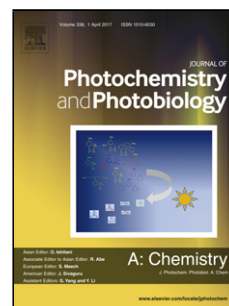


## Accepted Manuscript

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PII: S1010-6030(18)30856-6  
DOI: <https://doi.org/doi:10.1016/j.jphotochem.2018.07.047>  
Reference: JPC 11413

To appear in: *Journal of Photochemistry and Photobiology A: Chemistry*

Received date: 18-6-2018  
Revised date: 31-7-2018  
Accepted date: 31-7-2018

Please cite this article as: Mirko Matthias Lindic, Matthias Zajonz, Marie-Luise Hebestreit, Michael Schneider, W. Leo Meerts, Michael Schmitt, Excited state dipole moments of anisole in gas phase and solution, *Journal of Photochemistry & Photobiology, A: Chemistry* (2018), <https://doi.org/10.1016/j.jphotochem.2018.07.047>

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# Excited state dipole moments of anisole in gas phase and solution

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## Abstract

The excited state dipole moment of anisole has been determined in the gas phase from electronic Stark spectroscopy and in solution using thermochromic shifts in ethyl acetate. Electronic excitation increases the anisole dipole moment in the gas phase from 1.26 Debye in the ground state to 2.19 Debye in the electronically excited singlet state, leaving the orientation of the dipole moment practically unchanged. These values are compared to solution phase dipole moments. From variation of the fluorescence emission and absorption maxima with temperature, an excited state dipole moment of 2.7 Debye was determined. Several solvent polarity functions have been used in combination with experimentally determined cavity volumes at the respective temperatures. Both gas phase and condensed phase experimental dipole moments are compared to the results of *ab initio* calculations at the CC2 level of theory, using the cc-pVTZ basis set for the isolated molecule and using the COnductor-like Screening MOdel (COSMO), implemented in Turbomole, for the solvated anisole molecule.

### Keywords:

Excited state, Dipole moment, Stark spectroscopy, Thermochromic shifts

PACS: 33.20.-t, 33.15.Kr, 33.20.Sn, 31.10.+z

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## 1. Introduction

The use of dipole moments as measures for the distribution of electrons in molecules has successfully be applied for more than 100 years. The earliest designation of the concept of molecular dipoles goes back to Debye's paper of 1912 on a kinetic theory of insulators.[1] However, this concept is not uncontroversial, since for larger molecules higher terms of the multipole expansion may be needed to properly describe molecular electronic properties. The success of the model can be traced back to the fact, that the overall dipole moment can be constructed from atomic dipoles, which are centered at the atomic positions and point along the chemical bonds, the so called bond dipoles.[2] The main problem concerning the molecular dipole moments, however, results from the fact, that their experimental determination should preferably be performed in the vapor phase to avoid interaction with the surrounding solvent. Many substances of interest decompose thermally, before their vapor pressure is high enough to allow for the experimental determination of the dipole. In these cases determination of the molecular dipole in dilute solutions is the only possibility. For the ground state several schemes exist, to obtain vapor-phase dipole moments from solution measurements.[3] They can be applied to strongly dilute solutions with nonpolar solvents. For the excited state, the situation is much more complex, since mutual solvent-solute interactions are a prerequisite in many techniques used for the determination of excited state dipole moments in solution.[4]

The knowledge of excited state dipole moments of molecules and of transition dipole moments connecting ground and excited states are important prerequisites for the understanding of resonance

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