Torsion-Vibration, Torsion-Rotation, and Vibration-Rotation Interaction Constants for CH<sub>3</sub>OH from *Ab Initio* Calculations, Li-Hong Xu<sup>1</sup>, J.T. Hougen<sup>2</sup> and R.M. Lees<sup>1</sup>, <sup>1</sup> *University of New Brunswick* and <sup>2</sup> *National Institute of Standards and Technology* — This is a progress report on our effort to investigate the possibility of obtaining useful spectroscopic information from *ab initio* calculations. Previously, we have shown<sup>[1]</sup> that quantum chemistry results for methanol at the top and bottom of the torsional barrier could be used to determine the  $\cos 3\gamma$  dependence of the torsional potential energy (*i.e.*, the barrier height) to better than 0.5 %, and the  $\cos 3\gamma$  dependence of the rotational constants (three diagonal and one off-diagonal) to accuracies ranging from 7 % to 40 %. Results for acetaldehyde were about ten times worse, though these large discrepancies could be improved significantly by an empirical adjustment procedure. We then have shown<sup>[2]</sup> that G98 delivered very smooth force constant plots as a function of angle along the internal rotation coordinate (defined to be 0° at the bottom and 60° at the top of the barrier), and that when symmetrized coordinates (in the permutation inversion group  $G_6$ ) were used, these plots exhibited the  $\sin 3\gamma$  or  $\cos 3\gamma$  behavior expected from the symmetry species of the pair of vibrational coordinates multiplied by the force constant. In the present paper we investigate algebraically the meaning of various off-diagonal elements occurring in a Hessian matrix obtained by rotating the Cartesian Hessian matrix (containing second derivatives of the potential surface) to a coordinate system consisting of  $3N-7$  small-amplitude vibrations (where  $N$  is the number of atoms in the molecule), one large-amplitude vibration (the torsion), three overall rotations of the molecule, and three translations of the molecule. We then compute these elements numerically using quantum chemistry methods. Finally we discuss how these elements can be applied to analyses of vibration-torsion-rotation bands of methanol.

1. L.-H. Xu, R.M. Lees, and J.T. Hougen, *J. Chem. Phys.* **110**, 3835-3841 (1999).
2. L.-H. Xu, J.T. Hougen, R.M. Lees, and M.A. Mekhtiev, *J. Mol. Spectrosc.* **214**, 175-187 (2002).

MO-POS-72

Progress Report on the Measurement of Cesium Electron-Impact Cross Sections Using a Magneto-Optical Trap\*, T.J. Reddish<sup>1</sup>, J.A. MacAskill<sup>1</sup>, C. McGrath<sup>1</sup>, D.P. Secombe<sup>1</sup>, M. Lukomski<sup>1</sup>, J. Teeuwen<sup>1</sup>, S. Sutton<sup>1</sup>, W. Kedzierski<sup>1</sup>, J.W. McConkey<sup>1</sup>, W.A. van Wijngaarden<sup>2</sup>, I. Bray<sup>3</sup>, <sup>1</sup> *University of Windsor*, <sup>2</sup> *York University* and <sup>3</sup> *Murdoch University, Australia* — A trapped Cesium atom target, prepared using a magneto-optical trap (MOT), is exposed to a broad monochromatic beam of electrons. Since the infrared fluorescence from the trap is directly proportional to the number of atoms in the trap, the measurement of the decrease in the fluorescence signal, due to the interaction of the electron beam, provides a straightforward method of determining electron-impact cross sections. This technique, pioneered by Lin and co-workers<sup>[1]</sup>, does require knowledge of the absolute target density. The choice of an appropriate pulsing scheme enables one to obtain either the ground state (Cs 6<sup>2</sup>S<sub>1/2</sub>) total cross section or that for the 6<sup>2</sup>P<sub>1/2</sub> excited state; ionisation cross sections may also be determined. The first results (100-400 eV) showed good agreement with convergent close coupling calculations<sup>[2]</sup>. Improvements to the experimental setup and new results at lower electron energies will be presented at the conference.

1. R.S. Schapp, *et al* *Phys. Rev. Lett.* **76** (1996) 4328.
2. J.A. MacAskill *et al* *J. Elec. Spec. Rel. Phen.* **123** (2002) 173.

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**MO-POS-73**

Modeling of Collision-Induced Light Scattering using Mathematica/Programme Mathematica pour le calcul de l'intensité de la diffusion de la lumière induite par les chocs\*, **Andrew Senchuk** and George Tabisz, *University of Manitoba* — Collision-induced light scattering has been of great interest for many years due to the insights it gives on the physics of molecular interactions and dynamics. Calculation of the scattered intensities usually involves the manipulation and coupling of Cartesian tensors describing the multipole polarizability of the atoms or molecules together with tensors describing their interaction. As more complicated effects between the atoms and the field and/or higher order interactions between the atoms themselves are considered, the ranks of the resulting tensors become large. Consequently the resulting complexity, arising from the sheer number of terms that need to be considered, makes the calculation impractical in all but the lowest order cases. However, the effect of the higher order interactions cannot necessarily be dismissed as being negligible. To make the problem more tractable, one can re-express the theory in terms of irreducible spherical tensors, whose symmetry properties allow only a limited number of terms for a particular polarizability, and couple according to the Wigner coefficients. This is advantageous, as software packages, like Mathematica, exist which are able to calculate these very quickly. Thus we present results of modeling collision-induced light scattering using Mathematica in spherical tensor formalism. Our program handles arbitrary order polarizability tensors and can calculate interactions up to second-order.

\* This work is being supported by CIPI.

**MO-POS-74**

Variational Calculations of Four-Body Molecular Systems, Z.-C. Yan, University of New Brunswick — Fully nonadiabatic calculations are performed for various four-body two-center molecular systems, using variational method in Hylleraas coordinates. The systems under study include  $H_2$ ,  $HeH^+$ ,  $MuH$ , and their isotopes. Our studies demonstrate that the traditional Hylleraas coordinates, which has been used widely for one-center atomic systems, can be equally well applied to two-center molecular systems. High-precision energy eigenvalues will be reported.

**MO-POS-75**

Intensity-Dependent Optical Rotation by Molecules/ Rotation Optique par les Molécules Dépendante sur l'Intensité de la Lumière\*, **R. Cameron** and G.C. Tabisz, *University of Manitoba* — Chiral molecules rotate light through a forward scattering event. Single photon scattering, which is known as ordinary optical rotation, is independent of the light intensity  $I$ . We used a polarimeter in a heterodyne experiment to measure the optical rotation of solutions at 308 nm with high-intensity laser pulses. In three of the molecules that we studied (uridine, thymidine and cytidine) we found an intensity-dependent effect. The effect only appeared in molecules that had an absorption line near 308 nm; in other molecules that had no absorption line near 308 nm, such as sucrose, no intensity-dependent effect was observed. The intensity-dependent optical rotation in the three molecules was cumulative with each laser pulse and persisted with a time constant that was on the order of seconds and characteristic of the molecule.

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**MO-POS-76**

Atomic Metastable Production Following Fragmentation of S-Containing Molecules\*, **W. Kedzierski**, S. Amlin, X. Liao, R.J. Murray, J. Mutus, and J.W. McConkey, *University of Windsor* — A special xenon-matrix detector which is selectively sensitive to  $S(1S)$  atoms has been used to monitor dissociation of sulfur containing molecules into this fragment following controlled electron impact over an incident energy range from threshold to 400eV. A crossed-beam apparatus with a pulsed electron beam is used to obtain time-of-flight, and hence energy, spectra of metastable S fragments. Cross sections have been made absolute by comparison with previously obtained data from COS targets <sup>[1]</sup>.

1. Kedzierski *et al*, *J. Phys. B*, **34**, 4027 (2001).

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**MO-POS-77**

Trace Gas Detection Using Cavity Enhanced Absorption\*, **Jeff Seabrook** and D. Tokaryk, *University of New Brunswick* — This presentation describes our application of an integrated cavity output spectrometer (ICOS) to trace gas detection. The principles behind cavity enhanced absorption and details of our implementation will be presented. In addition, we will discuss this technique's potential for determining number densities of the trace gases we hope to monitor. This technique also shows promise as an easy to use, and highly sensitive absorption spectroscopy tool. The near infrared region offers us the opportunity to detect weak vibrational transitions in many atmospheric species such as  $CO$ ,  $CO_2$  and  $H_2S$ . We will present our preliminary investigations into the detection of the pollutant hydrogen sulfide, and of our spectroscopy of the extremely weak and highly perturbed (012) vibrational transition of this molecule.

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**MO-POS-78**

An Atomic Source for Degenerate Fermi Gas Experiments\*, **Swati Singh**<sup>1</sup>, S. Aubin<sup>2</sup>, P. Scrutton<sup>2</sup>, M. Extavour<sup>2</sup>, S. Myrskog<sup>2</sup> and J.H. Thywissen<sup>2</sup>, <sup>1</sup>*McMaster University and* <sup>2</sup>*University of Toronto* — Even though all the constituents (electrons, protons, neutrons) of an atom are fermions, fermionic atoms are much less abundant in nature than bosonic atoms. In order to make a degenerate Fermi gas of Potassium 40 (40K) atoms, we had to make our own atomic source using potassium enriched to 3% 40K, instead of the natural 0.01% abundance. We present the experimental challenges faced in building and testing of a "dispenser" source for K-40 that can be used for the experiment. We also present recent progress in other areas of the experiment, towards magneto-optical trapping and pure magnetic trapping of potassium.

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**MO-POS-79**

Mixed Sample Ion Trapping: Analysis and Evolution of Trapped Species\*, **Jérémie J. Choquette**<sup>1</sup> and R.I. Thompson<sup>2</sup>, <sup>1</sup>*University of Calgary* and <sup>2</sup>*NSERC* — Sympathetic laser cooling of trapped ions shows promise as a tool for low temperature studies of atoms and molecules. However, by its very nature it requires the generation and storage of mixtures of ions. Our work is currently focused on some of the issues and challenges of generating, storing, and analysing mixed samples involving magnesium, noble gas, nitrogen, and carbon monoxide ions. This presentation will outline our techniques for loading and buffer gas cooling of atomic and molecular ions from solid and gas phase sources. It will outline the 'q-scan' ion trap mass spectrometric technique that we use to analyse our trapped samples, and will provide a detailed discussion of the temporal evolution of these mixed samples which results from charge transfer reactions involving the trapped species and background gases in the vacuum system.

\* This work is being supported by NSERC.

**MO-POS-80**

Spectral Clustering in the NMR Spectrum of a Gaseous System\*, **Geoffrey Archibald**, Simon, E. Brief and M.E. Hayden, *Simon Fraser University* — We have observed unanticipated spectral clustering effects in the NMR spectrum of room temperature thermally polarized  $^3He$  gas at 1.5 Tesla. At least three distinct lines form when  $^3He$  is adulterated with the highly paramagnetic gases  $NO$  or  $O_2$ . These lines shift in frequency yet remain remarkably narrow when linear field gradients are applied. Unlike previous reports of spectral clustering, this behaviour cannot be explained solely in terms of the dipolar fields of the  $^3He$  atoms. Instead, the effects we observe appear to be mediated by electronic spins associated with the paramagnetic adulterants.

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