

Stark Effect in the Benzene Dimer

Melanie Schnell,^{*,†} P. R. Bunker,^{‡,§} Gert von Helden,[§] Jens-Uwe Grabow,^{||} Gerard Meijer,^{§,⊥}
and Ad van der Avoird[⊥]

[†]Max-Planck-Institut für Struktur und Dynamik der Materie, Center for Free-Electron Laser Science, and The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, D-22761 Hamburg, Germany

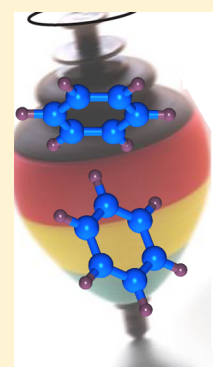
[‡]Steeacie Laboratory, National Research Council of Canada, Ottawa, Ontario K1A0R6, Canada

[§]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

^{||}Institut für Physikalische Chemie und Elektrochemie, Gottfried Wilhelm Leibniz Universität Hannover, Callinstrasse 3A, D-30167 Hannover, Germany

[⊥]Theoretical Chemistry, Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

ABSTRACT: Ab initio calculations of the six-dimensional intermolecular potential have shown the benzene dimer to be an asymmetric top molecule at equilibrium with one benzene moiety forming the “stem” and the other a “tilted cap” in a T-shaped structure. Internal rotation of the cap about its C_6 axis is essentially free; the barriers for cap tilting and for internal rotation of the stem about its C_6 axis are hindered by successively higher barriers. In previous work we have validated these theoretical results using Fourier transform microwave spectroscopy in conjunction with dynamics calculations. We have also measured the Stark effect, and despite the fact that the equilibrium structure is that of an asymmetric top, the assigned transitions involving $K = 0$ exhibit a second-order Stark effect whereas those involving $K = 1$ exhibit a first-order Stark effect. This is typical for a symmetric-top molecule, but anomalous for an asymmetric-top molecule. We use symmetry arguments to explain how this asymmetric-top molecule can have a first-order Stark effect in certain states that have excitation of cap internal rotation. Cap internal rotation is essentially the twisting of the monomers relative to each other about the intermolecular axis, and such torsional motion occurs in other asymmetric top dimers such as benzene–CO and benzene– H_2O . These latter dimers will also have levels that exhibit a first-order Stark effect, which we can explain using our symmetry arguments.



INTRODUCTION

In a combined experimental and theoretical study^{1,2} we have explained the observed quartet tunneling splittings in the microwave spectrum of the benzene dimer (C_6H_6)₂, and of a mixed dimer (C_6D_6)(C_6H_6). Our explanation is based on making dynamics calculations using a two-dimensional cut of the full six-dimensional intermolecular potential that was obtained purely by ab initio calculation.^{3,4} The global minimum of the intermolecular potential is at the tilted T-shaped structure shown in Figure 1; in this figure we indicate the “cap” (with nuclei labeled 1 to 6) and “stem” (with nuclei labeled 1' to 6') of the dimer. There is essentially free internal rotation of the cap about its C_6 axis, with successively higher barriers for the tilt tunneling of the cap and for the internal rotation tunneling of the stem about its C_6 axis. As shown in refs 1 and 2, the observed quartet splittings are the result of a concerted tunneling motion involving internal rotation of the stem about its C_6 axis and cap tilting.

At equilibrium the benzene dimer is an asymmetric top molecule. In ref 4 the full six-dimensional ab initio intermolecular potential surface was used to calculate the vibration–rotation–tunneling states of (C_6H_6)₂. These VRT states were calculated for all 54 irreducible representations (irreps) of the full cluster tunneling group G_{576} ,^{5,6} the

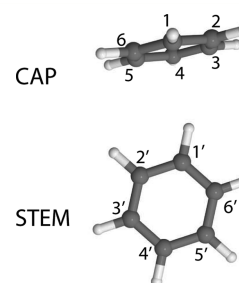


Figure 1. Nuclear labeled version of the equilibrium structure where the bonded carbon–hydrogen nuclei are numbered 1–6 in the cap and 1'–6' in the stem.

molecular symmetry (MS) group that applies if all intermolecular tunneling motions are feasible. Vibrationally averaged rotational constants A , B , and C were obtained both from the expectation values of the inverse inertia tensor and

Special Issue: Terry A. Miller Festschrift

Received: August 12, 2013

Revised: September 19, 2013

Published: September 19, 2013

from the differences between the energy levels calculated for total angular momentum $J = 0$ and $J = 1$. Also in these calculations we found that the benzene dimer behaves as an asymmetric rotor in its ground VRT state, as well as in some higher states. The value of the asymmetry parameter $B - C$ is slightly reduced by vibrational averaging. The rotational constants were only calculated for the VRT states belonging to the one-dimensional irreps $A_1^\pm, A_2^\pm, A_3^\pm, A_4^\pm$, however.

Asymmetric top molecules are not supposed to exhibit a first-order Stark effect, but we have observed that the benzene dimer does.^{1,2} In the present paper we describe the Stark measurements and we show, using symmetry arguments, how excitation of cap internal rotation leads to symmetry degenerate levels having a first-order Stark effect. Similar arguments would apply to other asymmetric top benzene complexes such as benzene-CO,⁷ benzene-N₂,^{8,9} benzene-H₂O,^{10,11} benzene-H₂S,¹² and benzene-SO₂.¹³

■ FIRST-ORDER STARK EFFECT

Watson¹⁴ showed that, in the absence of hyperfine splittings, the symmetry condition for a rovibronic level of symmetry Γ to have a first-order Stark effect is

$$\Gamma(\mu_f) \subset [\Gamma^2]_{\text{antisym}} \quad (1)$$

where $\Gamma(\mu_f)$ is the symmetry species of the space fixed components of the dipole moment operator (the one-dimensional irreducible representation having character +1 for all permutations of identical nuclei and character -1 for all permutation-inversions; see also section 14-5 of ref 15). The quantity on the right hand side is the antisymmetric square of the irreducible representation Γ . As a result, it is necessary but not sufficient that Γ be degenerate, and so, except in the case of accidental degeneracy, an asymmetric top molecule cannot have a first-order Stark effect. Watson also showed that this symmetry condition leads to the fact that nonpolar symmetric-top molecules do not have a first-order Stark effect.

We apply this symmetry condition to the benzene dimer, where it turns out that cap internal rotation tunneling and stem internal rotation tunneling have qualitatively different effects. One should not be surprised by this because cap internal rotation, which we will henceforth call “cap torsion”, and stem internal rotation, which we will henceforth call “stem rotation”, are qualitatively different internal motions. Cap torsion involves the twisting of the monomers about the intermolecular axis, and this tunneling also occurs in molecules such as benzene-CO, benzene-N₂, benzene-H₂O, benzene-H₂S, and benzene-SO₂. Stem rotation, on the other hand, is an internal rotation of the stem (or frame) of the dimer about an axis perpendicular to the intermolecular axis. To summarize our symmetry result, we find that low-barrier cap torsion tunneling gives rise to levels that have a first-order Stark effect, as is observed, whereas stem-rotation tunneling would not give rise to such levels even if the corresponding barrier were low.

To clearly contrast the effects of cap torsional tunneling versus stem rotational tunneling we will initially consider four different tunneling situations leading to the molecular symmetry (MS) groups $C_{6v}(\text{M})$, $C_{6h}(\text{M})$, G_{24} , and $D_{6h}(\text{M})$. The character tables of these groups (except for $C_{6h}(\text{M})$) are given in Appendix A of ref 15.

$C_{6v}(\text{M})$ Symmetry. If the benzene dimer had insuperable tunneling barriers for all the intermolecular rearrangements except cap torsion, it would have MS group symmetry $C_{6v}(\text{M})$

as is appropriate for benzene-CO. For this “only cap-tunneling” benzene dimer molecule the rotational states would be nondegenerate, but the rotation-torsion levels having torsional quantum number $K_{\text{cap}} = |k_{\text{cap}}| = 6n \pm 1$ would have rovibronic symmetry E_1 , and those having $K_{\text{cap}} = 6n \pm 2$ would have rovibronic symmetry E_2 ; the antisymmetric square of either of these is A_2 , the symmetry of μ_f . Thus such levels would have a first-order Stark shift. Rotation-torsion levels having $K_{\text{cap}} = 6n$ or $6n \pm 3$ would have rovibronic symmetry $A_1 + A_2$ or $B_1 + B_2$, respectively; the antisymmetric square of either of these reducible representations is also A_2 . However, the degeneracy of these levels is accidental (although systematic) and only occurs when such levels are significantly above the torsional barrier. Rotation-torsion levels in the ground torsional state with $K_{\text{cap}} = 0$ would be nondegenerate and would not have a first-order Stark shift. These symmetry results apply to the benzene-CO dimer, for which no Stark effect measurements have been made.⁷

$C_{6h}(\text{M})$ Symmetry. Alternatively, if the benzene dimer had insuperable tunneling barriers for all the intermolecular rearrangements except stem rotation, it would have MS group symmetry $C_{6h}(\text{M})$; this is an Abelian group of order 12. The elements map onto those of the point group C_{6h} as shown in Table 1. This hypothetical “only stem-rotation”

Table 1. Mapping of the Elements of the MS Group $C_{6h}(\text{M})$ onto Those of the Point Group C_{6h}

$C_{6h}(\text{M})$	C_{6h}
E	E
$(1'2'3'4'5'6')$	C_6
$(1'3'5')(2'4'6')$	C_3
$(1'4')(2'5')(3'6')$	C_2
$(1'5'3')(2'6'4')$	$(C_3)^2$
$(1'6'5'4'3'2')$	$(C_6)^5$
$(1'4')(2'5')(3'6')(14)(23)(56)^*$	i
$(1'5'3')(2'6'4')(14)(23)(56)^*$	$(S_3)^2$
$(1'6'5'4'3'2')(14)(23)(56)^*$	$(S_6)^5$
$(14)(23)(56)^*$	σ_h
$(1'2'3'4'5'6')(14)(23)(56)^*$	S_6
$(1'3'5')(2'4'6')(14)(23)(56)^*$	S_3

molecule has an MS group with the same order as the MS group $C_{6v}(\text{M})$ of the “only cap-torsion” molecule, but now because the antisymmetric square of any representation has to be “g”, whereas the symmetry of μ_f is A_u , no level would have a first-order Stark shift.

G_{24} Symmetry. If the benzene dimer had insuperable tunneling barriers for all the intermolecular rearrangements except cap torsion and cap tilt it would have MS group G_{24} . This is the MS group appropriate for the benzene-N₂, benzene-H₂O (see ref 16), benzene-H₂S, and benzene-SO₂ molecules. For the benzene dimer the permutation (78) should be replaced by $(2'6')(3'5')$ in Table A-27 of ref 15. For this “cap-torsion-and-cap-tilting” benzene dimer molecule the symmetry of μ_f is A_{2s} . The rovibronic symmetry is E_{1s} or E_{1a} if $K_{\text{cap}} = 6n \pm 1$, and E_{2s} or E_{2a} if $K_{\text{cap}} = 6n \pm 2$; the antisymmetric square of each of these irreducible representations is A_{2s} , and thus they would each have a first-order Stark shift. Levels with $K_{\text{cap}} = 3n$ would only have a first-order Stark shift if they were significantly above the torsional barrier, and levels in the ground torsional state with $K_{\text{cap}} = 0$ would be nondegenerate and not have a first-order Stark shift. These

symmetry results apply to the benzene–H₂O, benzene–H₂S, and benzene–SO₂ dimers, all of which have been observed to have levels with a first-order Stark shift.^{11–13} Our symmetry result means that the observed states having a first-order Stark effect in these three dimers must have torsional quantum number equal to $6n \pm 1$ or $6n \pm 2$.

$D_{6h}(M)$ Symmetry. In contrast to the above “cap-torsion-and-cap-tilting benzene dimer” molecule having MS group G_{24} , the “stem-rotation-and-cap-tilting” molecule has MS group $D_{6h}(M)$. The elements of the group contain those of the $C_{6h}(M)$ group in Table 1 plus elements like $(2'6')(3'5')(14)(25)(36)$, $(1'4')(2'3')(5'6')(14)(25)(36)$, $(1'4')(2'3')(5'6')(26)(35)^*$, and $(2'6')(3'5')(26)(35)^*$ that map onto C_2 , C_2' , σ_d , and σ_v elements, respectively, of the point group D_{6h} . The MS groups $D_{6h}(M)$ and G_{24} have the same order, but they are not isomorphic. Now, in a similar manner as for the only stem-rotation benzene dimer molecule discussed above, also for the stem-rotation-and-cap-tilting molecule there would be no level with a first-order Stark shift. This is because in $D_{6h}(M)$, the symmetry of μ_f is A_{1u} and the antisymmetric square of any representation has to be “g”.

G_{144} Symmetry. Experimental and theoretical results^{1–4} show that cap torsion, cap tilting, and stem rotation are all feasible intermolecular motions in the benzene dimer, and this leads to the MS group $G_{144} = G_{\text{cap}} \times G_{\text{stem}}$ as introduced in ref 17, where $G_{\text{cap}} = C_{6v}(M)$ and $G_{\text{stem}} = D_6(M)$. The irreducible representations of G_{144} are labeled $\Gamma_{\text{cap}} \times \Gamma_{\text{stem}}$, where Γ_{cap} are the irreducible representations of G_{cap} and Γ_{stem} are the irreducible representations of G_{stem} .¹⁷ The symmetry of μ_f in G_{144} is $A_2 \times A_1$, and there will be a first-order Stark effect in levels having symmetry $E_1 \times \Gamma$ or $E_2 \times \Gamma$, where Γ is any species of G_{stem} . Looking at the symmetry of the rovibronic levels in G_{144} and bearing in mind the very low internal temperature of the molecules in the supersonic jet (2 K) relative to the torsional barrier (6 cm^{-1}) lead to the conclusion that only levels having cap torsion quantum number $K_{\text{cap}} = 6n \pm 1$ or $6n \pm 2$ will have a first-order Stark effect.

G_{576} Symmetry. If all intermolecular motions were feasible, including cap turnover and benzene moiety exchange, the MS group would be the full cluster tunneling group G_{576} .^{5,6} This group contains the space fixed inversion operation E^* that gives the parity of the levels. The space fixed components of the dipole moment μ_f will have negative parity whereas the square of any representation must have positive parity. One would then say that no level has a first-order Stark shift. However, because cap turnover and benzene moiety exchange tunneling splittings are insignificant, the use of G_{576} leads to accidental degeneracies. For levels having $K_{\text{cap}} = 6n \pm 1$ or $6n \pm 2$ the accidental degeneracies are of the type $K^+ + K^-$, $G_7^+ + G_7^-$, $G_1^+ + G_1^-$, etc (see ref 4), and the antisymmetric square of such reducible representations does contain the symmetry of μ_f (A_1^-); they will thus have a first-order Stark shift.

■ STARK SHIFT MEASUREMENTS

The symmetry considerations discussed above were motivated by our Stark effect measurements on the benzene dimer, which are partly discussed in ref 2. We give some of the experimental details here again, with particular emphasis on the experimental setup and its relevance for determining a first-order Stark effect, to support our symmetry results. The measurements were made using the Coaxially Oriented Beam Resonator Arrangement (COBRA) Fourier transform microwave spectrometer in Hannover with the Coaxial Arrangement of Electrodes for Stark

effect Applied in Resonators (CAESAR).^{18,19} The CAESAR setup provides a very homogeneous electric field in the direction of the resonator axis so that the principal advantage of the longer transit time of the molecular jet in the coaxial arrangement of COBRA becomes applicable for Stark effect experiments where very narrow line widths are desired. In the CAESAR setup, the two resonators themselves are used as Stark electrodes, and additional ring electrodes are introduced to homogenize the electric field. Due to the large separation (approximately 0.6 m) of the resonator reflectors that are used as Stark electrodes (Figure 2), very weak homogeneous electric fields can be generated that allow stringent tests for a first-order Stark effect.

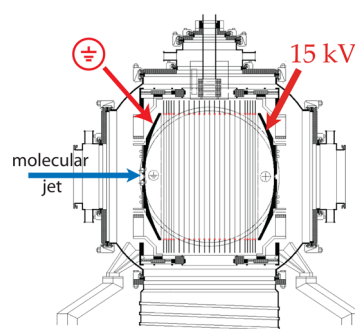


Figure 2. Schematic view of the CAESAR arrangement used for the Stark measurements.

We have performed measurements on a series of $K = 1$ transitions of the benzene dimer and found significant line shifts and broadening even at very low electric field strengths of only 0.02 V/m. This indicates that the observed first-order Stark effect is intrinsic to the energy levels involved and does not simply arise from avoided crossings with higher lying energy levels. Such avoided crossings typically appear at higher electric field strengths of a few kV/cm (10^5 V/m). A quantitative analysis of the linear Stark effect of the $K = 1$ transitions is complicated by the large number of M_J components that exhibit different Stark shifts and thus lead to the observed line broadening. Despite the high resolution provided by the CAESAR setup, the individual components cannot be resolved sufficiently well to perform a quantitative analysis. As a result of our G_{144} symmetry analysis, the fact that the $K = 1$ levels that we observe have a first-order Stark effect means that they must be in states that have cap torsional quantum number $K_{\text{cap}} = 6n \pm 1$ or $6n \pm 2$.

■ SUMMARY

Previous work has established that the benzene dimer is an asymmetric top at equilibrium with a tilted cap-on-stem T-shaped structure, yet we have found that the $K = 1$ states exhibit a first-order Stark shift that would normally be indicative of a symmetric top structure. We show that the appropriate symmetry degeneracy that is required for there to be a first-order Stark shift arises from cap torsion tunneling. Specifically, states having cap torsion quantum number $K_{\text{cap}} = 6n \pm 1$ or $6n \pm 2$ will have a first-order Stark shift. Thus the $K = 1$ states that we observe must have such a value for K_{cap} . The excitation of stem rotation tunneling, on the other hand, does not generate states having a first-order Stark shift despite such states having symmetry degeneracy. States having $K_{\text{cap}} = 0$ will not have the degeneracy required for them to show a first-order Stark shift.

These symmetry results are also applicable to other benzene complexes such as benzene–CO and benzene–H₂O.

AUTHOR INFORMATION

Corresponding Author

*M. Schnell: e-mail, melanie.schnell@asg.mpg.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.v.d.A. and P.R.B. are grateful to the Fritz Haber Institute for hospitality. A.v.d.A. also thanks the Alexander von Humboldt Stiftung for a Humboldt Senior Research Award. M.S. acknowledges financial support by the Deutsche Forschungsgemeinschaft and the Cluster of Excellence “The Hamburg Centre for Ultrafast Imaging” and by the Fonds der Chemischen Industrie via a Dozentenstipendium. J.-U.G. is grateful for support from the Deutsche Forschungsgemeinschaft and the Land Niedersachsen.

REFERENCES

- (1) Schnell, M.; Bunker, P. R.; von Helden, G.; Grabow, J.-U.; Meijer, G.; van der Avoird, A. Structure of the Benzene Dimer: Governed by Dynamics. *Angew. Chem., Int. Ed.* **2013**, *52*, 5180–5183.
- (2) Schnell, M.; Bunker, P. R.; von Helden, G.; Grabow, J.-U.; Meijer, G.; van der Avoird, A. Unraveling the Internal Dynamics of the Benzene Dimer: a Combined Theoretical and Microwave Spectroscopy Study. *Phys. Chem. Chem. Phys.* **2013**, *15*, 10207–10223.
- (3) Podeszwa, R.; Bukowski, R.; Szalewicz, K. Potential Energy Surface for the Benzene Dimer and Perturbational Analysis of π - π Interactions. *J. Phys. Chem. A* **2006**, *110*, 10345–10354.
- (4) van der Avoird, A.; Podeszwa, R.; Szalewicz, K.; Leforestier, C.; Bunker, P. R.; Schnell, M.; von Helden, G.; Meijer, G. Vibration-Rotation-Tunneling States of the Benzene Dimer: an *ab initio* Study. *Phys. Chem. Chem. Phys.* **2010**, *12*, 8219–8240.
- (5) Odutola, J. A.; Alvis, D. L.; Curtis, C. W.; Dyke, T. R. Permutation-inversion groups for dimers: Class structure and character table. *Mol. Phys.* **1981**, *42*, 267–282.
- (6) Schmied, R.; Lehmann, K. K. Computer-generated character tables and nuclear spin statistical weights: application to benzene dimer and methane dimer. *J. Mol. Spectrosc.* **2004**, *226*, 201–202.
- (7) Brupbacher, Th.; Bauder, A. Pure rotational spectrum and structure of the benzene-CO van der Waals complex. *J. Chem. Phys.* **1993**, *99*, 9394–9399.
- (8) Weber, Th.; Smith, A. M.; Riedle, E.; Neusser, H. J.; Schlag, E. W. High-resolution UV spectrum of the benzene-N₂ van der Waals complex. *Chem. Phys. Lett.* **1990**, *175*, 79–83.
- (9) Ohshima, Y.; Kohguchi, H.; Endo, Y. Pulsed-nozzle Fourier-transform microwave spectroscopy of the benzene-¹⁵N₂ complex. *Chem. Phys. Lett.* **1991**, *184*, 21–24.
- (10) Gutowsky, H. S.; Emilsson, T.; Arunan, E. Low-*J* rotational spectra, internal rotation, and structures of several benzene-water dimers. *J. Chem. Phys.* **1993**, *99*, 4883–4893.
- (11) Emilsson, T.; Gutowsky, H. S.; de Olivera, G.; Dykstra, C. E. Rotational patches: Stark effect, dipole moment, and dynamics of water loosely bound to benzene. *J. Chem. Phys.* **2000**, *112*, 1287–1294.
- (12) Arunan, E.; Emilsson, T.; Gutowsky, H. S.; Fraser, G. T.; de Olivera, G.; Dykstra, C. E. Rotational spectrum of the weakly bonded C₆H₆-H₂S dimer and comparisons to C₆H₆-H₂O dimer. *J. Chem. Phys.* **2002**, *117*, 9766–9776.
- (13) Taleb-Bendiab, A.; Hillig, K. W., II; Kuczkowski, R. L. Microwave spectrum of benzene-SO₂: Barrier to internal rotation, structure and dipole moment. *J. Chem. Phys.* **1992**, *97*, 2996–3006.
- (14) Watson, J. K. G. The Symmetry Condition for a First-Order Stark Effect. *J. Mol. Spectrosc.* **1974**, *50*, 281–285.
- (15) Bunker, P. R.; Jensen, P. *Molecular Symmetry and Spectroscopy*, 2nd ed.; NRC Research Press: Ottawa, 2006. See <http://www.nrcresearchpress.com/doi/book/10.1139/9780660196282>.
- (16) Gregory, J. K.; Clary, D. C. Quantum simulation of the benzene-water complex. *Mol. Phys.* **1996**, *88*, 33–52.
- (17) Špirko, V.; Engkvist, O.; Soldan, P.; Setzle, H. L.; Schlag, E. W.; Hobza, P. Structure and vibrational dynamics of the benzene dimer. *J. Chem. Phys.* **1999**, *111*, 572–582.
- (18) Grabow, J.-U.; Palmer, E. S.; McCarthy, M. C.; Thaddeus, P. Supersonic-jet cryogenic-resonator coaxially oriented beam-resonator arrangement Fourier transform microwave spectrometer. *Rev. Sci. Instrum.* **2005**, *76*, 093106–093106.
- (19) Schnell, M.; Banser, D.; Grabow, J.-U. Coaxially aligned electrodes for Stark-effect applied in resonators using a supersonic jet Fourier transform microwave spectrometer. *Rev. Sci. Instrum.* **2004**, *75*, 2111–2115.