

Transition Dipole Moments of PO

Antonio Carlos Borin^a (PQ), Adalberto Vasconcelos Sanches de Araújo^b (PG)

Universidade de São Paulo, Instituto de Química
Av. Prof. Lineu Prestes 748, 05508-000, São Paulo, SP, Brazil
(e-mail: ancborin@iq.usp.br^a, avsa2@hotmail.com^b)

Keywords: MRCI, Transition Dipole Moments, PO

INTRODUCTION

Phosphorus monoxide (PO) is a very important interstellar species found¹, for instance, in the circumstellar envelop of the VY CMA star and of the asymptotic giant branch oxygen star IK Tau, either characterized as rich oxygen environment. Despite of its relevance, little is known about the chemistry of PO formation. To understand it in the interstellar space, the rate coefficients for radiative association of P and O atoms is a need, for which the transition dipole moment function is a key information. In this work, the lowest-lying electronic states of PO and the most relevant electronic transitions were investigated by *ab initio* calculations at the MRCI level with extended basis sets. For the first time, transition dipole moment functions were also computed, which will be of great value for understanding the chemical aspects of PO formation in interstellar environments.

METHODS

Potential energy curves and transition dipole moments were calculated at the multireference configuration interaction (MRCI) level and full electron cc-pVQZ² basis sets, augmented with³ three s, three p, three d, and three f diffuse functions on the P atom. All P and C valence electrons and orbitals, plus one extra set of σ and π orbitals, were included in the active space. The calculations were carried out in the C_{2v} point group symmetry, with the MOLPRO⁴ software.

RESULTS AND DISCUSSION

The computed potential energy curves and transition dipole moment function are plotted in Figure 1. The $X^2\Pi$ is the ground electronic state ($R_e = 1.489 \text{ \AA}$, $\omega_e = 1243 \text{ cm}^{-1}$), with the $B^2\Sigma^+$ electronic state being the lowest-lying doublet excited state ($T_e = 3.75 \text{ eV}$, $R_e = 1.494 \text{ \AA}$, $\omega_e = 1042 \text{ cm}^{-1}$), in agreement with experimental findings⁵. As to the transition dipole moment, its value at the asymptotic atomic limit is zero, because both

electronic states dissociate into the same atomic dissociation channel.

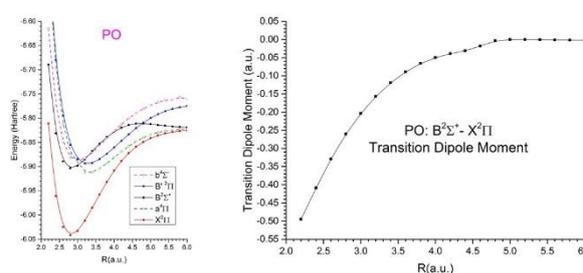


Figure 1. Potential energy curves for the lowest-lying electronic states of PO and the $B^2\Sigma^+ - X^2\Pi$ dipole transition moment function.

CONCLUSIONS

The results presented in this contribution are relevant for the computing the rate coefficients for radiative association of P and O atoms, from which the chemical aspects related to P and O association can be better understood. Franck-Condon factors, Einstein coefficients, and radiative lifetimes for the first excited electronic states.

ACKNOWLEDGMENTS

The authors are grateful for the support given from the CNPq.

¹ T. Kamínski, C. A. Gottlieb, K. H. Young, K. M. Menten, N. A. Patel, 2013, *Ast. Journal*, 209, 38 (2013).

² T. H. Dunning, *J. Chem. Phys.*, 90, 1007, (1989); D. E. Woon, T. H. Dunning, *J. Chem. Phys.*, 98, 1358, (1993).

³ H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs Comput. Mol. Sci.*, 2, 242, (2012).

⁴ A. Spielfiedel, N. C. Handy, *Phys. Chem. Chem. Phys.*, 1, 2401, (1999).

⁵ K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV Constant of Diatomic Molecules*. Van Nostrand Reinhold, New York, 1979.