FINAL TECHNICAL REPORT

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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., H_2CO, NH_2, H_2O) and also collisions of two rotors (e.g., H_2–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 l–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 H_2, CO, HCN, HN_2^+, H_2CO, NH_3, CS, OCS, HC_3N, SiO (including vibrational excitation), H_2O, CH_3CN, SO_2, C_3H_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 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

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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 HN_2^+, HCO_2^+, C_3N, and C_4H 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

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