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Hemamali Perera
University of Nevada, Las Vegas

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ROTATIONAL ENERGY TRANSFER IN CO + He COLLISIONS

by

Hemamali Perera

Bachelor of Science
University of Peradeniya, Sri Lanka
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Hemamali Perera

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Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative

ABSTRACT

Rotational Energy Transfer in CO+He Collisions

By

Hemamali Perera

Dr. Balakrishnan Naduvalath, Examination Committee Chair
Associate Professor of Chemistry
University of Nevada, Las Vegas

Rotational energy transfer is an important process in a variety of astrophysical environments including the interstellar medium, photo-dissociation regions, and cool stellar atmospheres. The knowledge of the rates of rotational energy transfer in collisions at low temperatures is required to understand the relative intensities of rotational transitions observed in emission from dense interstellar clouds. Specifically, it is necessary to know the rate coefficients for energy transfer between different rotational levels of CO in collisions with the major interstellar species such as H_2, H, and He in order to estimate the radiative cooling rate as applied to the cooling mechanism in the interstellar medium.

Accurate quantum mechanical calculations were carried out to investigate the excitation and de-excitations of rotational levels in a hetero-nuclear molecule at low temperatures by taking the He + CO system as an illustrative example. Collisions between CO molecule in its electronic ground state and He atom provide an ideal test case for comparisons between experiment and theory, because the potential energy surface that governs the collision dynamics has been calculated accurately. The collision dynamics calculations were performed by solving the time-independent Schrödinger equation employing the close coupling method. The rate constants for rotational energy transfer were obtained by Boltzmann averaging the corresponding cross sections. The calculations were performed to investigate the collision energy dependence of total removal of cross sections for rotational levels of $j_i = 0.....12$ in the ground vibrational state ($\nu = 0$) of CO and $j_i = 0, 1, 4$, and 6 in the excited $\nu = 2$ vibrational level of CO. It is found that the van der Waals well in the interaction potential supports a number of shape resonances which significantly influence the relaxation cross sections at energies less than the well depth. The computed results are compared with available experimental and theoretical data.

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Every person has their own stories during their stay in Graduate school. My success in research, dedication and hard work ended up contributing my calculated results in the Journal of Chemical Physics B, titled 'Quenching of rotationally excited CO in cold and ultra-cold collisions with H, He and H_2'. First of all I would like to express my sincere thanks and gratitude to my academic advisor, Dr. Balakrishnan Naduvalath for his constant encouragement, advice and enthusiastic guidance throughout my graduate studies and thesis project. "Thank you for everything you have done for me. It was an absolute pleasure to work for you and work with you in your research group."

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CHAPTER 1

INTRODUCTION

1.1 Purpose of the study

Rotational energy transfer due to atom-molecule or molecule-molecule inelastic collisions is an important process in a variety of astrophysical environments including interstellar clouds, photo-dissociation regions and cool stellar/planetary atmospheres. In these environments, excitation and de-excitation of rotational levels of molecules by collision with an atom or a molecule will play a major role in the cooling mechanism. In order to understand the cooling mechanisms, it is essential to understand the rates of rotational energy transfer in collisions over a wide range of temperatures. The molecular systems in these astrophysical environments include a variety of species; therefore, it is impossible to find the properties of such complex systems analytically. Molecular dynamics simulation circumvents this problem by using valid numerical methods. It represents an interface between laboratory experiments and theory and can be understood as a virtual experiment.

However, advanced atmospheric modeling and spectral synthesis of extra-solar giant planets (EGPs), cool dwarf stars, such as brown dwarfs (BDs), and other cool astrophysical environments require an array of accurate molecular data for the determination of overall and state-to-state cross sections and rate coefficients. The present work provides an explicit comparison between experimental and theoretical rate coefficients over a wide range of temperatures and initial rotational levels. Although the purpose of the present paper is to provide relevant data for astrophysical modeling, there are other areas of importance such as cooling and trapping of molecules and the creation of Bose-Einstein condensates of atoms and molecules[1].

1.2 Significance of the study

Atoms and molecules with their emission at specific frequencies act as probes on the conditions of the early Universe in order to gain an understanding of how galaxies and clusters form.[2] Currently, there still is not a good understanding of these formations. In order to answer these questions we must follow the collapse of initial perturbations in density. A density perturbation that collapses without cooling quickly comes into virial equilibrium. To collapse further requires cooling. Thus, the objects formed are controlled by cooling, predominantly a molecular phenomenon and therefore is called cooling mechanism by the gas-phase chemistry of molecule formation and destruction. As a result it is necessary to know the rate coefficients for energy transfer between atom-molecule collisions in order to estimate the radiative and collisional cooling rate as applied to the cooling mechanism in the interstellar medium.

The gas and dust that exist in open space between stars and galaxies is called interstellar medium. An interstellar cloud is a denser-than-average region of the interstellar medium. Depending on the density, size, and temperature of a given cloud, the species in it can be neutral, ionized (i.e. a plasma), or molecular (molecular clouds). Neutral and ionized clouds are sometimes referred to as diffuse clouds, while molecular clouds are also known as dense clouds. There are more than 142 different species detected in the interstellar medium[3]. The interstellar medium consists of about 90% H_2 and 10 % He. CO is the second most prevalent molecule in the interstellar medium having an abundance of $\approx 10^{-4}$ relative to H_2. Moreover, CO is the most abundant dipolar molecule, so rotational transitions observed in emission from $^{12}C^{16}O$ and its isotopomers are used to locate and map dense interstellar clouds both in the Milky Way and other galaxies.

When a star forms in a molecular cloud, the stellar ultraviolet (UV) radiation has a profound effect on the interstellar medium. Photo-dissociation is one of the major processes through which molecules are broken down but new molecules are being formed because of the vacuum present in the interstellar medium. The UV photons energetic enough to ionize hydrogen will create a sharply bounded ionized hydrogen region around the star, but less energetic UV photons are still energetic enough to photo-dissociate molecules and ionize atoms such as carbon, silicon, and sulfur. Thus, just outside the ionized hydrogen region, the soft UV radiation creates a so-called "photo-dissociation region" (PDR) where hydrogen is neutral, but low ionization potential atoms are ionized and molecules such as CO are photo-dissociated. The relative distribution of atomic, molecular, and ionized gas in certain star formation regions confirms the presence of PDRs. UV radiation causes these interstellar medium gases to excite to a high energy state by photo-dissociation. These excited atoms and molecules reach ground state either by radiative transition or collisional de-excitation leading to the cooling mechanism in the interstellar medium.

In interstellar environments, collisional excitation of CO by H, He and H_2 followed by emission is a powerful cooling mechanism[4]. Moreover, due to the relatively high abundance of CO, emission from rotational states of CO with j>0 provides an important cooling mechanism in the interstellar medium. Comparisons of the emission intensities from different rotational levels and different isotopomers of CO enable to identify the physical conditions in different regions of the interstellar medium. Therefore, it is necessary to know the rate coefficients for energy transfer between different rotational levels of CO in collisions with the major interstellar species such as H_2, H, and He in order to estimate the physical conditions in different regions of the interstellar medium and to estimate the radiative cooling rate. Moreover, knowledge of the rates of rotational energy transfer in collisions at various temperatures is also needed to understand many gas-phase phenomena. Data for rotational energy transfer processes are needed to predict and explain the final quantum state populations of exothermic reactions and chemical lasers. Rotational energy transfer rates influence many fundamental processes and are of particular significance. Processes influenced include sound propagation, absorption, dispersion in a gas medium, the population evolution of non-equilibrium systems like the high temperature environment of flames, the viscosity of a gas, optical pumping processes, and the pressures broadening of spectral linewidths[5].

In addition, it is not practical to measure the rate coefficients for such collisions over a wide range of initial rotational states and temperatures in laboratory since the temperature of the interstellar medium ranges from about 3 K to tens of thousands Kelvin. As a result, there is a need to compute the rate coefficients for a wide range of initial rotational states and temperatures by using valid theoretical methods for modeling astrophysical environments.

1.3 Review of experimental and theoretical studies on He + CO system

The collisions between CO molecules in their ($X^1\Sigma^+$) electronic ground state and He atoms have been the subject of many experimental and theoretical studies, making it a good candidate for benchmark calculations. He-CO is one of the few heavy rotor-noble gas atom systems for which it is possible to calculate the potential energy surface accurately. Many experimental methods have been used to investigate the rotational energy transfer in CO in self-collisions and in collisions with rare-gas (Rg) atoms. The availability of experimental results has been extremely useful in the development of reliable theoretical methods.

The availability of molecular beam and laser techniques has begun to provide very detailed information about collisions in which translational kinetic energy is transferred to rotational degrees of freedom in the electronic ground state. Antonova et al.[6], in one such approach, used a crossed beam apparatus to detect CO state-specifically with a resonantly enhanced multi-photon ionization scheme. Using this approach they derived relative integral cross sections for rotational excitation of CO from its two lowest rotational levels, $X^1\Sigma^+, \nu = 0,\ j = 0$ and 1, in collisions with He at collision energies of 72 and 89 meV.

The He-CO system has been the subject of a large number of experimental and theoretical investigations in determining the vibrational relaxation efficiency in mixtures of He and CO. Recently, a number of papers have been published by Reid et al.[7], addressing the anomalous behavior of the rate coefficient for vibrational relaxation of CO $(\nu = 1)$ by collisions with both ^{3}He and ^{4}He.

Experimental and theoretical results have been carried out for CO-X systems (with X= CO, Ne, He) in order to obtain rotational relaxation cross sections in the 5-100 K temperature interval by Amaral et al.[8]A progression, $\sigma_{r,CO-CO} > \sigma_{r,CO-Ne} > \sigma_{r,CO-He}$ has been identified at the higher temperatures, which changes at T < 20 K to the following progression $\sigma_{r,CO-CO} < \sigma_{r,CO-Ne} < \sigma_{r,CO-He}$. For CO-He collisions, good accordance is found with available theoretical and experimental data in the 20-100 K temperature intervals.

Indeed, very few experiments have directly provided state-to-state rate coefficients or cross sections for rotational energy transfer in collisions between CO and He. State-to-state rate coefficients or cross sections provide rotational energy transfer between defined initial and final states. Belikov et al.[9] have derived such rate constants by observing the evolution of CO rotational level populations in the environment of a free jet expansion, in which the main gas is He. However, such methods are not state resolved and the interpretation of their observations is complex and relies on the details of assumed state-to-state rate coefficient matrix. Smith et al.[10] have published experimental data on CO-He rotational energy transfer using the infrared-infrared (IR-IR) double resonance (DR) technique at room temperature. CO was excited into specific rotational levels $(\mathrm{j_i})$ in $(\nu = 2)$ ranging from $\mathrm{j_i} = 2 - 9$ and populations monitored in $\mathrm{j_f} = 1 - 10$. They found that their data for state-to-state rate coefficients could be fitted extremely well using the calculated rate coefficients, and found strong evidence for the accuracy of the He-CO potential surface of Heijmen et al.[11]

Recently, Carty et al.[12] reported experimental rate coefficients at different temperatures for RET in collisions between CO $(v = 2, j = 0, 1, 4, \text{ and } 6)$ and He using the infrared-vacuum ultraviolet double-resonance technique. The measurements were performed at five temperatures (15, 27, 63, 149 and 294 K) and provide information to test the validity of theoretical results at temperatures lower than 30 K for which no prior experimental results were available. Measurements at such low temperatures are advantageous because the results of the collisions should be particularly sensitive to the attractive part of the potential energy surface.

On the other hand, accurate theoretical data requires precise potential-energy surfaces (PES) and reliable dynamical treatment of the collision processes. Two PES calculations[11,13] have been recently reported for the He-CO system, but doubts still remain that any one potential surface is preferred. Reid et al.[7] reported coupled states (CS) scattering calculations using the Heijmen et al.[11] potential, which has been improved upon at very low energies by Balakrishnan et al.[1] and Zhu et al.[14] who used the more accurate close-coupling (CC) technique. Balakrishnan et al.[1] reported quantum mechanical coupled channel scattering calculations using Heijmen et al.[11] potential energy surface for the ro-vibrational relaxation of CO in collisions with He atoms. The calculated results for the vibrational relaxation of CO $(v = 1)$ are in good agreement with available experimental results.

Cecchi-Pestellini et al.[15] reported a large set of close-coupling (CC) and infinite order sudden (IOS) approximation calculations using the Heijmen et al.[11] potential for energy transfer between rotational levels of CO in collision with He atoms for energies between

5 and 600 cm^{-1}. The results of Cecchi-Pestellini et al.[15] are in good agreement with the available experimental data.

Florian et al.[16] investigated the rotational relaxation in ultra-cold collisions for highly initially excited rotational states, j = 80-230, using the coupled states (CS) method. It is computationally not tractable to perform quantum mechanical close coupling (CC) calculations for such large values of j. Therefore to obtain the desired large-j scattering data both the coupled states (CS) and the effective potential (EP) approximations were adopted for obtaining qualitatively reliable cross sections in the limit of ultra-cold temperatures. This effort was motivated by the possibility of studying molecular collisions at cold and ultracold temperatures particularly as methodologies are currently being developed to cool and trap neutral polar molecules.

The close coupling calculations performed in the present work provide state-to-state cross sections and total removal of cross sections as a function of collision energy as well as total removal rate coefficients and state-to-state rate coefficients over a wide range of temperatures for $\nu = 0$ and 2 vibrational levels of CO in collisions with He using the Heijmen et al.[11] interaction potential. The rotational relaxation studies in this work, have considered rotational levels as high as $j = 12$ for $\nu = 0$.

1.4 Scope of the study

This study aims at a full theoretical understanding of rotational energy transfer processes in collision between He atom and the CO molecule for collision energies ranging from 10^{-6} – 10^{4} cm^{-1}. The objective of the present work is to examine the dynamics of rotationally inelastic energy transfer in He-CO system employing time independent quantum mechanical methodologies, and then comparing these results with existing published experimental and theoretical results.

The findings of this study will illustrate the behavior of rotational energy transfer rate constants over a wide range of temperatures for He + CO inelastic collisions within the $v = 0$ and $v = 2$ vibrational levels. Carty et al.[12] have recently reported experimental results of rotational excitation and de-excitation collisions for the $v = 2$ vibrational level of CO. They compared their results with those reported by Cecchi-Pestellini et al.[15] who reported calculations for the $v = 0$ vibrational level. The present calculations for $v = 2$ will enable a direct comparison with the experimental results of Carty and also test the validity of neglecting the vibrational motion of the CO molecules as in the calculation by Cecchi-Pestellini et al.[15]

CHAPTER 2

METHODOLOGY

2.1 Quantum mechanical approach

The quantum mechanical method involves solutions of the time-independent Schrödinger equation (1), which is used to compute cross sections and rate coefficients.

$$\left(\hat{H}-E\right)\Psi\left(R,r,\theta\right)=0 \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where $\hat{H}$ is the Hamiltonian operator for the atom-diatom system, E is the total energy for the system which represents the sum of the kinetic energy (E_k), and vibration rotation energy (ε_{vj}); $\Psi\left(R,r,\theta\right)$ is the wave function of the atom-diatom system. Calculations of cross sections and rate coefficients of He + CO collisions are computed as a function of kinetic energy for different rotational and vibrational levels.

The atom-diatom Hamiltonian ($\hat{H}$) in the center of mass frame, is given by equation (2).

$$\hat{H} = -\frac{\hbar^2}{2\mu \mathrm{R}}\frac{\partial^2}{\partial R^2}R+\frac{l^2}{2\mu \mathrm{R}^2}+\hat{H}_{CO}+V_{\mathrm{int}}\left(R,r,\theta\right) \quad\ldots\ldots\ldots\ldots(2)$$

$$\mu=\frac{\mathrm{m_{He}}\,(\mathrm{m_C}+\mathrm{m_O})}{\mathrm{m_{He}}+\mathrm{m_C}+\mathrm{m_O}} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where μ is the reduced mass of the helium atom with respect to the CO molecule. In equation (2), the various terms are defined as follows: r is the distance between the carbon and oxygen atoms, R is the distance between the helium atom and the center of mass of the molecule, θ is the angle between r and R, and l is the orbital angular momentum of the He + CO system.

A schematic representation of the Jacobi co-ordinate system for the He-CO system is shown in Figure.1.

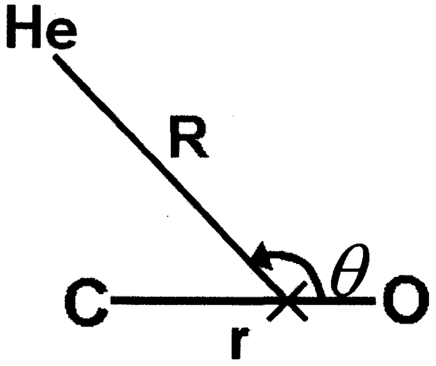

Figure 1.

The He-CO interaction potential $V_{\text{int}}\left(R,r,\theta\right)$ is an important ingredient in our quantum mechanical scattering calculations. The interaction potential can be expanded in terms of Legendre polynomials, as in equation 4, in which $V_\lambda(R,r)$ term describes the radial part and $P_\lambda(\cos\theta)$ term describes the angular dependence of the potential.

$$V_{\text{int}}\left(R,r,\theta\right)=\sum_{\lambda}V_\lambda(R,r)P_\lambda(\cos\theta)\text{..........................}(4)$$

In order to examine the anisotropy of the He-CO interaction potential, the leading terms in the Legendre polynomial expansion of the interaction potential will be analyzed in Chapter 3. The He-CO interaction potential of Heijmen et al.[11] was used because it includes the variation of the interaction potential with respect to the stretching of the CO bond. It is also considered to be superior to the other potentials that are available for this system especially in reproducing the bound state energies of the He-CO complex.

The $\hat{H}_{CO}$ term in equation (2) is given by

$$\hat{H}_{CO} = -\frac{\hbar^2}{2\mu_{CO}r}\frac{\partial^2}{\partial r^2}r + \frac{j(j+1)}{2\mu_{CO}r^2} + V_{CO}(\,r\,)\text{........................}(5)$$

where μ_{CO} is the reduced mass of the CO molecule, j is the rotational angular momentum, and $V_{CO}(\,r\,)$ is the interaction potential of the isolated CO molecule.

In the close coupling (CC) method[17], the wave function $\Psi(\,R,r,\theta\,)$ in equation (1) is expanded in terms of the rotational and vibrational wave functions of the diatomic molecule as follows,

$$\Psi(\,R,r,\theta\,) = \Sigma_{v,j,l} C^J_{vjl}(R)\chi_{vj}(r)Y_{jm}(\theta,\phi)Y_{lm_l}(\theta,\phi)\text{........}(6)$$

where $C^J_{vjl}(R)$ is the expansion coefficient for motion along R, $\chi_{vj}(r)$ is the vibrational wave function of the diatomic molecule, $Y_{jm}(\theta,\phi)$ is the rotational wave function of the diatom, and $Y_{lm_l}(\theta,\phi)$ is the rotational wave function for the atom-molecule system.

Substitution of equation (2) and equation (6) into equation (1) leads to the final close-coupled radial Schrödinger equations.[17]

$$\left[\frac{d^2}{dR^2} + k^2_{vj} - \frac{l(l+1)}{R^2}\right] * C^J_{vjl}(R) = 2\mu\sum_{v'j'l'}\langle vjl|\; V_{\text{int}}(R,r,\theta)\,|v'j'l'\rangle C^J_{v'j'l'}(R)$$

$$\text{....}(7)$$

where the term within the angular brackets on the right hand side is the matrix elements of the interaction potential between the ro-vibrational wave functions. For practical calculations it is convenient to adopt the total angular momentum representation introduced by Arthurs and Dalgarno[17] in which the total angular momentum is given by $J = l + j$. For a given (j, l) combination, total angular momentum quantum numbers $J = |j-l| \ldots\ldots |j+l|$ needs to be included in the close-coupling calculations. The quantity $k_{vj}^2 = \frac{2\mu}{\hbar^2}\left(E - \varepsilon_{vj} \right)$ is the wave vector in the incoming channel where E is the total energy, and ε_{vj} is the ro-vibrational energy of CO molecule. Asymptotic solution of the Schrödinger equation yields the scattering matrix S_{vjl}^J which contains all the relevant information about elastic and inelastic scattering amplitudes. Thus for each value of energy (E), solutions of equation (7) yields the unknown coefficients for $C_{vjl}^J(R)$ which is related to the scattering amplitude and the scattering matrix S_{vjl}^J.

The total cross sections for transitions from an initial rotational-vibrational state labeled by vj to a final vibrational-rotational state labeled by $v'j'$ can be expressed in terms of the scattering matrix S_{vjl}^J,

$$\sigma_{vj \to v'j'}(E_k) = \frac{\pi}{(2j+1)k_{vj}^2} \sum_{J=0}^{J_{\max}} (2J+1) \sum_{l=|J-j|}^{|J+j|} \sum_{l'=|J-j'|}^{|J+j'|} \left| \delta_{jj'} \delta_{ll'} \delta_{vv'} - S_{vjl;v'j'l'}^J \right|^2 \ldots(8)$$

The total removal cross section from a given initial state as a function of the collision energy $E_k = E - \varepsilon_{vj}$ is obtained as follows;

$$\sigma_{vj}^{removal}(E_k) = \sum_{j \neq j'} \sigma_{vj \to v'j'}(E_k) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

where the summation includes only rotationally inelastic transitions in the same vibrational level. State-to-state and total rate coefficients are obtained by averaging the corresponding cross sections over a Boltzmann distribution of velocities of the incident atom:

$$k_{v,j\to v'j'}(T)=\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\left(\frac{1}{k_BT}\right)^2\int_0^\infty \sigma_{v,j\to v'j'}(E_k)E_k\exp(-E_k/k_BT)dE_k\text{.......}(10)$$

where T is temperature and k_B is the Boltzmann constant. The thermally averaged cross sections at a given temperature T are obtained by dividing the rate coefficients with the thermal velocity $[(8k_BT/\pi\mu)^{1/2}]$.

2.2 Computational details

The quantum mechanical scattering calculations were performed using the non-reactive scattering program called MOLSCAT developed by Hutson and Green[18]. MOLSCAT solves the coupled channel Schrödinger equation described above and calculates the state-to-state cross sections for rotational and vibrational transitions. The outcome of a molecular collision process is described quantum-mechanically by the S-matrix [equation (7)], which contains information on the probability amplitudes and phases for the various possible outcomes. Experimental observables, such as differential and integral cross sections, can be written in terms of S-matrix elements. MOLSCAT does this by solving the time-independent Schrödinger equation using the close coupling (CC) method, coupled states (CS) approximation and infinite order sudden (IOS) method. Among this the CC method provides the most accurate results. The time-independent Schrödinger equation is solved by the CC method in this study. A difficulty in using the CC method is that it is computationally feasible only for systems which have a rather small number of rotational and vibrational levels accessible at collision energies of interest.

The MOLSCAT program requires information about the collision system of interest. In particular, the types of collision partners for example, linear rigid rotors, vibrating diatomic molecules, or asymmetric top rotors. In addition it is necessary to provide the program which rotational (and possibly vibrational) levels of each to include in the expansion of the total wavefunction $\{ \Psi(R,r,\theta) \}$ as well as to describe the intermolecular forces between the two collision partners at the collision energies of interest. Other input parameters may be used to provide finer control of the calculation, specify optional processing such as the calculation of line shape cross sections, or options such as saving the S-matrices to a data file in order to be used to calculate further scattering properties. Details of the input parameters used in the calculations are given in the Appendix.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Radial and angular dependence of the He – CO interaction potential

In order to examine the dependence of the radial and angular expansion terms of the interaction potential of the system, we computed the leading terms in the angular expansion of the interaction potential [equation (4)] for different values of λ with the inter-nuclear distance r fixed at its equilibrium value, $r_{eq} = 2.132$ a.u. The first five V_λ's with $\lambda = 0-4$ are shown in fig. 2.

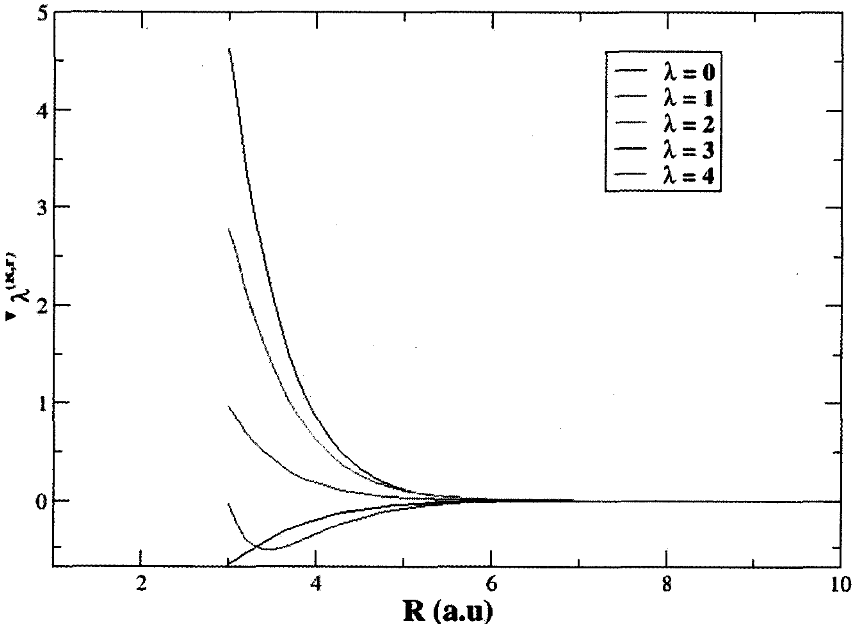

Fig. 2: Angular expansion coefficients of the interaction potential for He-CO System as a function of R at $r = r_{eq}$.

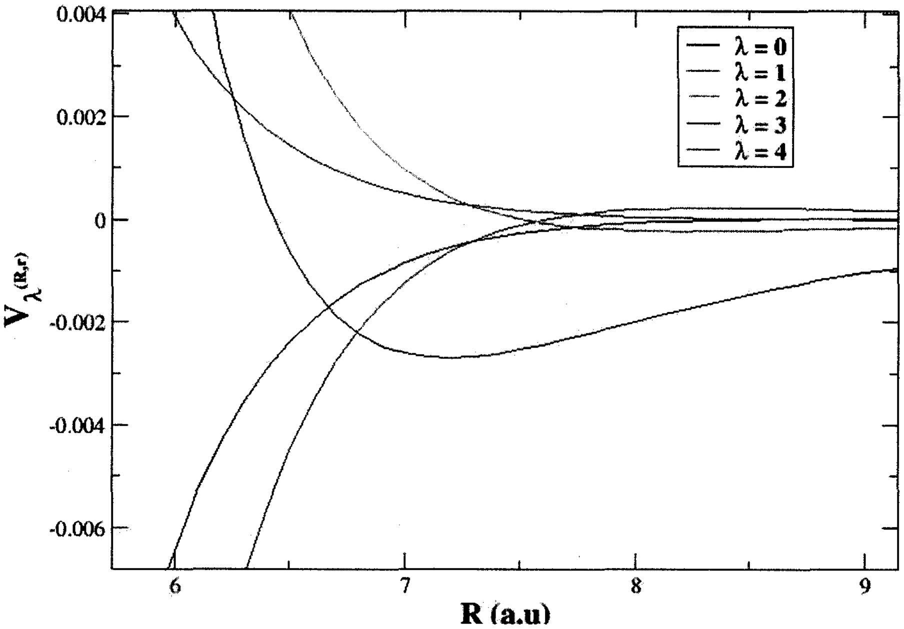

Fig. 3: Angular expansion coefficients of the interaction potential for He-CO System as a function of R = 5.5 – 9.0 a.u

As shown in Fig. 2 and Fig. 3 the spherically symmetric term, V_0 is repulsive at short range but has an attractive part in the long-range due to Van der Waals interaction. The radial terms of higher λ coefficients such as V_1, V_2, V_3 and V_4 are responsible for driving the rotational transitions. Since higher V_λ terms are smaller one would expect that low energy rotational transitions of the CO molecule is mostly controlled by the first few terms in the angular expansion. Each $V_\lambda(R,r)$ term is connected to a Δj term, where $\Delta j = j_f - j_i$, is the change in the rotational quantum number of the CO molecule as illustrated graphically in 3.3 section. The efficiency of higher Δj transition is determined by the magnitude of higher $V_\lambda(R,r)$ terms.

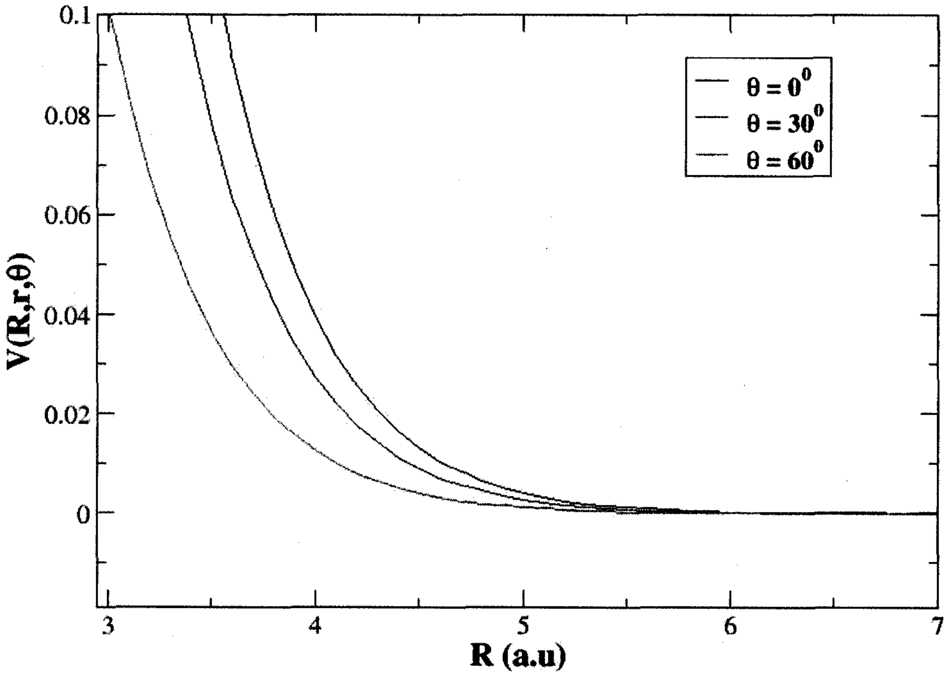

Fig. 4: Radial dependence of the He-CO interaction potential for different angles: $\theta = 0^0$, 30^0 and 60^0 as a function of R at $r = r_{eq}$.

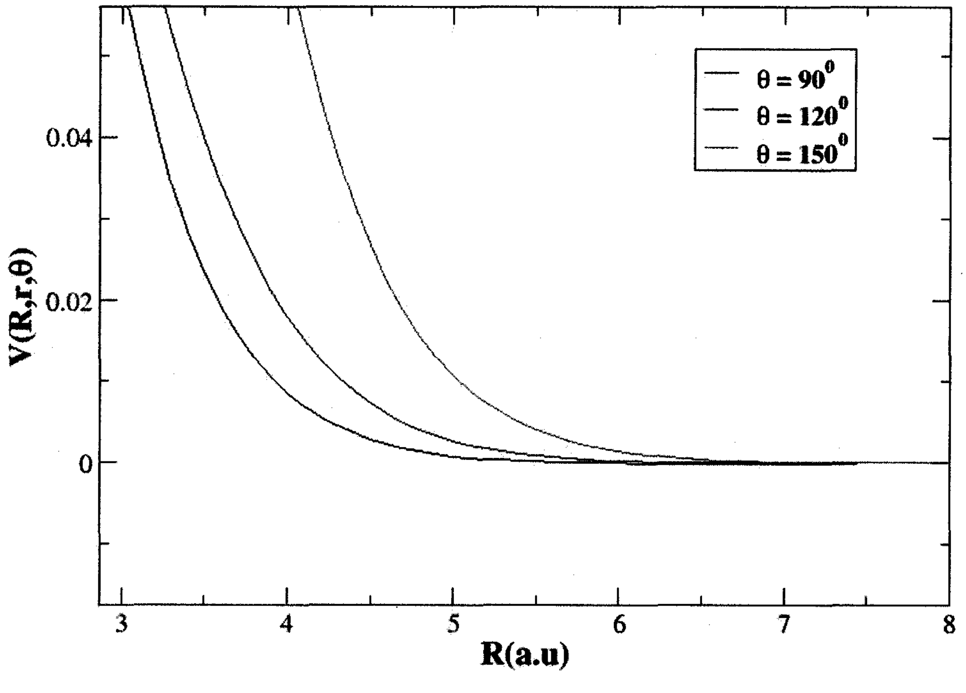

Fig. 5: Radial dependence of the He-CO interaction potential for angles, $\theta = 90^0$, 120^0 and 150^0 as a function of R at $r = r_{eq}$.

Figure 4 and Figure 5 provide radial dependence of the of He - CO interaction potential for angles, $\theta = 0^0, 30^0, 60^0, 90^0, 120^0$, and 150^0. It is seen that the potential varies significantly with the angle of approach of He to the CO molecule.

3.2 Cross sections and rate coefficient results for $(\nu = 0)$ state of CO

The calculations presented here were carried out over a period of one year, in a variety of computers at UNLV chemistry department. The calculations are computer intensive and the first few months of my time was devoted to familiarizing with FORTRAN programming and UNIX/LINUX operating system in which the MOLSCAT program was implemented.

Also the convergence tests, testing of the program and to get the final production calculations it took more than 6 months. Some high energy calculations with higher values of angular momentum took about 2 months of dedicated computer time.

We first present results for He + CO collisions in which the vibrational level of the CO molecule is taken to be zero. A large number of convergence tests have been carried out to ensure convergence of the cross sections and rate coefficients with respect to the basis set size as well as other parameters that enter into the solution of the Schrödinger equation. Figure 6 compares the collision energy dependence of total quenching cross-sections of rotationally-inelastic, vibrationally-elastic collisions of CO calculated using Equation 8. Calculations have been performed for ten initial rotational states, $(\nu = 0,\ j_i = 1, 2, ... 10)$ of He + CO non-reactive collisions as a function of collision energy in the range $10^{-6} - 10^4$ cm^{-1}. The cross sections from each initial rotational state of CO are summed over all final rotational states to obtain the total removal cross section as a function of collision energy as given by Equation 8. The cross sections vary inversely with collision energy as the collision energy approaches zero for energies lower than 10^{-4} cm^{-1}. This is due to the onset of the Wigner regime[19] for which ($\sigma \sim$ *const. / velocity*).

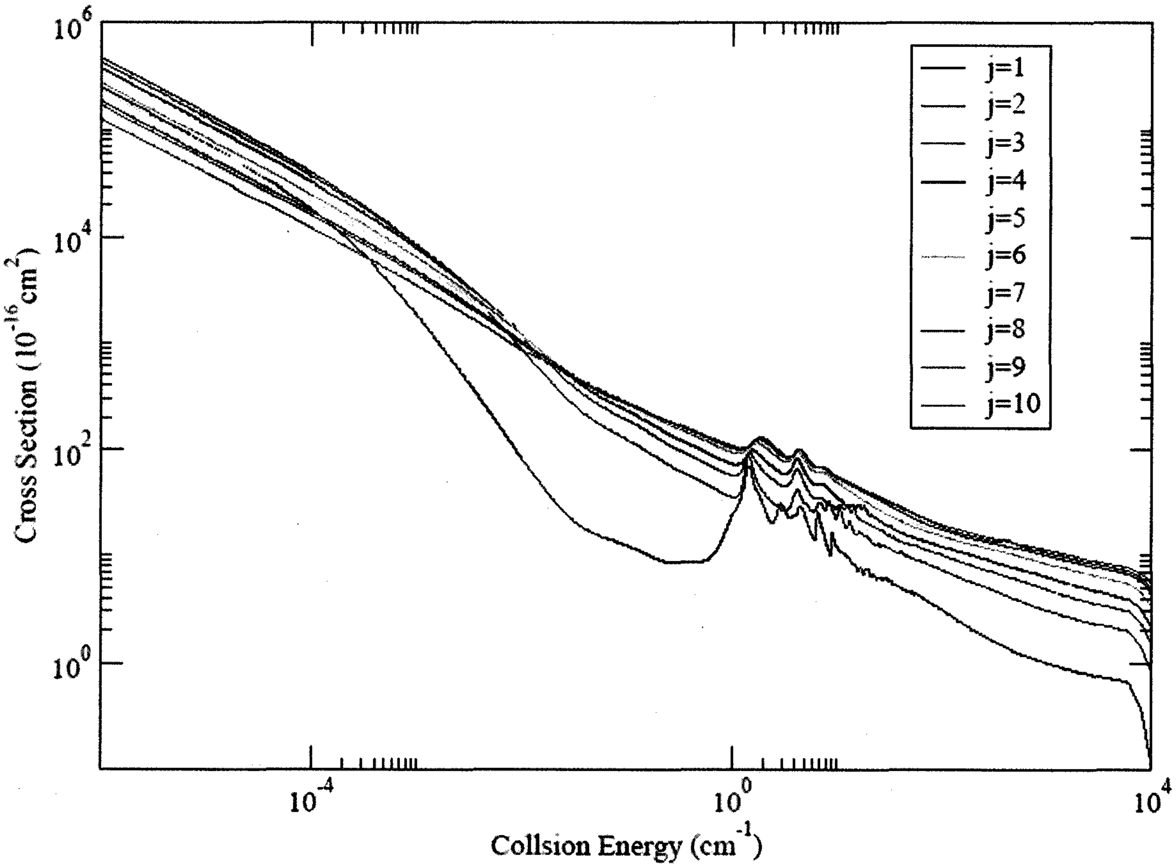

Figure 6: Cross sections for quenching of the $\nu = 0$, $j_i = 1, 2, ...$ 10 levels of CO in collisions with He as a function of the collision energy.

The van der Waals well in the interaction potential supports a number of shape resonances which significantly influence the relaxation cross sections at energies less than the van der Waals well depth (1-20 cm^{-1}). The narrow oscillations that are observed

(Figure 6) in the energy range 1.0-10.0 cm^{-1} are due to shape resonances supported by the formation of quasibound levels or van der Waals complexes. These long-lived complexes allow multiple collisions to occur, which strongly enhance the rotational relaxation processes and may give rise to open-channel (shape) and closed-channel (Feshbach) resonances. The experimental cross sections for total removal of CO from selected rotational levels are obtained by dividing their measured rate coefficients by the mean relative velocities $[(8k_B T / \pi\mu)^{1/2}]$ at the temperatures of the experiments.

State-to-state cross sections for $j = 0 \rightarrow 1$ rotational excitation in the $\nu = 0$ vibrational level of CO are compared in Figure 7 with the results of Cecchi-Pestellini et al.[15] as a function of the collision energy. The agreement between present calculations and calculations by Cecchi-Pestellini et al.[15] is found to be excellent.

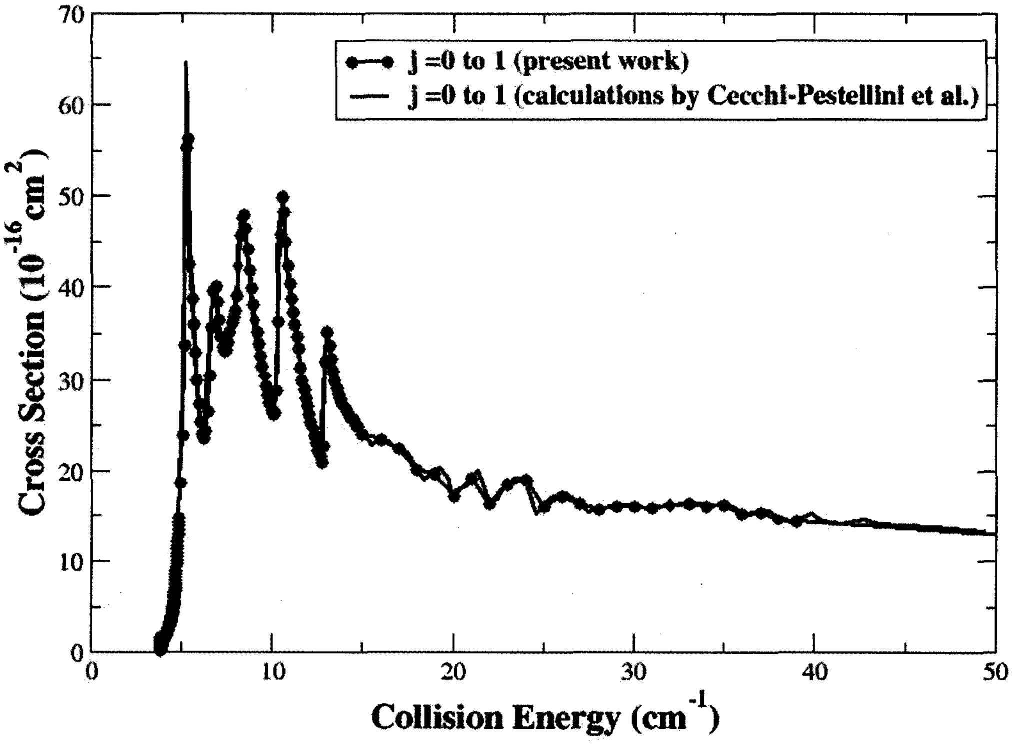

Figure 7: Rotational excitation cross section as a function of the collision energy

The quenching rate coefficients for He-CO (j) for j = 1-10 are computed using Equation 9. The rate coefficients as a function of the temperature in the range of 10^{-3} - 100K are shown in Figure 8. The enhancement in the rate constants for T=1-10K is due to the presence of shape resonances.

The quenching rate coefficients are finite in the limit of low temperatures because the corresponding cross section varies inversely with velocity as explained by Wigner's law ($\sigma \sim$ *const. / velocity*). In addition, the calculated results for j = 1 have been compared with the previous theoretical calculations performed by Cecchi-Pestellini et al.[15] and the agreement is excellent.

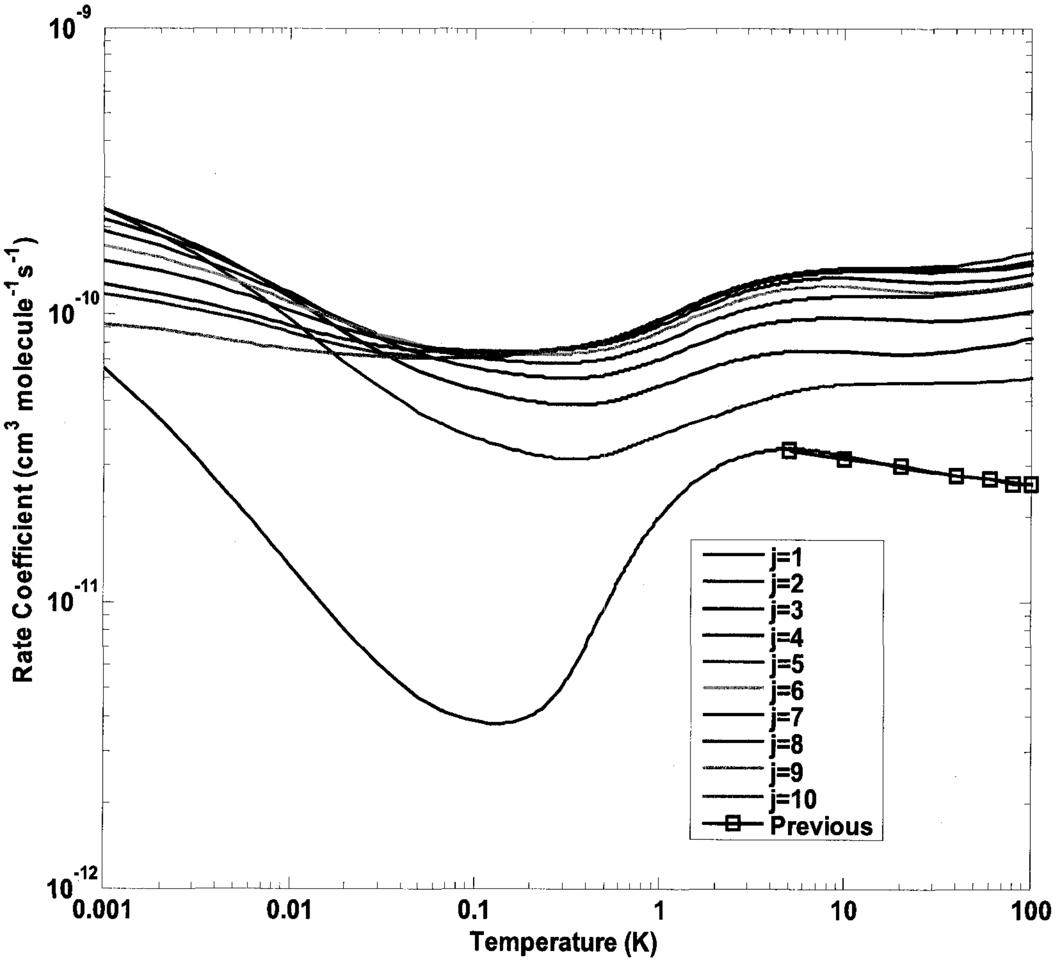

Figure 8: Quenching rate coefficients for initial $v = 0$, j = 1....10 states of CO in collision with He atoms. Solid lines: present calculations; Line with squares: previous calculations by Cecchi-Pestellini et al.[15]

We would also like to emphasize that theoretical calculations can be used to calculate rate coefficient values at very low temperatures even though experimental techniques have not been developed to measure rate coefficients at such low temperatures. Since results are generally sensitive to details of the interaction potential at low energies comparison between theory and experiment can be used to derive precise intermolecular potentials.

3.3 State-to-state rate coefficient results for $(\nu = 2)$ state of CO

State-to-state cross sections are thermally averaged over the kinetic energy distribution to yield the corresponding rate coefficients at a temperature T as given by Equation 10. A comparison of measured and calculated results has been provided for excitation and de-excitation rate coefficients for CO as a function of final rotational levels. Figures 9 to 12 provide comparison between the present calculations and experimental data of Carty et al.[12] for state-to-state rotational transitions in CO $(\nu = 2)$ for initial rotational levels $j_i = 0, 1, 4$ and 6 at a temperature of 294K.

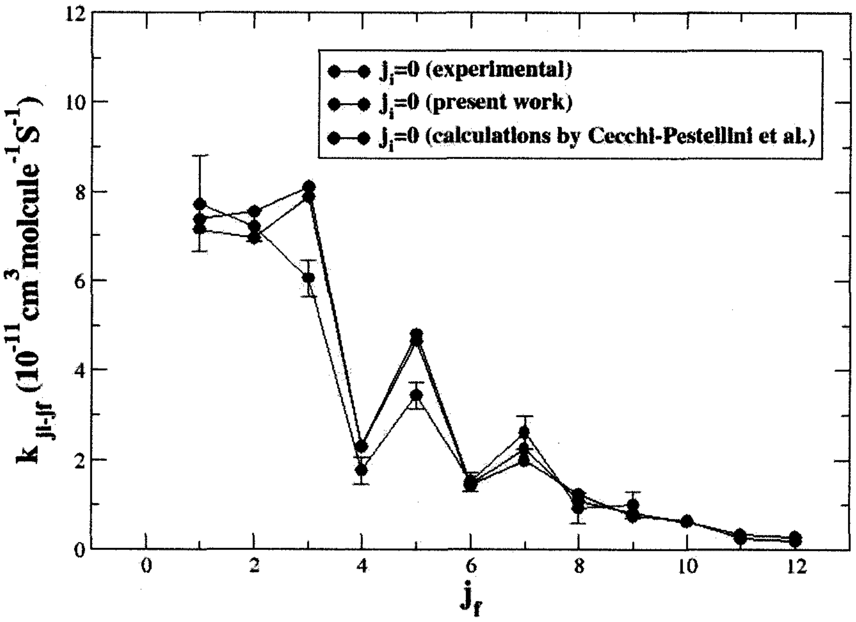

Figure 9: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 0$ at 294K

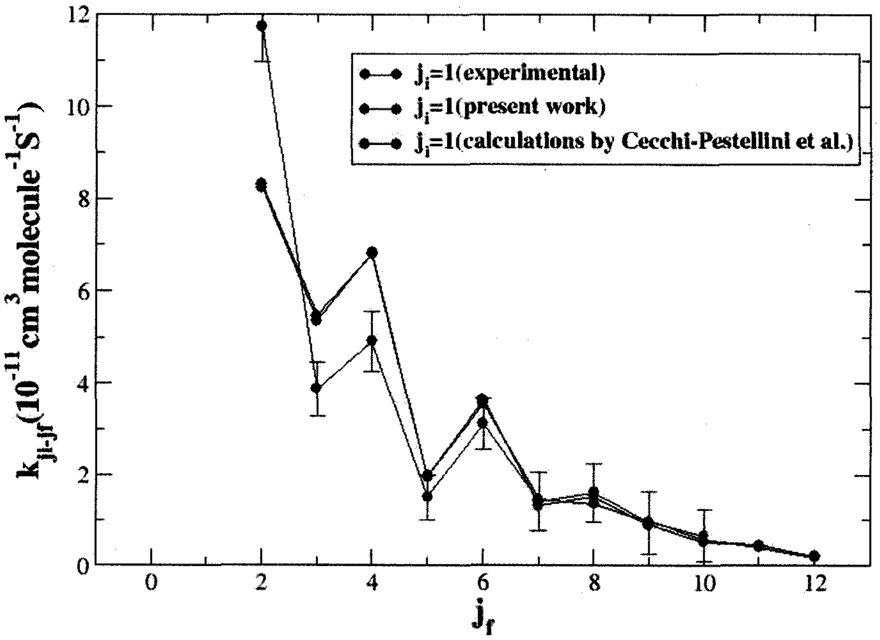

Figure 10: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 1$ at 294K

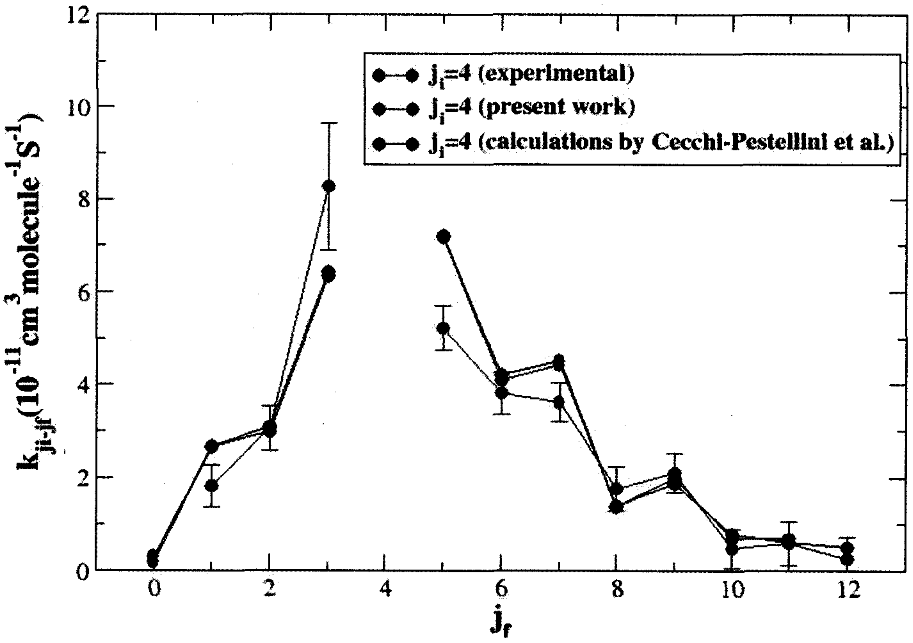

Figure 11: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 4$ at 294K

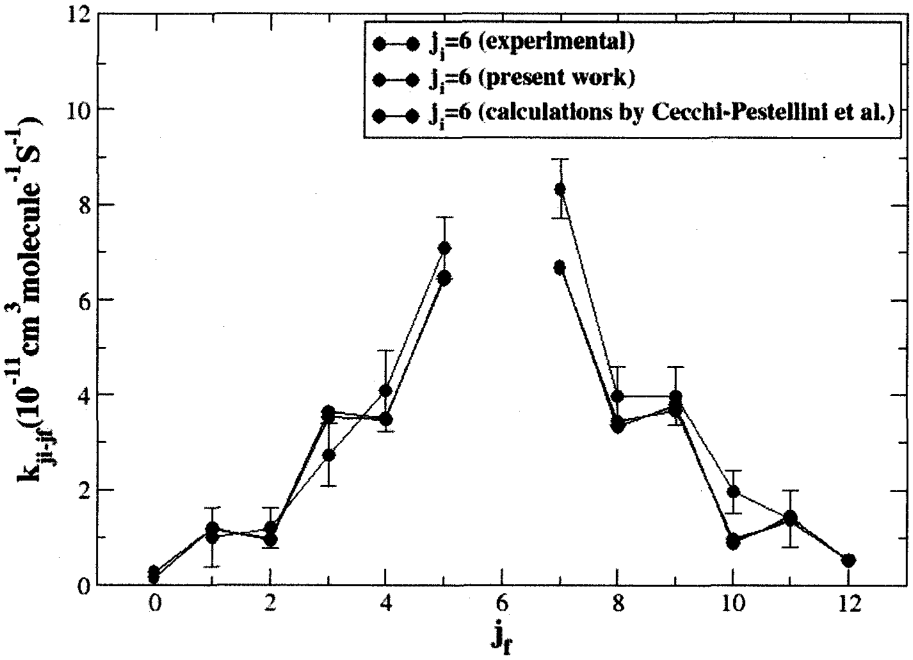

Figure 12: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 6$ at 294K

Experimental results are given by red circles with error bars in Fig. 9 to 12 and the present results are shown by black circles. The results of Cecchi-Pestellini et al.[15] obtained for $v = 0$ of CO are shown by blue circles. The agreement between theory and experiment is found to be excellent.

Figures 9 and Figures 10 display state-to-state excitation rate coefficients as a function of final rotational levels of the CO molecule and Figures 11 and Figures 12 display state-to-state de-excitation rate coefficients on the left side and excitation rate coefficients on the right hand side as a function of final rotational levels of the CO molecule. Note that the state-to-state rate coefficients display an oscillatory structure due to the anisotropy of the He-CO interaction potential.

This anisotropy shows that the state-to-state rate coefficients oscillate with Δj, giving favorable outcome to odd Δj versus even Δj, as found by Antonova et al.[6] where

$\Delta j = j_f - j_i$, is the change in the rotational quantum number of the CO molecule. The observation that odd Δj transitions are favored in rotationally inelastic CO-He collisions, is especially apparent at T=294K and less apparent at T=63K and T=15K; this demonstrates that the CO-He interaction potential must be particularly anisotropic.

Figures 13 to16 display similar comparison between experiment and theory for state-to-state rate coefficients at 63K and Figures 17-19 at 15K.

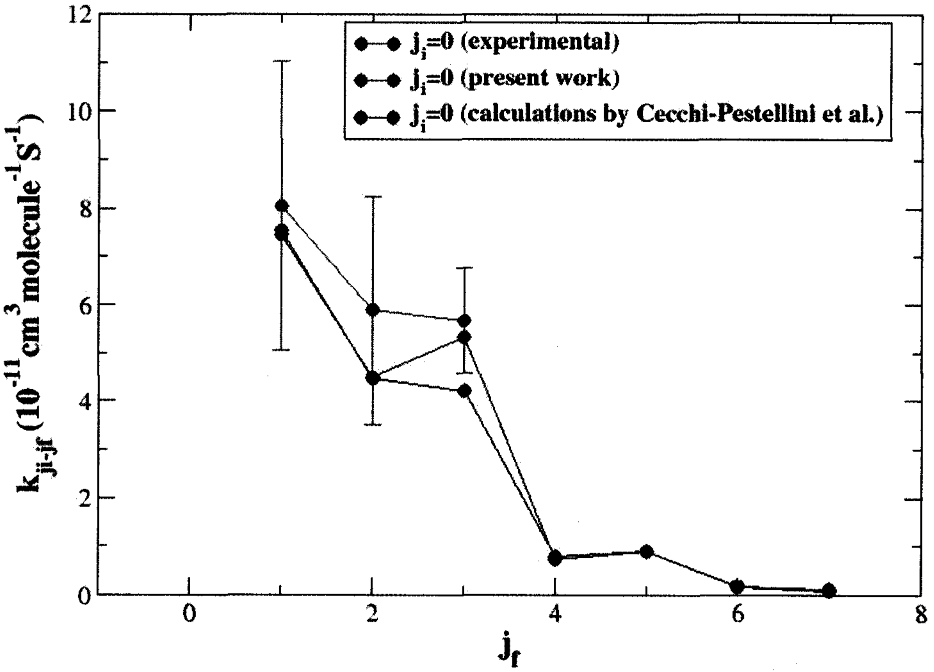

Figure 13: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 0$ at 63K

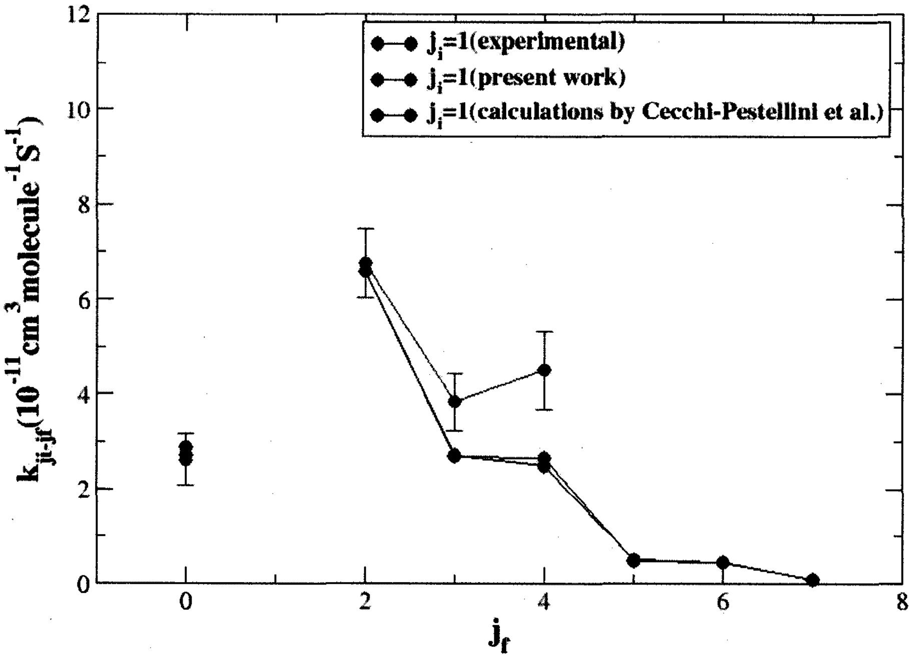

Figure 14: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 1$ at 63K

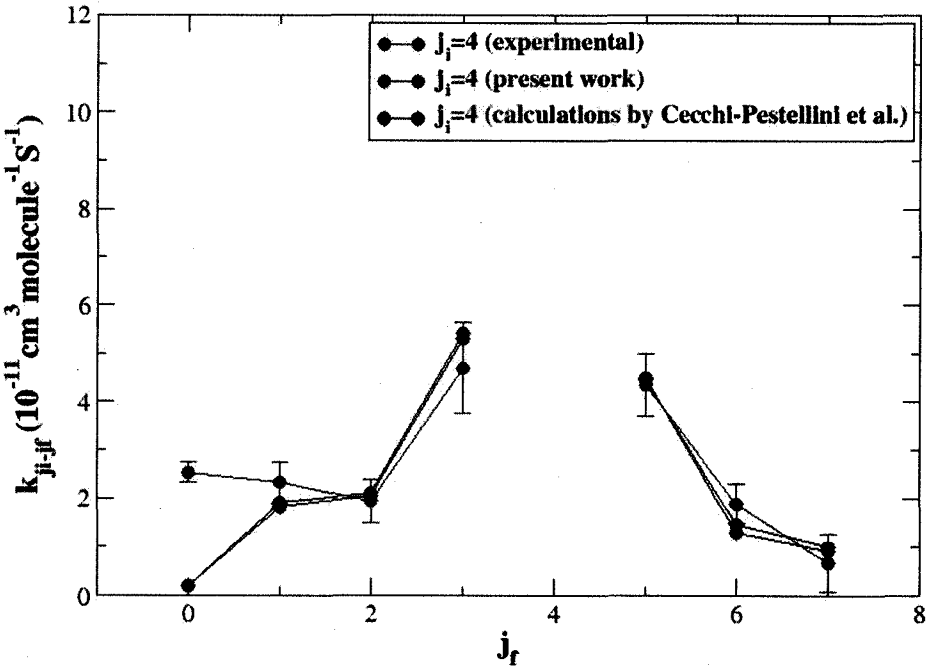

Figure 15: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 4$ at 63K

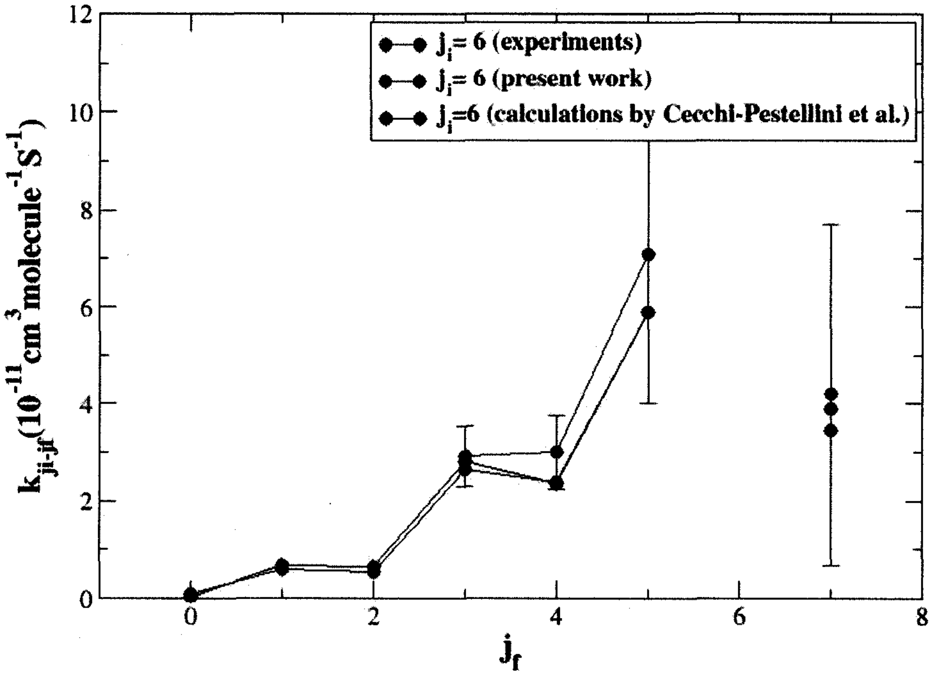

Figure 16: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 6$ at 63K

The oscillatory behavior of rate coefficients ($k_{j_i-j_f}$) versus Δj transitions becomes narrower so the rate coefficients become suppressed, as the temperature lowers from 63K to 15K. Measurements at such low temperatures are important because the collision results should be particularly sensitive to the attractive part of the potential energy surface.

Overall, there is very good agreement between the experimental and theoretical results illustrated in figures 9 to 19. The small differences, particularly at low temperature may be due to inaccuracies in the Heijmen et al.[11] potential energy surface that was used in the present calculations and calculations by Cecchi-Pestellini et al.[15]. There is an excellent agreement between present theoretical results and calculations by Cecchi-Pestellini et al.[15] shown here except at a few points in Figures 17 and Figures 19. For example, a slight discrepancy occurs in Figure 17, at $j_f = 3$, where the values of theoretical and calculations by Cecchi-Pestellini et al.[15] are somewhat larger. The differences may be due to the fact that calculations of Cecchi-Pestellini et al.[15] are carried out for the $v = 0$ vibrational level of CO whereas the present calculations are performed for $v = 2$ vibrational level. Results illustrate that rotational excitation/de-excitation rate constants are not strongly sensitive to the initial vibrational level of CO molecule at least for low vibrational levels. The present results are in agreement with the results of Yang et al.[20]

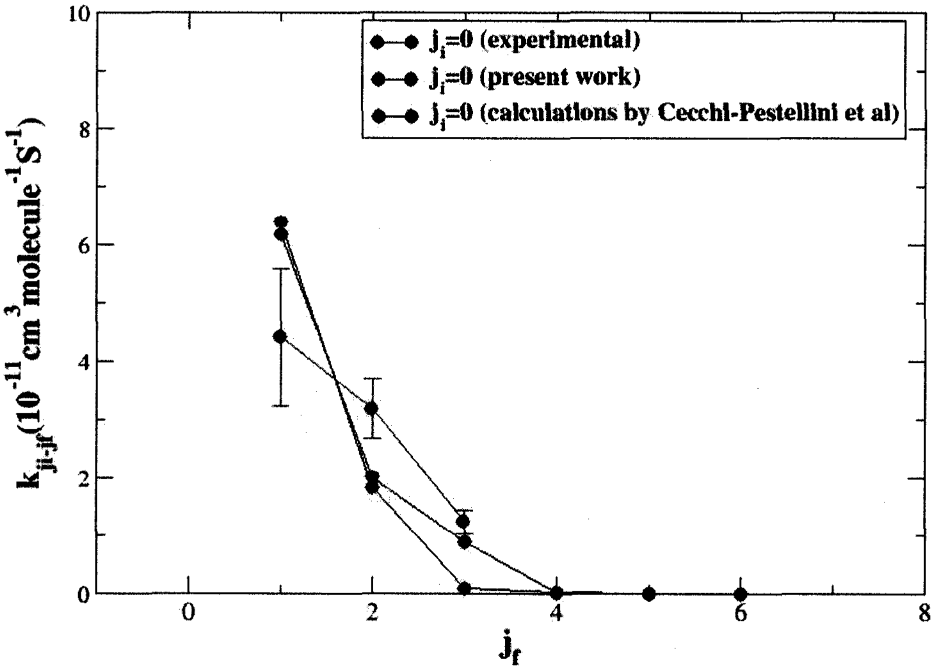

Figure 17: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 0$ at 15K

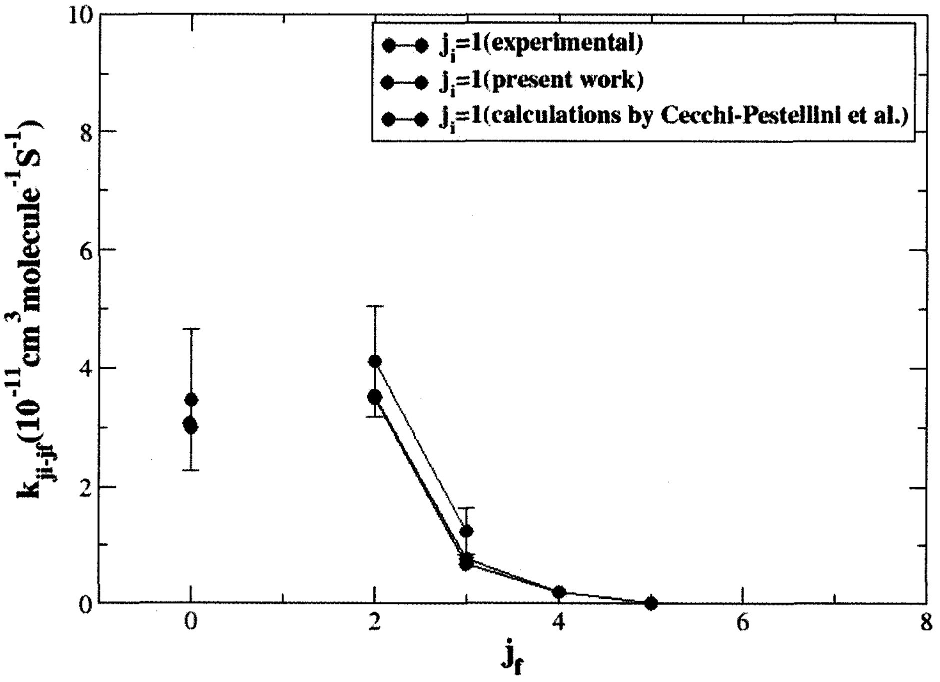

Figure 18: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 1$ at 15K

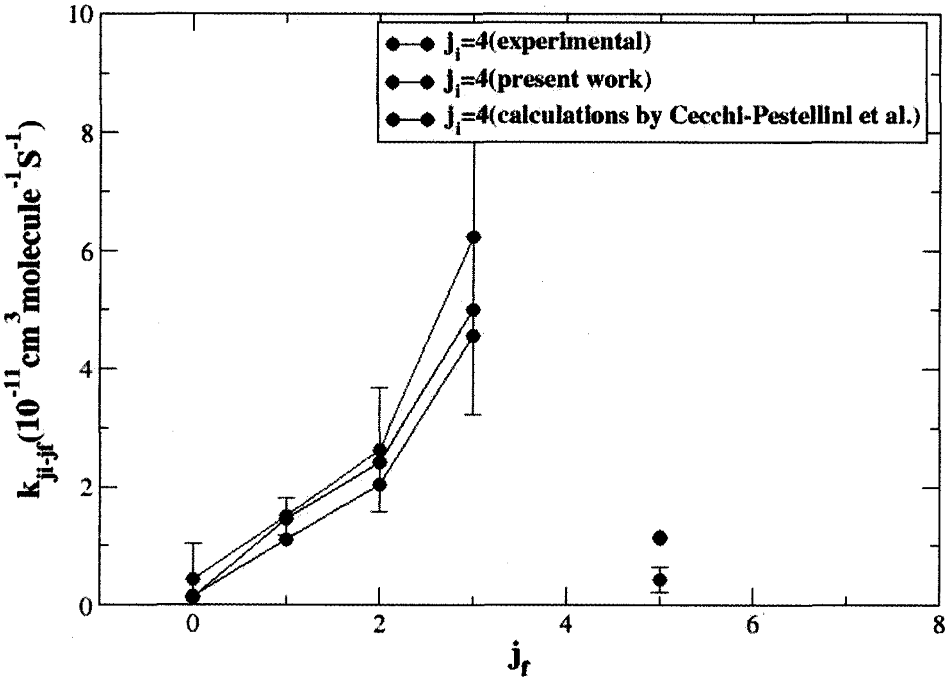

Figure 19: State-to-state rate coefficients as a function of final rotational quantum number for initial rotational level $j_i = 4$ at 15K

CHAPTER 4

SUMMARY AND CONCLUSIONS

4.1 Summary and Conclusions

The primary purpose of this study is to investigate the rotational energy transfer in atom-molecule collisions using the He + CO system as an illustrative example. Cross sections for the quenching of CO molecules from ro-vibrational levels $\nu = 0$, $j_i = 1, 2, \ldots.. 10$ in He-CO collisions have been calculated using an explicit quantum mechanical close-coupling approach with the interaction potential of Heijmen et al.[11] The total removal cross sections show resonance structures at low energies due to the van der Waals well.

The quenching rate coefficients attain finite values in the limit of low temperature in accordance with Wigner threshold law. The state-to-state rate coefficients from selected rotational levels $j_i = 0,\ 1, 4, 6$ of CO $(\nu = 2)$ have been calculated at 15, 63 and 294K using the coupled channel method. The calculated state-to-state rate coefficients are found to be in excellent agreement with previous calculated results of Cecchi-Pestellini et al.[15]. Computed results are also in excellent agreement with the experimental results validating the accuracy of He-CO potential surface by Heijmen et al.[11] and the computational scheme employed. Since, very good agreement exists between present theoretical calculations with CO in its $\nu = 2$ vibrational state and calculations by Cecchi-Pestellini et al.[15] for $\nu = 0$, the rotational energy transfer appears to be independent of initial vibrational levels, at least for low vibrational quantum numbers. Low temperature rotational energy transfer in CO molecules plays an important role in many interstellar environments. We believe that the data presented here will be useful for modeling astrophysical environments where He-CO collisions induce rotational transitions in the CO molecule.

APPENDIX

FORMAT OF INPUT DATA

MOLSCAT consists of 3 blocks of NAMELIST data in the following order named as &INPUT, &BASIS and &POTL. &INPUT block provides overall control of the calculation such as collision energies, partial wave limits, print options, optional calculations and choice of tolerances for the numerical propagator. &BASIS block describes the collision type, the rotation-vibration basis set and dynamical approximations. &POTL block describes the intermolecular potential. In &INPUT data, reduced mass for collision in atomic mass units is listed by URED variable. The URED parameter for He-CO system is 3.5 amu (atomic mass unit) as given by equation (3). The total energies at which scattering calculations are performed are controlled by the array ENERGY and the variables NNRG, DNRG and EUNITS. If DNRG=0.0, calculations will be performed for the NNRG energies listed in the ENERGY array. If DNRG is not 0.0, calculations will be performed at NNRG equally spaced energies, DNRG apart, starting at ENERGY (1). The default maximum allowed value of NNRG is currently 100 but it can be increased if needed. The units of ENERGY and DNRG are determined by the integer variable EUNITS, we used EUNITS = 1 which corresponds to energy in cm^{-1}. In the present work calculations have been performed for a wide range of energies extending from 10^{-6} to10^{4} cm^{-1}.

It is necessary to choose a suitable numerical method for solving the coupled equations and for many systems a good choice is the Hybrid modified log-derivative Airy propagator of Manolopoulos and Alexander[21] which is listed by INTFLG parameter. In the absence of special circumstances, INTFLG = 8 is a good choice, infact INTFLG = 8 was used in the present work and it is particularly useful for systems which have strong long range interactions and it is recommended as a general-purpose propagator for cross section calculations. RMIN and RMAX are used to choose the starting and finishing points for integrating the coupled equations, thus the input value of RMAX is the smallest distance at which the propagator may terminate. In some modes, since MOLSCAT may determine RMIN, and RMAX internally, one needs to carry convergence tests by varying RMIN and RMAX values for different total angular momentum (JTOT) values. In most of the present calculations, RMIN = 1 au was used and RMAX was varied from 30 au to 100 au depending on the energy of the calculation.

It is necessary to do calculations for a range of total angular momentum (J) partial waves; they are labeled by the variable JTOT. MOLSCAT has built-in loops over total angular momentum JTOT and symmetry type M. M is used differently for different decoupling schemes, M takes values of 1 and 2 for odd and even parity label respectively for generating close-coupling equations. The loop over JTOT is controlled by the three input variables JTOTL, JTOTU and JSTEP as the lowest, highest and the increment, respectively. The program will loop from JTOTL to JTOTU in steps of JSTEP. In most cases in the present calculations JTOTL =0 and JTOTU was varied from 5 to 180 depending on the total energy of the calculation. In particular, one needs to consider only a small number of partial waves at low energies. However at low energies results are more sensitive to details of the interaction potential as well as other parameters that enter into the numerical solution of the Schrödinger equation. In particular, large RMAX and small increment in R are needed for accurate results at low energies. At higher energies, a large number of partial waves are needed to obtain converged cross sections.

In &BASIS data, information about the rotational or vibrational levels are provided. The type of basis functions and the coordinate system needed to describe the interaction potential depend on the nature of the colliding species. The collision type is described by an internal variable ITYP. ITYP = 7 was used in the present work which describes collision of a vibrating diatomic molecule with a structureless atom with different potentials for different rotational levels. In &POTL data, the length scaling factor used internally by MOLSCAT is denoted by RM. Variables that control the integration, such as RMIN, RMAX are in units of RM and it is specified in units of Angstroms (RM = 1.0) or atomic units (RM = 0.5291770644). The potential is expanded in angular functions appropriate to the collision type and specified by MXLAM parameter. MXLAM describes the number of angular terms in the potential expansion. In scattering calculations the angular dependence of the potential is represented as an expansion in Legendre polynomials as explained in methodology.

REFERENCES

1. N. Balakrishnan and A. Dalgarno, R. C. Forrey, J. Chem. Phys. **113**, 621-627 (2000)

2. S. Lepp, P. C. Stancil and A. Dalgarno, J. Phys. B, At. Mol. Opt. Phys. **35,** R57-R80 (2002)

3. E. Herbst, J. Phys. Chem., **109**, 4017 (2005)

4. B. Yang, H. Perera, N. Balakrishnan, R. C. Forrey and P. C. Stancil, J. Phys. B. At. Mol. Opt. Phys. **39**, S1229-A1239 (2006)

5. S. P. Phipps, T. C. Smith, G. D. Hager, M. C. Heaven, J. K. McIver, and W. G. Rudolph, J. Chem. Phys. **116**, 9281 (2002)

6. S. Antonova, A. Lin, A. P. Tsakotellis, and G. C. McBane, J. Chem. Phys. **110**, 2384 (1999)

7. P. Reid, C. J. S. M. Simpson, and H. M. Quiney, Chem. Phys. Lett. **246**, 562 (1995); J. Chem. Phys. **107**, 9929 (1997), J. P. Reid and C. J. S. M. Simpson, Chem. Phys. Lett. **280**, 367 (1997)

8. G. A. Amaral, F. J. Aoiz, L. Banares, J. Barr, V. J. Herrero, B. Martinez-Haya, M. Menendez, G. A. Pino, I. Tanarro, I. Torres, and J. E. Verdasco, J. Chem. Phys. **109**, 9402-9413 (2005)

9. M. M. Ahern, D. A. Steinhurst, and M. A. Smith, Chem. Phys. Lett. **300**, 681 (1999), A. E. Belikov and M. A. Smith, J. Chem. Phys. **110**, 8513 (1999), A. E. Belikov, M. L. Strekalov, and A. V. Storozhev, Chem. Phys. Lett. **304**, 253 (1999), A. E. Belikov, Mol. Phys. **98**, 343 (2000); A. E. Belikov, A. V. Storozhev, M. L. Strekalov, and M. A. Smith, ibid. **99**, 559 (2001)

10. T. C. Smith, D. A. Hostutler, G. D. Hager, M. C. Heaven, and G. C. McBane, J. Chem. Phys. **120**, 2285 (2004)

11. T. G. A. Heijmen, R. Moszynski, P. E. S. Wormer, and A. Vander Avoird, J. Chem. Phys. **107**, 9921 (1997)

12. D. Carty, A. Goddard, I. R. Sims and I. W. M. Smith, J. Chem. Phys., **121**, 4671 (2004)

13. R. Kobayashi, R. D. Amos, J. P. Reid, H. M. Quiney, and C. J. S. M. Simpson, Mol. Phys. **98**, 1995 (2000)

14. C. Zhu, N. Balakrishnan, and A. Dalgarno, J. Chem. Phys. **115**, 1335 (2001)

15. C. Cecchi-Pestellini, E. Bodo, N. Balakrishnan, A. Dalgarno, Astrophysical J. **571**, 1015 (2002)

16. P. M. Florian, M. Hoster, and R. C. Forrey, Phys. Rev. A **70**, 032709 (2004)

17. A. M. Arthus and A. Dalgarno, Proc. R. Soc. London, Ser. A **256**, 540 (1963), W. A. Lester, Jr., in Dynamics of Molecular Collisions, Part A, edited by W. H. Miller (Plenum, New York, 1976), pp. 1-32

18. J. M. Hutson and S. Green, MOLSCAT computer code, version 14 (1994), distributed by Collaborative Computational Project No. 6 of the Engineering and Physical Sciences Research Council (UK)

19. E. P. Wigner, Phys. Rev. **73**, 1002 (1948)

20. Benhui Yang and P. C. Stancil, N. Balakrishnan, R. C. Forrey, J. Chem. Phys. **123,** 134326 (2005)

21. D. E. Manolopoulos and M. H. Alexander, J. Chem. Phys. **86**, 2044 (1987)

VITA

Graduate College
University of Nevada, Las Vegas
Hemamali Graduate Student

Home Address:
9127 Heavenly Valley Ave
Las Vegas, Nevada 89147

Degrees:
Bachelor of Science, General Science, 1994
University of Peradeniya, Sri Lanka

Publications:

Quenching of rotationally excited CO in cold and ultracold collisions with H, He and H_2
Benhui Yang, Hemamali Perera, N Balakrishnan, R C Forrey and P C Stancil,
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Thesis Title: Rotational Energy Transfer in CO+He collisions

Thesis Examination Committee:
Chairperson, Dr. Balakrishnan Naduvalath, Associate Professor, Ph. D.
Committee Member, Dr. Clemens Heske, Ph. D.
Committee Member, Dr. Dennis W. Lindle, Ph. D.
Committee Member, Dr. Stephen Lepp, Ph. D.