

Close-coupling study of rotational energy transfer of CO($v=2$) by collisions with He atoms

Benhui Yang* and P. C. Stancil†

*Department of Physics and Astronomy and the Center for Simulational Physics
The University of Georgia, Athens, Georgia 30602-2451*

N. Balakrishnan‡

Department of Chemistry, The University of Nevada, Las Vegas, Nevada 89154

R. C. Forrey§

*Department of Physics, Penn State University,
Berks-Lehigh Valley College, Reading, Pennsylvania 19610*

Abstract

Quantum close-coupling scattering calculations of rotational energy transfer in vibrationally excited CO due to collisions with He atom are presented for collision energies between 10^{-5} and ~ 1000 cm^{-1} with CO being initially in vibrational level $v = 2$ and rotational levels $j = 0, 1, 4,$ and 6 . The He-CO interaction potential of Heijmen *et al.* [J. Chem. Phys. **107**, 9921 (1997)] was adopted for the calculations. Cross sections for rovibrational transitions and state-to-state rotational energy transfer from selected initial rotational levels were computed and compared with recent measurements of Carty *et al.* [J. Chem. Phys. **121**, 4671 (2004)] and available theoretical results. Comparison in all cases is found to be excellent, providing a stringent test for the scattering calculations as well as the reliability of the He-CO interaction potential by Heijmen *et al.*

*Electronic address: yang@physast.uga.edu

†Electronic address: stancil@physast.uga.edu

‡Electronic address: naduvala@unlv.nevada.edu

§Electronic address: rcf6@psu.edu

I. INTRODUCTION

Rotationally-inelastic, vibrationally-elastic collisions of molecular species by atoms or molecules, so-called rotational energy transfer (RET), is an important process in a variety of astrophysical environments including interstellar clouds, photodissociation regions, and cool stellar/planetary atmospheres. Inherent in the majority of model atmosphere/synthetic spectra studies is the assumption of local thermodynamic equilibrium (LTE), i.e. that the level populations of the atoms and molecules can be described by a Boltzmann distribution. There is reason to suspect departure from LTE in extrasolar giant planets (EGPs) and cool dwarf stars, such as brown dwarfs (BDs), due to a low abundance of electrons and the strong irradiation from their companion stars. However, advanced atmospheric modeling and spectral synthesis of EGPs, BDs, and other cool astrophysical environments requires an extensive array of accurate molecular data, i.e. state to state cross sections and rate coefficients. A large portion of the data are either currently unavailable (as the requisite experiments or calculations have not been carried out) or the available data are insufficient to meet the demands required by the modeling applications. Comprehensive experimental and theoretical studies of such processes are now becoming feasible.

The He-CO collisional system has been the subject of numerous experimental [1–5] and theoretical [6–17] studies, making it a good candidate for benchmark calculations. Two recent potential energy surface (PES) calculations [9, 10] have been reported in recent years in an effort to reduce uncertainties in the electronic structure part of the theory, but doubts still remain that any one potential surface is preferred [3]. Reid *et al.* [8] reported coupled states (CS) scattering calculations using the Heijmen *et al.* [9] potential, which have been improved upon at very low energies by Balakrishnan *et al.* [11] and Zhu *et al.* [12], who used the more accurate close-coupling (CC) technique. Krens [14, 15] reported that different CS approaches, Legendre expansions of the PES, and treatments of the vibrational wave functions yield significantly different results for this system. In particular, the J -labeled CS approximation where J is the total angular momentum quantum number yielded better results compared to the l (orbital angular momentum quantum number) labeled CS approximation. Krens [15] also showed the importance of including higher-order terms in the Legendre expansion of the interaction potential as well as using accurate rotational level j -dependent (centrifugal distorted) CO vibrational wave functions in accurately describing

the dynamics. Cecchi-Pestellini *et al.* [16] reported a large set of CC and infinite order sudden (IOS) approximation calculations using the Heijmen *et al.* potential. To reduce the computational expenses, the CC calculations were restricted to vibrational level $v = 0$ and the IOS approximation was used for $v = 1 - 6$. Florian *et al.* [17] investigated rotational relaxation in ultracold collisions for very large initially excited rotational states, $j = 80 - 230$, using the CS method. This latter effort was motivated by the possibility to study molecular collisions at cold and ultra-cold temperatures as schemes are currently being developed to efficiently cool and trap neutral polar molecules. All the studies mentioned above used the interaction potential of Heijmen *et al.* [9]. For the Kobayashi *et al.* [10] surface, only vibrational quenching calculations of $v = 1$ have been performed [10] which appear to be consistent with similar calculations made with the Heijmen *et al.* surface.

Very recently, Carty *et al.* [5] reported experimental rate coefficients and thermally averaged cross sections 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 provide the most extensive set of rate coefficients for rotationally inelastic collisions between CO and helium atoms and therefore provide an ideal ground for benchmarking theoretical results. The measurements were performed at five temperatures (15, 27, 63, 149, and 294 K) and for the first time provide opportunities to test the validity of theoretical results at temperatures lower than 30 K for which no prior experimental results were available. In the absence of detailed theoretical calculations of rotational transitions within the $v = 2$ manifold, Carty *et al.* compared their results with the theoretical results of Cecchi-Pestellini *et al.* [16] which were computed within the $v = 0$ vibrational level of the CO molecules. Though the comparisons showed good agreement with experimental results, an explicit comparison of theory and experiment is lacking.

The aim of this paper is to extend the work of Cecchi-Pestellini *et al.* [16] to provide rotational state-to-state data for CO ($v = 2$) collisions with He using the CC method and to provide an explicit comparison with experimental results of Carty *et al.* [5]. The paper is organized as follows: Section II gives a brief review of the theoretical methodologies used in the current study. The results of the calculations and discussion of the results are given in Section III, and Section IV concludes.

II. COMPUTATION METHODOLOGY

In this section we briefly outline the quantum close-coupling method [18–20] used in the present calculations for the rotational excitation of CO by He atoms. The reader is referred to Ref. [21] for more detailed discussions of the methodology.

The Hamiltonian for the He-CO system can be written as

$$\hat{H} = \hat{H}_{\text{CO}} - \frac{1}{2\mu} \nabla_R^2 + V(r, R, \theta) \quad (1)$$

where r is the distance between the carbon and oxygen atom, R is the distance from the CO center of mass to the He atom, and μ is the reduced mass of the helium atom with respect to CO. $\hat{H}_{\text{CO}} = -\frac{1}{2m} \nabla_r^2 + u(r)$ is the vibration-rotation Hamiltonian for the isolated CO molecule, where m is the reduced mass of CO and $u(r)$ is the diatomic CO potential. Its eigenfunctions are products of rotational wave functions Y_{jm_j} and vibrational wave functions $\chi_{vj}(r)$, where j and m_j are the rotational quantum number and its projection on the space-fixed axis. The vibrational wave function $\chi_{vj}(r)$ as well as the rovibrational energy levels ϵ_{vj} of the CO molecule are determined numerically by solving the radial r nuclear Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{j(j+1)}{2mr^2} + u(r) - \epsilon_{vj} \right] \chi_{vj}(r) = 0. \quad (2)$$

In Eq. (1), the kinetic energy of the relative collision motion can be separated into a radial part and an orbital angular momentum term, and the total scattering wave function of the He-CO system is expanded in terms of functions of radial and angular coordinates. Substitution of the total wave function into the stationary Schrödinger equation with the total Hamiltonian of the He-CO system (Eq. (1)) yields a set of coupled second-order differential equations, where the coupling is represented by matrix elements of the intermolecular potential.

It is convenient to adopt the total angular momentum representation introduced by Arthurs and Dalgarno [18] where the total angular momentum \mathbf{J} , is composed of the angular momentum of the CO molecule \mathbf{j} , and the orbital angular momentum of the collision complex \mathbf{l} : $\mathbf{J} = \mathbf{l} + \mathbf{j}$. Then the coupled equations become block diagonal in J and independent of its projection, M , on the space-fixed axis. Asymptotic solution of the Schrödinger equation yields the scattering S matrix which contains all the relevant information about He-CO scattering. The total cross sections for transitions from an initial rotational-vibrational state

labeled by vj to a final rotational-vibrational state labeled $v'j'$ can be expressed in terms of the scattering matrix, S ,

$$\sigma_{vj \rightarrow v'j'}(E_{vj}) = \frac{\pi}{(2j+1)k_{vj}^2} \sum_{J=0} (2J+1) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |\delta_{jj'} \delta_{ll'} \delta_{vv'} - S_{jj'l'l'vv'}^J|^2, \quad (3)$$

where $k_{vj} = \sqrt{2\mu(E - \epsilon_{vj})}/\hbar$ is the wave vector in the incoming channel and E the total energy.

The total removal cross section (rotationally inelastic cross section) as a function of collision energy $E_{vj} = E - \epsilon_{vj}$ from a given initial state is obtained as:

$$\sigma_{vj}^{\text{removal}}(E_{vj}) = \sum_{j' \neq j} \sigma_{vj \rightarrow v'j'}(E_{vj}), \quad (4)$$

where the summation includes only rotationally inelastic transitions in the same vibrational level.

By integrating the collision energy dependence of the state-to-state cross sections with a Maxwell-Boltzmann distribution of velocities of the incident atom, the state-to-state rate coefficients are given by

$$r_{vj \rightarrow v'j'}(T) = \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} \frac{1}{(k_B T)^2} \int_0^\infty \sigma_{vj \rightarrow v'j'}(E_{vj}) \exp(-E_{vj}/k_B T) E_{vj} dE_{vj}, \quad (5)$$

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

III. RESULTS AND DISCUSSION

All the close-coupling calculations reported here were performed using the nonreactive scattering code, MOLSCAT [22]. Though we have performed full rovibrational calculations involving a large number of open and closed rovibrational channels, since the purpose of the paper is benchmarking, we present only rotationally-inelastic, vibrationally-elastic results to provide a detailed comparison with the experimental data of Carty *et al.* [5]. We adopted the He-CO interaction potential of Heijmen *et al.* [9] which includes the variation of the interaction potential with respect to the CO bond stretching coordinate. It is considered to be superior to the other potentials [23–25] that are available for this system especially in

reproducing the bound state energies of the He-CO complex. The potential has a van der Waals minimum of -23.734 cm^{-1} at a separation of 3.46 \AA between He and the center of mass of CO with a skew angle of 48.4° and with the CO bond length fixed at the equilibrium value $r_e=1.128 \text{ \AA}$.

The coupled-channel equations were integrated using the modified log-derivative Airy propagator of Alexander and Manolopoulos [26] with a variable step size. The wave function was propagated to a maximum intermolecular separation of $R = 100 \text{ \AA}$. Calculations were performed for collision energies between 10^{-6} cm^{-1} and 1000 cm^{-1} in order to evaluate thermally averaged rate constants from 10^{-5} to 294 K . At each energy a sufficient number of total angular momentum partial waves have been included to ensure convergence of the cross sections. The maximum value of J employed in the calculation was 50. The basis set used consisted of 36 rotational states in the ground vibrational state of CO, 31 rotational levels of $v = 1$, 26 rotational levels of $v = 2$, and 11 states in the vibrational closed channel, $v = 3$, or B3(35,30,25,10) in the notation of Ref. [27].

A. Cross sections for the removal of CO from selected rotational levels

We have performed calculations of the collision energy dependence of state-to-state cross sections for four initial rovibrational states of $v=2$, $j=0, 1, 4$, and 6 . From Eq. (4), the cross sections from each initial rotational state of CO ($v=2$) are summed over all final rotational states to obtain the total removal cross section as a function of relative translational energy. The results are depicted in Fig. 1 for $j = 0, 1, 4$, and 6 . For initial levels $j=0$ and 1 and incident energies less than the van der Waals well depth ($\sim 20 \text{ cm}^{-1}$), the cross sections exhibit oscillations as a function of the kinetic energy characteristic of resonances. As discussed by Reid *et al.* [8], the low collision energy regime fosters the formation of quasi-bound levels or van der Waals complexes. These long lived complexes allow multiple collisions to occur and strongly enhance the vibrational and rotational relaxation process and influence the open-channel (shape) [28] and closed-channel (Feshbach) [29] resonances. The thresholds for the opening of closed rotational channels are indicated in the figure which for the lowest energies have a close correspondence to some of the resonances. For $v = 2$, $j = 0$, the excitation cross section, including the location of the resonances, is nearly identical to that presented by Cecchi-Pestellini *et al.* [16] for $v = 0$, $j = 0$. This is not surprising given that

the bound-state rotational energies for the He-CO complex are very similar for both the $v = 0$ and $v = 1$ manifolds [9], and presumably also for $v = 2$ as well. For the energies above 30 cm^{-1} , the cross sections vary slowly with increasing collision energy.

The resonances due to the van der Waals interaction become suppressed with increase in initial diatom rotation and are not as prominent as those for initial rotational levels $j=0$ and 1 as shown in Figs. 1c and 1d for rotational levels $j=4$ and 6. At higher energies the cross sections vary slowly with increasing energy, while at very low energies, rotational quenching dominates, which is seen in the insets to follow the typical Wigner behavior.

Our close-coupling results are compared with the measurements of Carty *et al.* [5] in Fig. 1. Generally, our theoretical values are in good agreement with the experimental data, especially at higher collision energies. Note that the experimental cross sections for total removal of CO from selected rotational levels are thermally averaged and obtained by dividing their measured rate coefficients by the mean relative velocities at the temperatures of the experiments. The predicted resonance structure is therefore unobservable in these measurements. Carty *et al.* also compared their experimental results to the thermally-averaged cross sections of Cecchi-Pestellini *et al.* [16] for $v = 0$ and a single value from Krems [14] for $v = 3, j = 0$. Good agreement was also found suggesting, at least for low vibrational quantum numbers, that the RET process is insensitive to the CO vibrational state.

In Fig. 1b, comparison is also made to the only previously published cross section for RET for CO($v = 2$) by Bodo *et al.* [13] for $j = 1$ between 10^{-5} and 1 cm^{-1} . For this collision energy range, the only available RET channel is deexcitation to $v' = 2, j' = 0$ for which we find very good agreement.

B. State-to-state rate coefficients

State-to-state cross sections are thermally averaged over the kinetic energy distribution to give state-to-state rate coefficients of CO at a temperature T as described by Eq. (5). The resulting state-to-state RET rate coefficients for initial rovibrational states ($v = 2, j=0, 1, 4,$ and 6) are presented in Figs. 2-6 and compared with the experimental results [5] at temperatures 15, 27, 63, 149, and 294 K, respectively. In nearly all cases, the theoretical rate coefficients show good agreement with the experimental values at all five temperatures.

The present CC rate coefficients exhibit similar general features as noticed by Carty *et al.* [5]. For all initial rotational states ($j=0, 1, 4,$ and 6) the rotationally inelastic state-to-state rate coefficients show a general decrease with increasing $|\Delta j| = |j' - j|$. Superimposed on this general trend, the theoretical rate coefficients also display some oscillations with Δj , with a propensity to prefer odd Δj over even Δj . The preference for odd over even Δj has been discussed by Carty *et al.* [5] and McCurdy *et al.* [30] and it occurs due to the strong anisotropy of the He-CO interaction potential. This propensity, however, is not evident at 15 and 27 K possibly due to the influence of the quasi-bound resonances. The vanishing of propensities near resonance energies was previously noted by Lee and Bowman [31] in the H-CO collision system. Further it can be seen that the distribution of the rate coefficients with Δj narrows as the temperature is reduced.

While there is a general agreement between theory and experiment, there are some discrepancies for certain transitions at certain temperatures. These differences may be due to inaccuracies in the Heijmen *et al.* potential energy surface though this is less likely due to the very good agreement found for most transitions. Further, Smith *et al.* [4] performed very similar calculations using the same potential and a combination of CC and CS methods, but adopted a rigid rotor approximation. Their state-to-state rate coefficients at 297 K are nearly identical to the current results at 294 K. The remaining discrepancies between theory and experiment may therefore lie in the relaxation kinetics model used to extract the rate coefficient values from the experimental data [5]. In their model, a two-level system was adopted which required corrective and normalization procedures for some transitions. As it is often these transitions which show the largest disagreement with the current calculations, the two-level model may be inadequate. Nevertheless, the very good agreement for most transitions for the wide range of temperatures, is very encouraging and suggests that the Heijmen *et al.* [9] surface is adequate for extensive collisional studies.

IV. CONCLUSION

Cross sections for the total removal of CO molecules from selected levels ($v=2, j=0, 1, 4,$ and 6) of the He-CO system have been calculated using an explicit quantum mechanical close-coupling approach with the interaction potential of Heijmen *et al.* [9]. The total removal cross sections show resonance structures at intermediate energies due to the van der

Waals well. Both the cross sections and state-to-state rate coefficients at $T = 15, 27, 63, 149,$ and 294 K show good agreement with experimental results, validating the accuracy of He-CO potential surface by Heijmen *et al.* [9] as well as the present scattering calculations. The observation that the theoretical cross sections and state-to-state rate coefficients from selected rotational levels of $v=0$ (Cecchi-Pestellini *et al.* [16]) and $v = 2$ (present work) for RET are very similar indicates that vibrational motion, at least for small vibrational quantum numbers, has minimal effect on the RET process for CO molecule scattering with He atoms.

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Figure Captions

- Fig. 1. Cross sections for the total removal of CO from selected rotational levels j in collisions with He atoms as functions of collision energy: (a) $j = 0$, (b) $j = 1$, (c) $j = 4$, (d) $j = 6$. Lines with open circles: current CC calculations; solid circles with error bars: measurement [5]. In the inset to (b), solid line: current CC calculations; dashed line: CC calculation of Bodo *et al.* [13]. Filled boxes correspond to the rotational threshold energies for the opening of closed-channels from left to right (a) $j' = 1, 2, 3, 4$, and 5; (b) $j' = 2, 3, 4$, and 5; (c) $j' = 5, 6$, and 7; and (d) $j' = 7, 8$, and 9.
- Fig. 2. State-to-state rate coefficients for rotationally inelastic collisions of CO($v=2$) with He atom at 15 K: (a) $j = 0$, (b) $j = 1$, (c) $j = 4$. Lines with open circles: current CC calculations; solid circles with error bar: measurements [5].
- Fig. 3. Same as Fig. 2, except for 27 K.
- Fig. 4. State-to-state rate coefficients for rotationally inelastic collisions of CO($v=2$) with He atom at 63 K: (a) $j = 0$, (b) $j = 1$, (c) $j = 4$, (d) $j = 6$. Symbols are same as in Fig. 2.
- Fig. 5. Same as Fig. 4, except for 149 K.
- Fig. 6. Same as Fig. 4, except for 294 K.

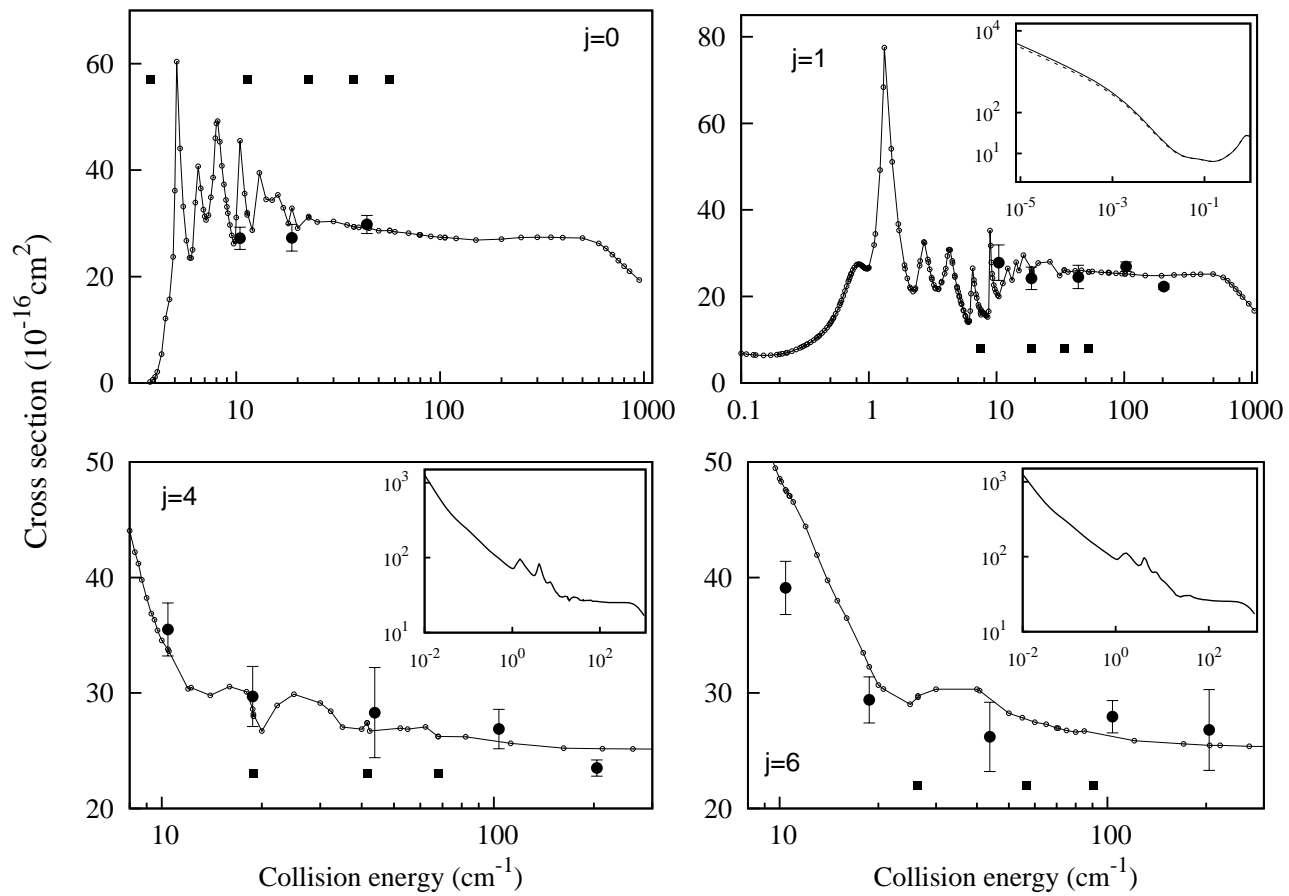


Fig. 1

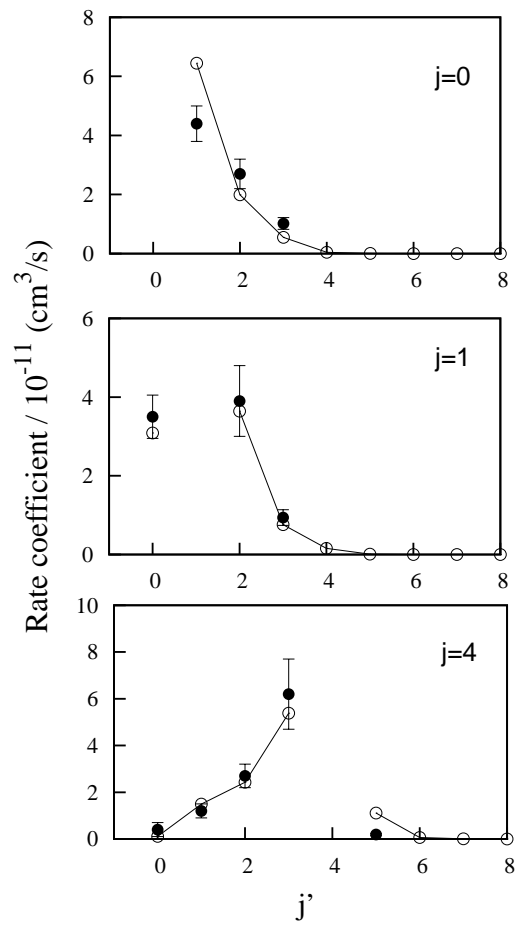


Fig. 2

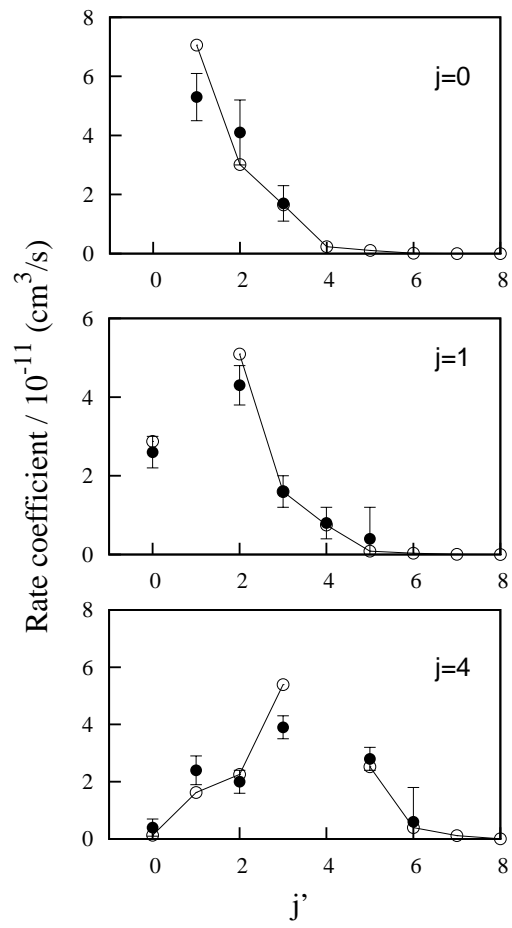


Fig. 3

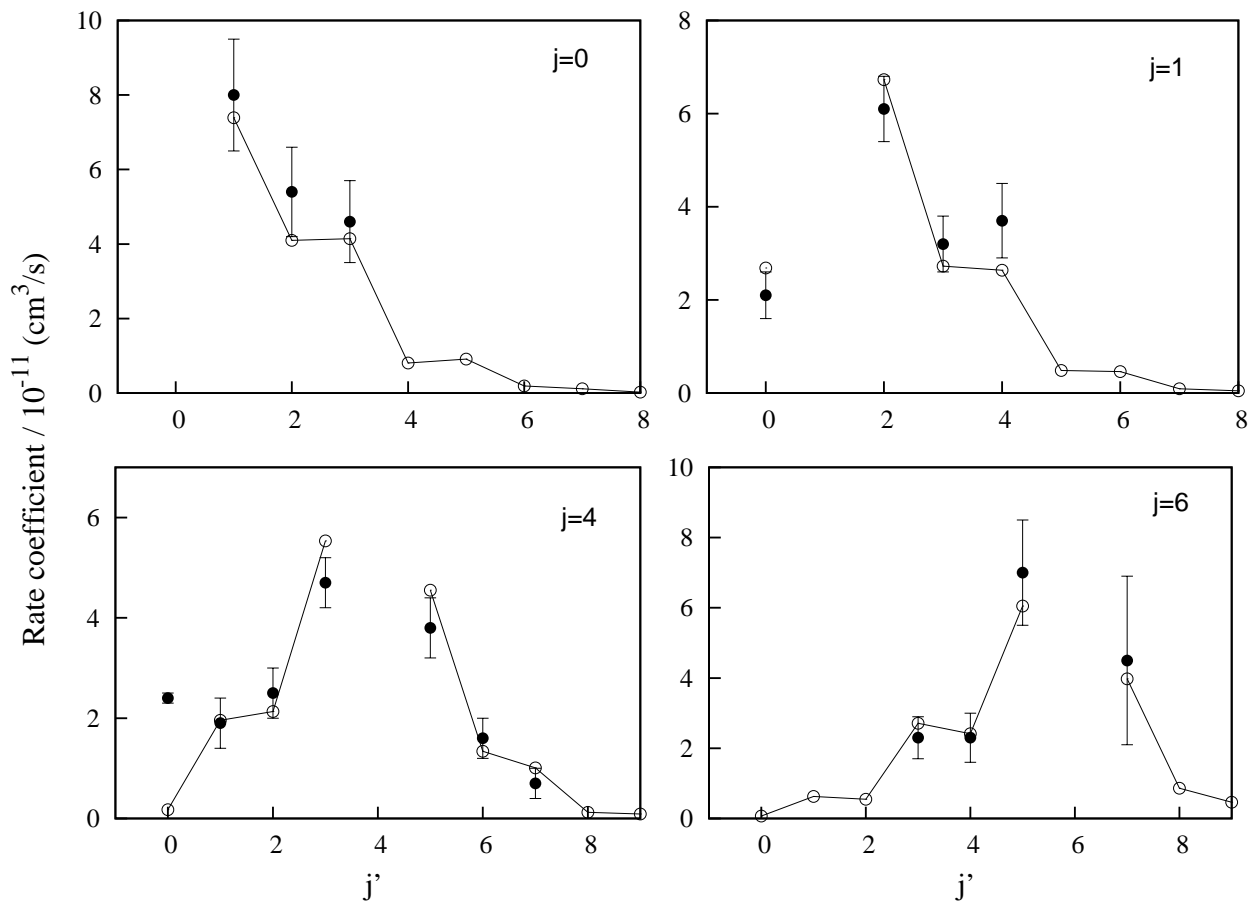


Fig. 4

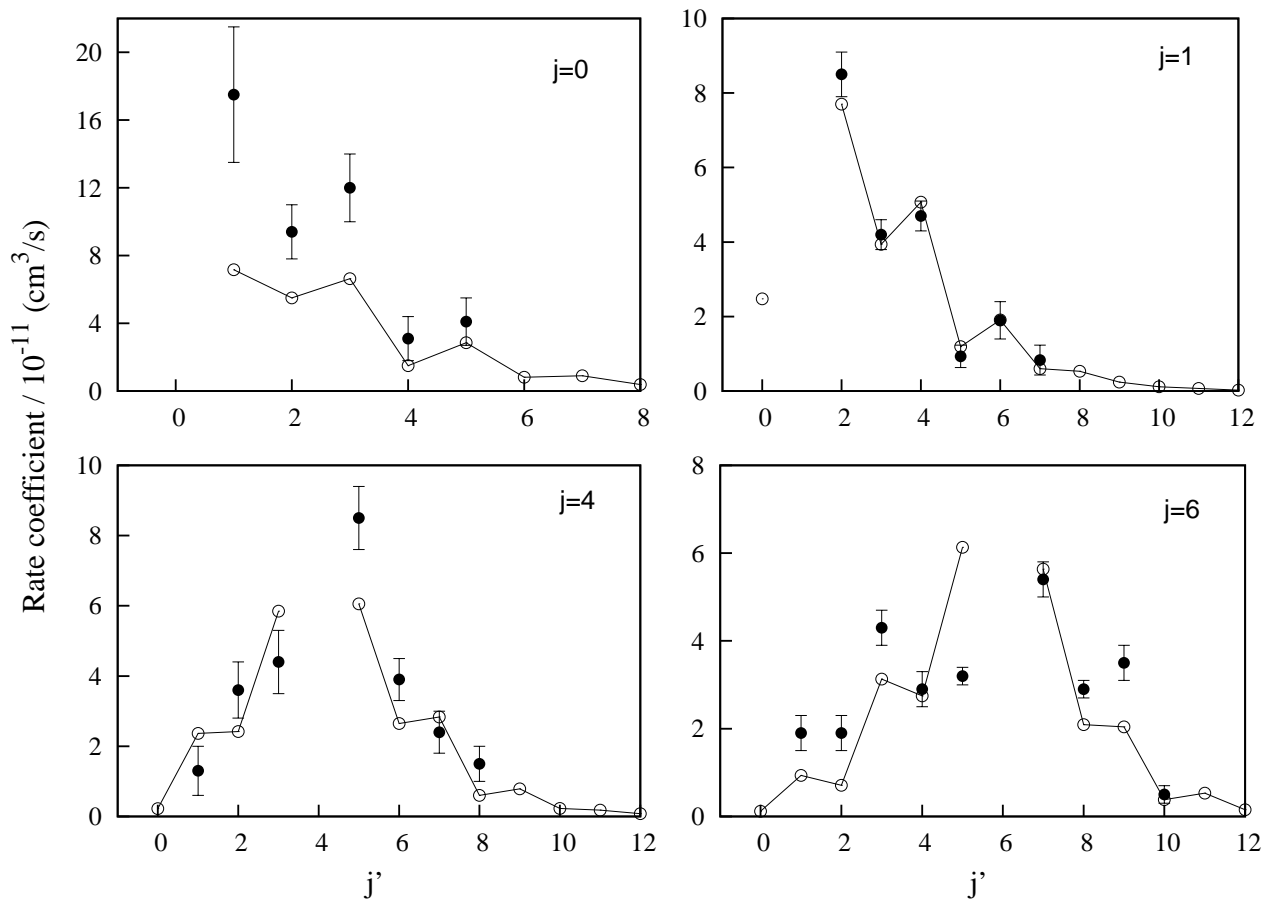


Fig. 5

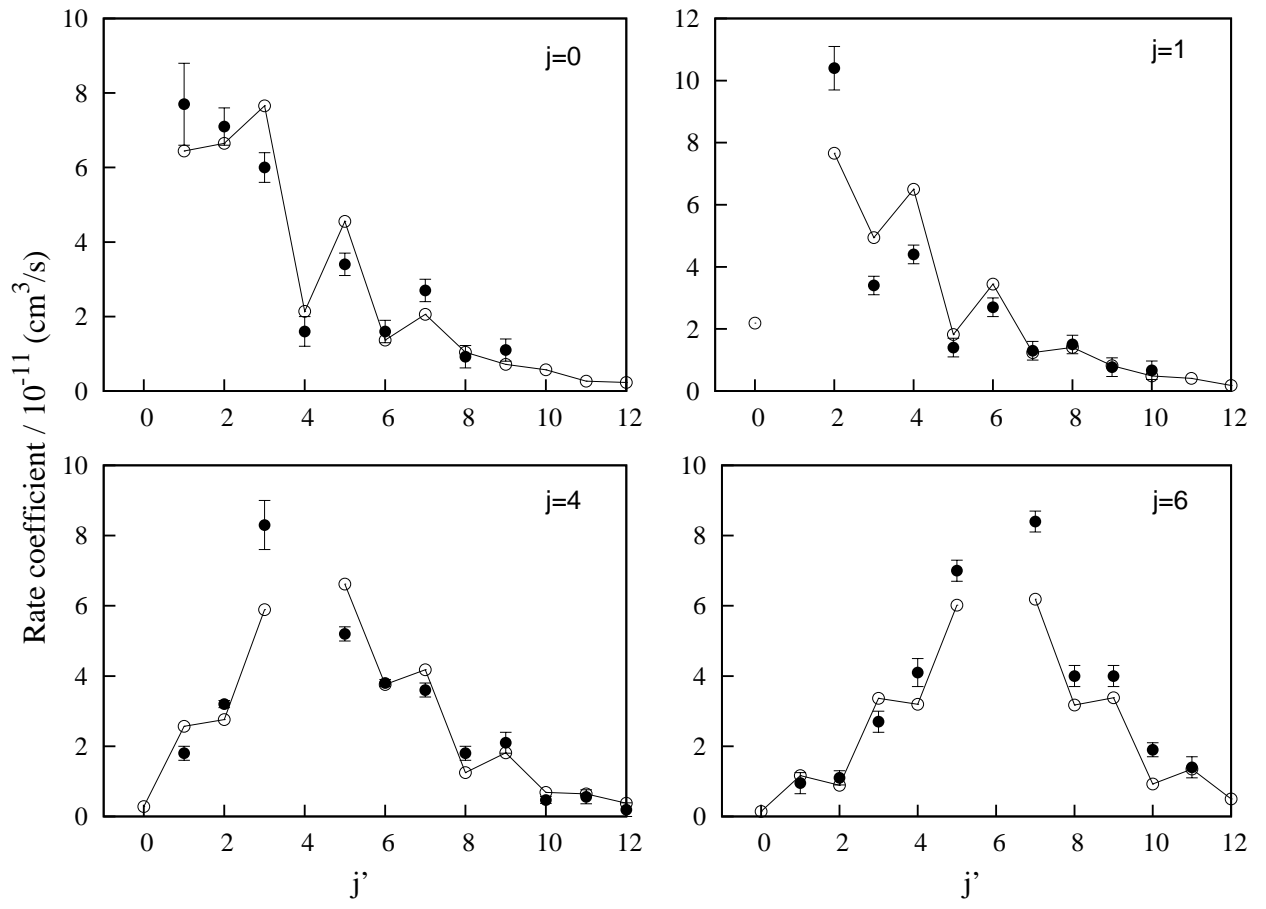


Fig. 6