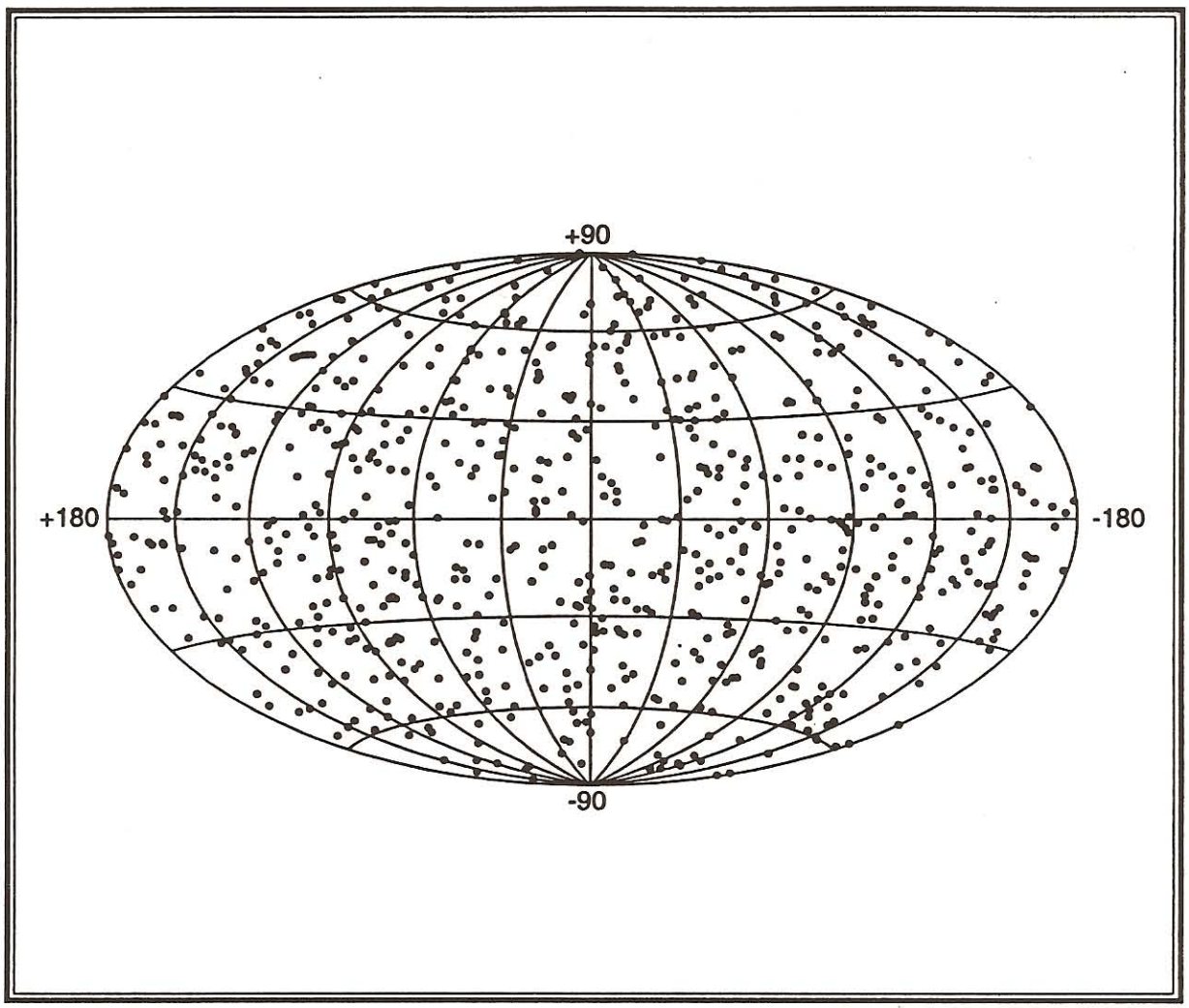
BULLETIN
OF THE AMERICAN PHYSICAL SOCIETY



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22755.3 cm^{-1} and 22772.5 cm^{-1} which correspond to threshold energies for the dissociating molecular states to $3p_{1/2}$ and $3p_{3/2}$ sodium atomic levels respectively. The ground state dissociation energy of the Na_2 molecule has been estimated and is in good agreement with the recent experimental and theoretical values.

* Supported by the NSRDB, Pakistan and the ICTP, Trieste, (Italy) under the ICAC scheme.

16:18

G7 10 Subthermal Molecular Spin-Orbit Distributions in the Atmosphere. P.S. ARMSTRONG[1], S.J. LIPSON, W.A.M. BLUMBERG, J.A. DODD[1], J.R. LOWELL, and R.M. NADILE, Phillips Laboratory, Hanscom AFB, MA, and [1]Stewart Radiance Laboratory, Bedford, MA -- The populations in the two spin-orbit manifolds of nitric oxide in the earth's thermosphere have been found to depart by as much as a factor of two (or hundreds of degrees K) from the ratio expected from thermal equilibrium. Absolute spin-orbit specific densities of NO($X^2\Pi$, v=1) have been determined from high-resolution (1 cm^{-1}) IR earth limb spectra obtained in the CIRRIS 1A Space Shuttle experiment for the 100-200 km region. Nonlinear least-squares spectral fitting was used to analyze the NO(Δv=1) emissions near 5.3 μm. The sublevel population ratio represents a third degree of freedom, along with vibration and rotation, that is not in equilibrium with the local kinetic temperature. The subthermal distributions most likely result from NO(v=0) + O collisions, which are the major source of NO(v=1) in the thermosphere. Thus, the present measurements provide new information on NO + O collision dynamics and the dissociation of the NO_2 transition states, suggesting a relationship with subthermal NO sublevel distributions observed in NO_2 photodissociation. It may be possible to use observed spin-orbit population ratios as diagnostic probes of NO(v) collisional and chemiluminescent excitation mechanisms, and for the reinterpretation of prior atmospheric NO measurements.

This work was supported by the Air Force Office of Scientific Research and the Ballistic Missile Defense Organization.

16:30

G7 11 *Electronic Mass Scaling and Badger's Rule.* J.D. MORGAN III, D.R. HERSCHBACH, *Dept. of Chemistry, Harvard University.* — In 1934 R.M. Badger[1] observed that for the great majority of ground and excited states of molecules, harmonic stretching constants are approximately proportional to the inverse cube of the bond length R. Since then much numerical fitting of experimental data has been done to verify and refine 'Badger's Rule', but its theoretical justification has remained elusive. Insight into the origin of Badger's Rule is gained by imagining the electronic mass m to be a continuous variable. In a system of heavy particles (such as nuclei) and light particles of a single kind (such as electrons or muons) of mass m, all interacting by Coulombic potentials, a simple scaling argument implies that the energy levels are proportional to m, neglecting non-adiabatic effects, and the typical length scales are proportional to $1/m$. Thus a harmonic stretching constant, which is the second derivative of the energy with respect to the bond distance, is proportional to m^3, which in turn is proportional to R^{-3}. The muonic case, with $m_\mu \simeq 207\, m_e$, illustrates the robustness of Badger's Rule even in regimes undreamt of in the 1930's.

[1]R.M. Badger, *J. Chem. Phys.* **2**, 128 (1934); **3**, 710 (1935).

16:42

G7 12

Semiclassical mechanics of H_2^+ beyond the Born Oppenheimer approximation D. W. Noid, J. Müller, and J. Burgdörfer . University of Tennessee and Oak Ridge National Laboratory

Most previous structure calculations of H_2^+ have been performed using the Born Oppenheimer (BO) separation of nuclear and electronic degrees of freedom as a starting point. We show that the unrestricted classical dynamics of the H_2^+ molecule molecule possesses regions of phase space which are stable. A new adiabatic invariant, which differs from the one discussed for the separable problem with fixed nuclei, is presented. We have performed semiclassical EBK quantization of H_2^+ without invoking a BO separation. The breakdown of the BO approximation for highly excited states is discussed. This work was supported in part by the National Science Foundation and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. and through Contract No. DE-F605-87ER40361 with the University of Tennessee.

Supplementary Papers

G7 13 The Nature and Utility of Laser Optogal-vanic Transitions in Spectroscopy.* P. MISRA, X. ZHU and A.H. NUR, Howard University. - The laser optogalvanic (OG) effect provides a good solution for laser wavelength calibration inadequacies in the visible and near UV regions. We have recorded over 200 laser-assisted OG neon transitions in the 337-598 nm region. A large number of the OG transitions recorded occurred in the near UV as compared to the yellow and red regions. The polarity of the OG waveforms in certain cases can be understood in terms of population of neon atoms in metastable energy levels. The laser OG transitions - in conjunction with simultaneously recorded etalon fringes - have allowed calibration of tunable dye lasers to within 0.3 cm^{-1} accuracy and enabled precise analysis of rotationally-resolved spectra of jet-cooled free radicals.

*Supported by EPA grant R81-9720-010, NASA grant NAGW-2950 and the Collaborative Core Unit of Howard University's Graduate School of Arts and Sciences.

G7 14 Molecular Spectroscopy of Supersonically Cooled Transient Species.* P. MISRA, X. ZHU, M.M. KAMAL and A.H. NUR, Howard University. - Transient molecular species, namely the alkoxy and alkylthio radicals, have been generated in a supersonic beam and probed with a tunable dye laser. Well-resolved laser excitation and wavelength-resolved emission spectra of the jet-cooled radicals have been recorded. Molecular parameters characterizing both the ground and excited electronic states have been determined following a comprehensive vibronic and rotational analyses of the laser-induced fluorescence spectra.

*Supported by EPA grant R81-9720-010, NASA grant NAGW-2950 and the Collaborative Core Unit of Howard University's Graduate School of Arts & Sciences.

SESSION G8: DAMOP: RYDBERG ATOMS
Tuesday afternoon, 19 April 1994
Washington Room B at 14:30
W. Cook, presiding

14:30

G8 1 Steps in the Microwave Ionization of Highly Excited Hydrogen Atoms. S. Y. LUIE AND J. E. BAYFIELD, University of Pittsburgh. --- Quasi-