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# The Effect of Non-equilibrium Kinetics on Oxygen Chemistry in the Interstellar Medium

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## ABSTRACT

It has been suggested that in photon-dominated regions, oxygen chemistry is initiated by the  $\text{O}+\text{H}_2 \rightarrow \text{OH}+\text{H}$  reaction. The reaction has an energy barrier of about 0.4 eV with ground state reactants and it is slow at low temperatures. There is strong experimental evidence that vibrational excitation of the  $\text{H}_2$  molecule increases the reactivity significantly. We present extensive quantum calculations of cross sections and rate coefficients for the  $\text{O}+\text{H}_2(v)$  reaction for  $v = 0 - 3$  of the  $\text{H}_2$  molecule and show that the vibrational excitation of the molecule has a significant effect on reactivity, especially at low temperatures.

## 1. Introduction

The study of photodissociation regions or photon-dominated regions (PDRs) has attracted considerable attention in recent years. Its importance is derived from the fact that far-ultraviolet (FUV) photons penetrate the clouds, heat the gas, and influence the chemical and energy balance of the neutral interstellar medium. They also play significant role in star forming processes in galaxies (Hollenbach & Tielens 1997). Theoretical models (Tielens & Hollenbach 1985; van Dishoeck & Black 1988; Sternberg et al. 1989; Le Bourlot et al. 1993; Sternberg et al. 1997) of this phenomenon have been developed and used for the interpretation of different events occurring in the neutral interstellar medium. Detailed analysis of the relevant chemical reactions in dense molecular clouds exposed to intense far-ultraviolet radiation has been given by Sternberg and Dalgarno (1995).

Chemistry of PDR differs significantly from usual ion-molecular chemical reactions. Because of the FUV flux, nonthermal processes are very important and vibrationally excited  $\text{H}_2$  (denoted as  $\text{H}_2^*$ ) can play significant role in PDR chemistry. When the gas is hot ( $T > 500$  K), the activation energy for reactions of atoms and radicals with  $\text{H}_2$  and  $\text{H}_2^*$  can be overcome and these reactions are dominated. Recombination and charge transfer reactions can also significantly contribute to the ionization balance.

In this work, we give an overview of quantum calculations of the  $\text{O}+\text{H}_2(v)$  reaction for vibrational levels  $v = 0-3$  to explore the effect of vibrational excitation of  $\text{H}_2$  on the reaction rates.

## 2. Results and discussion

The quantum scattering calculations were performed using the ABC reactive scattering program (Scouteris, Castillo & Manolopoulos 2000). We have extensively adapted this program for a number of atom-diatom reactions over the last few years, including the  $\text{O}+\text{H}_2$  reaction (Balakrishnan 2004; Sultanov & Balakrishnan 2005; Weck & Balakrishnan 2005). While the  $\text{O}+\text{H}_2$  reaction is amenable to numerically exact quantum calculations without any decoupling approximations, such calculations become computer intensive for excited vibrational levels. In our previous studies (Balakrishnan 2004; Sultanov & Balakrishnan 2005) we have demonstrated that the simpler  $J$ -shifting approximation (Bowman 1991) can be used to compute cross sections and rate coefficients for the  $\text{O}+\text{H}_2$  reaction without losing much accuracy. Therefore, most of the results for vibrationally excited  $\text{H}_2$  shown here are computed using the  $J$ -shifting approximation. The  $J$ -shifting method works well for systems which involve an energy barrier as in the case of the present system. We will explicitly show the validity of the  $J$ -shifting approximation by comparing with results from numerically exact calculations. More details of the calculations are given in our recent article (Sultanov & Balakrishnan 2005).

The  $\text{O}+\text{H}_2$  reaction involves two lowest adiabatic potentials,  ${}^3A'$  and  ${}^3A''$ . While an explicit quantum calculation must include non-adiabatic coupling between the two surfaces, such effects have been shown to be negligible for the present system using both the trajectory surface hopping method as well as coupled wave packet calculations. Thus, the results shown here are computed separately on the  ${}^3A'$  and  ${}^3A''$  potential surfaces of Rogers et al. (2000) and scaled by a multiple surface coefficient of  $1/3$ . That is, the total cross sections and rate coefficients are given by  $1/3({}^3A' + {}^3A'')$ .

In Fig.1 we compare results for  $\text{O}+\text{H}_2(v = 0)$  reaction from the full quantum calculations and the  $J$ -shifting method (Balakrishnan 2004) with the experimental and theoretical results of Garton et al. (2003). The theoretical results of Garton et al. are obtained using the time-dependent quantum mechanical approach in which the coupled-states approximation was used to reduce the computer time. It is seen that all three theoretical results agree well with each other and also with the experimental results. Fig. 1 also illustrates that the error introduced by the  $J$ -shifting method is within 10-15% which is within the uncertainty of astrophysical models predictions.

In Fig. 2 we show integral cross sections for the  $\text{O}+\text{p-H}_2(v = 0-3)$  (left panel) and  $\text{O}+\text{o-H}_2(v = 0-3)$  (right panel) reactions as functions of the incident kinetic energy. It

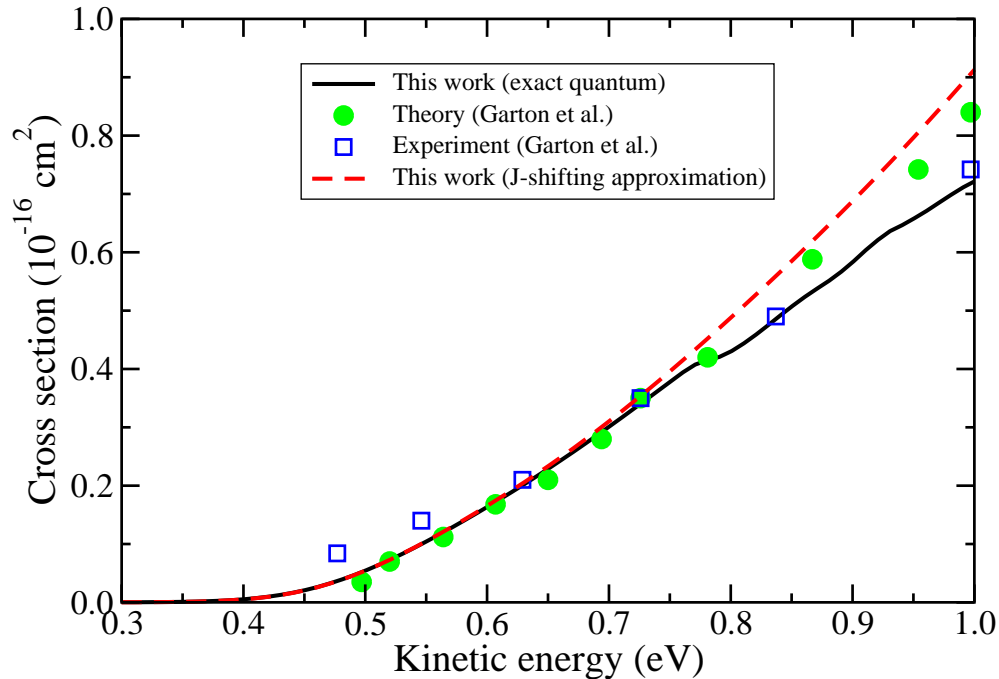


Fig. 1.— Comparison of reaction cross sections for the  $O(^3P)+H_2(v = 0, j = 0)$  from the present calculations (Balakrishnan 2004) and Garton et al. (2003) as functions of the incident kinetic energy.

is seen that vibrational excitation has a dramatic effect on reactivity. The effect is much larger at low kinetic energy than at high kinetic energies. This is because at low energies the reaction is dominated by tunneling. Since the energy barrier for the reaction is substantial, tunneling probability is much smaller. Vibrational excitation lowers the adiabatic barrier for the reaction and tunneling occurs much more favorably at low energies.

As seen in the right panel of Fig. 2, vibrational excitation has an even more dramatic effect on ortho- $H_2$  results at low energies. We believe that this is due to the slightly higher internal energy of o- $H_2$  which effectively leads to lower barrier height for the reaction. Rate coefficients are obtained by Boltzmann averaging the cross sections at a given temperatures. Tabulated values of the rate coefficients in the temperature range 100-4000 K are reported in our recent publication (Sultanov & Balakrishnan 2005). It has been found that vibrational excitation has a dramatic effect on reactivity at low temperatures with rate coefficient increasing by a about 11 orders magnitude between  $v = 0 - 3$  of  $H_2$ . The effect is less significant at high temperatures. For example, at 4000 K, the rate coefficients for  $v = 0$

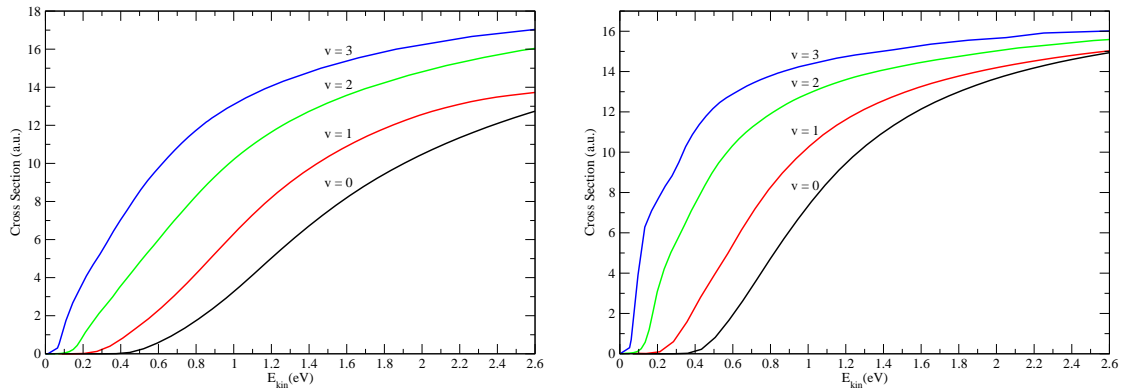


Fig. 2.— Reaction cross section vs. energy for the  $O(^3P)+H_2(v)$  reaction for  $v = 0 - 3$ . Left panel: results for  $p\text{-}H_2$  reaction; right panel: results for  $o\text{-}H_2$  reaction.

and  $v = 3$  differ only by an order of magnitude. Thus, non-equilibrium effect become more important at lower temperatures than at higher temperatures.

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## REFERENCES

- Hollenbach, D. J., Tielens A. G. G. M. 1997, *Annu. Rev. Astron. Astrophys.*, 35, 179  
 Tielens, A. G. G. M., & Hollenbach, D. 1985, *ApJ*, 291, 722  
 van Dishoeck, & E. F., Black, J. H. 1988, *ApJ*, 334, 771  
 Sternberg, A., Dalgarno, A. & Lepp, S. 1989, *ApJ*, 320, 676  
 Le Boulrot, J., Pineau des Forêts, G., Roueff, E., & Flower, D. R. 1993, *A&A*, 267, 233  
 Sternberg, A., Yan, M. & Dalgarno, A. 1997, *Molecules in Astrophysics: Probes and Processes*, E. F. van Dishoeck, Dordrecht: Kluwer, 1997, 141  
 Sternberg, A., & Dalgarno, A. 1995, *ApJS*, 99, 565  
 Scouteris, D., Castillo, J. F., & Manolopoulos, D. E. 2000, *Comput. Phys. Commun.*, 133, 128  
 Balakrishnan, N., 2004, *J. Chem. Phys.* 121, 6346  
 Sultanov, R. A., & Balakrishnan, N., 2005, *Astrophysical Journal* 629, 305  
 Weck, P. F., & Balakrishnan, N., 2005, *J. Chem. Phys.* 123, 144308  
 Bowman, J. M. 1991, *J. Phys. Chem.*, 95, 4960  
 Rogers, S., Wang, D., Kupperman, A., & Walch, S. 2000, *J. Phys. Chem. A*, 104, 2308  
 Garton, D. J., Minton, T. K., Maiti, B., Troya, D., & Schatz, G. C., 2003, *J. Chem. Phys.*, 118, 1585