FINAL TECHNICAL REPORT

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Title of proposal: Theoretical molecular studies of astrophysical interest

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Institution: The Trustees of Columbia University in the City of New York

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When work under this grant began in 1974 there was a great need for state-to-state collisional excitation rates for interstellar molecules observed by radioastronomers. These were required to interpret observed line intensities in terms of local temperatures and densities, but, owing to lack of experimental or theoretical values, estimates then being used for this purpose ranged over several orders of magnitude. A problem of particular interest was collisional excitation of formaldehyde; Townes and Cheung had suggested that the relative size of different state-to-state rates (propensity rules) was responsible for the anomalous absorption observed for this species.

We believed that numerical molecular scattering techniques (in particular the close coupling or coupled channel method) could be used to obtain accurate results, and that these would be computationally feasible since only a few molecular rotational levels are populated at the low temperatures thought to prevail in the observed regions. Such calculations also require detailed knowledge of the intermolecular forces, but we thought that those could also be obtained with sufficient accuracy by theoretical (quantum chemical) techniques.

Others, notably Roy Gordon at Harvard, had made progress in solving the molecular scattering equations, generally using semi-empirical intermolecular potentials. Work done under this grant generalized Gordon's scattering code, and introduced the use of theoretical interaction potentials obtained by solving the molecular Schrodinger equation. Earlier work had considered only the excitation of a diatomic molecule by collisions with an atom, and we extended the formalism to include excitation of more general molecular rotors (e.g., \( \text{H}_2\text{CO}, \text{NH}_2, \text{H}_2\text{O} \)) and also collisions of two rotors (e.g., \( \text{H}_2-\text{H}_2 \)).

Solution of the molecular scattering equations is computationally quite expensive. As this work progressed a number of approximate molecular scattering
methods were suggested by other workers, e.g., the effective potential method of Rabitz, the coupled states approximation of Kouri and McGuire, and the decoupled 1–dominant method of Alexander. As we had obtained accurate close coupling cross sections for several systems, we were in a good position to test these approximate methods. In collaboration with D. Kouri (Univ. of Houston) we also helped develop and test accuracy of the infinite order sudden approximation.

With support from this grant collisional excitation rates have now been obtained for a number of systems of astrophysical interest, including $\text{H}_2$, CO, HCN, HN$^+_2$, H$_2$O, NH$_3$, CS, OCS, HC$_3$N, SiO (including vibrational excitation), H$_2$O, CH$_3$CN, SO$_2$, C$_3$H$_2$, and SiC$_2$. In general, work has progressed toward more complex species (i.e., with more internal degrees of freedom). Most of these calculations considered only excitation by collisions with He atoms rather than $\text{H}_2$ which is the dominant interstellar species. Although it has been argued that rates for excitation by these are similar, it is still important to do accurate calculations for the latter; increasing computational power should make this feasible.

It has still not been possible to obtain experimental values for the state-to-state collisional excitation rates of interest in radioastronomy. In order to obtain some check of the theoretical methods we have therefore considered other experimental data which measure related rotational relaxation phenomena. The most widely available such data (and which are also closely related to the desired rotational excitation rates) are pressure broadened linewidth parameters. We have therefore studied the theoretical calculation of line broadening cross sections. Less extensive work has also been done with NMR relaxation rates and Senftleben–Beenaaker effects. Comparison of theoretical and experimental values has generally been quite satisfactory, confirming the accuracy of the theoretical methods.

In the mid 70s and early 80s some of the most exciting work in radioastronomy
was the discovery of 'exotic' species in space, i.e., radicals, ions, and metastable isomers which are too reactive to have been studied in terrestrial labs. It became apparent that our expertise with quantum chemical methods could be useful in identifying some of these species. Work supported by this grant was seminal in identifying $\text{HN}_2^+$, $\text{HCO}_2^+$, $\text{C}_3\text{N}$, and $\text{C}_4\text{H}$ in interstellar space from quantum chemical predictions of their spectral constants. In the mid 80s this grant also supported some related laboratory studies.

A number of publications have resulted from work supported by this grant, and these are listed below. Many of these publications are widely cited, both in the astrophysical and the chemical physics literature.

PUBLICATIONS resulting from research supported by NASA Grant NSG 7105


3. S. Green, B.J. Garrison, and W.A. Lester, "Hartree–Fock and Gordon–Kim Interaction Potentials for Scattering of Closed–Shell Molecules and Atoms: ($\text{H}_2\text{CO,He}$) and ($\text{H}_2\text{,Li}^+$)", J. Chem. Phys. 63, 1154–1161 (1975).


16. S. Wilson and S. Green, "Theoretical Studies of the Butadiynyl and
Cyanoethynyl Radicals: Support for the Identification of C₃N in IRC+10216",

17. R. Ramaswamy, H. Rabitz, and S. Green, "Low Temperature Rotational

18. S. Green, "Rotational Excitation in Collisions Between Two Rigid Rotors:
Alternate Angular Momentum Coupling and Pressure Broadening of HCl by

19. R. Goldflam, S. Green, and D.J. Kouri, "Computational Tests of the Coupled
States Angular Momentum Decoupling Approximation for NMR Spin–Lattice

20. S. Green, "Comment on Fitting Ab Initio Intermolecular Potentials for

21. S. Chapman and S. Green, "Rotational Excitation of Linear Molecules by
Collisions with Atoms: Comparison of Classical and Quantum Methods", J.

22. R. Goldflam, S. Green, and D.J. Kouri, "Infinite Order Sudden Approximation
for Rotational Energy Transfer in Gaseous Mixtures", J. Chem. Phys. 67,

23. R. Goldflam, D.J. Kouri, and S. Green, "On the Factorization and Fitting of

24. S. Green, R. Ramaswamy, and H. Rabitz, "Collisional Excitation of Interstellar

25. S. Green, B.J. Garrison, W.A. Lester, and W.H. Miller, "Collisional Excitation


36. H. Schor, S. Chapman, S. Green, and R.N. Zare, "Dynamics of the Collinear 
37. S. Green, "Vibrational Dependence of Pressure Induced Spectral Linewidths and 
Lineshifts: Application of the Infinite Order Sudden Scattering Approximation", 
38. S. Green and D.G. Truhlar, "Rotational Excitation of Hydrogen Molecules by 
(1979).
39. S. Green, "Surprisal Analysis of Rotational–Translational Energy Transfer: 
(Suppl.) 42, 103–141 (1980).
41. S.E. Cummins, M. Morris, and P. Thaddeus, "On C_4H Versus Vibrationally 
42. S. Green, "Theoretical Microwave Spectral Constants C_2N, C_2N^+, and C_3H", 
43. S. Wilson and S. Green, "Theoretical Microwave Spectral Constants for C_3H^+ 
44. S. Wilson and S. Green, "Theoretical Studies of the HeCN^+ and NeCN^+ 
45. S. Green, "Energy Transfer in NH_3–He Collisions", J. Chem. Phys. 73, 2740 
(1980).
46. S. Green and L.D. Thomas, "On The Use of Pressure Broadening Data to 
Assess the Accuracy of CO–He Interaction Potentials", J. Chem. Phys. 73, 5391 
(1980).


93. S. Green, "Calculation of pressure broadened spectral line shapes including collisional transfer of intensity", NATO advanced research workshop, in press.