

Photoelectron Spectroscopy of *m*-Xylylene Anion

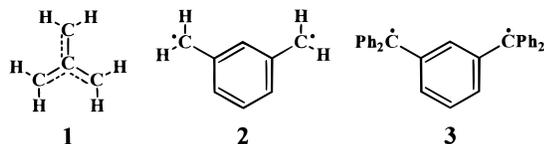
Paul G. Wenthold,* Joseph B. Kim, and W. C. Lineberger*

Contribution from JILA, University of Colorado and National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440

Received July 11, 1996[⊗]

Abstract: The 351-nm photoelectron spectrum of the negative ion of 1,3-benzoquinodimethane (*m*-xylylene) is reported. Features are observed in the photoelectron spectrum corresponding to formation of the 3B_2 , 1A_1 , and 1B_2 states of *m*-xylylene. The electron affinity of the triplet ground state is found to be 0.919 ± 0.008 eV, and vibrational frequencies of 290, 540, and 1500 cm^{-1} are obtained. The active modes are assigned to α -carbon bending, ring deformation, and methylene bending, respectively. The 1A_1 state is found to lie 9.6 ± 0.2 kcal/mol higher in energy than the ground state, in good agreement with theoretical predictions. Vibrational frequencies of 265, 1000, and 1265 cm^{-1} are found for this state. The 1B_2 is estimated to be <21.5 kcal/mol higher in energy than the ground state. Density functional calculations have been carried out on the negative ion, indicating that the 2B_1 ion is a minimum on the potential energy surface, lying 2.9 kcal/mol lower in energy than the 2A_2 ion, which is a transition state.

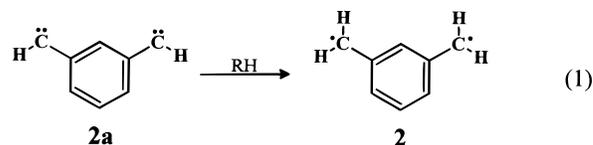
Recent approaches to the design and construction of magnetic organic compounds (organoferrromagnets) have utilized biradicals, such as trimethylenemethane (TMM) derivatives or *m*-benzoquinodimethanes (*m*-xylylenes), as “ferromagnetic coupling units.”¹ These types of linkages are used because the parent biradicals, TMM (**1**) and *m*-xylylene (**2**), are known to possess triplet ground states,^{2,3} and thus serve as high spin linkages. Moreover, the singlet–triplet energy splittings for these biradicals (ΔE_{ST}) are believed to be large (*ca.* 0.5 eV),^{4–7} so small perturbations in their structure will not change the nature of the ground state. The high spin preference in these molecules is predicted by simple qualitative theory,⁸ and is a result of electron repulsion that destabilizes the singlet states.



The physical properties of these high-spin biradicals have been of considerable interest. In particular, TMM (**1**) has been the subject of experimental studies for 30 years, and of theoretical studies nearly 20 years longer. EPR measurements by Dowd showed that the biradical had a triplet ground state,^{2,9} and in subsequent experiments, the proton hyperfine coupling^{10,11} and rate of ring closure of the ground state^{12,13} were determined.

More recently, Maier and co-workers^{14,15} have obtained the infrared spectrum of the ground state of **1**. Assignments of the vibrational modes were readily made on the basis of results from *ab initio* calculations. Additional vibrational information for the triplet and planar singlet states of TMM has come from the recently reported photoelectron spectrum of the TMM negative ion.⁴ Moreover, using a simple thermochemical cycle, the heat of formation of TMM could be determined from the measured electron affinity. Altogether, the experimental studies listed here, along with more than a dozen computational studies,¹⁶ have led to a substantial understanding of the properties and electronic structure of this biradical.

In contrast, little is known experimentally or theoretically about *m*-xylylene, **2**. Elegant ESR studies by Wright and Platz³ demonstrated that **2** has a triplet ground state, as predicted by theory. For these experiments, the biradical was generated from the double hydrogen atom transfer reaction of the corresponding (bis)carbene, **2a**, with the ethanol matrix utilized for the study (eq 1). The (bis)carbene **2a** was prepared by photolysis of the corresponding bis(diazo) compound.¹⁷ Migirdicyan and Bau-



det¹⁸ reported the electronic spectrum of **2**, generated by UV photolysis of *m*-xylene in a hydrocarbon matrix at 77 K. From the vibrational structure observed in the fluorescence spectrum, vibrational frequencies of 530 and 988 cm^{-1} were obtained. These were assigned to ring deformation and ring-breathing modes of the ground state biradical.¹⁸ Finally, a lower limit of 76 kcal/mol for the heat of formation of **2** was determined by

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.
 (2) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.
 (3) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628.
 (4) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.
 (5) Fort, R. C., Jr.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549.
 (6) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791.
 (7) Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273.
 (8) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
 (9) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.
 (10) Dowd, P.; Sachdev, K. *J. Am. Chem. Soc.* **1967**, *89*, 715.
 (11) Dowd, P.; Gold, A.; Sachdev, K. *J. Am. Chem. Soc.* **1968**, *90*, 2715.
 (12) Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977**, *99*, 6438.

(13) Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799.
 (14) Maier, G.; Reisenauer, H. P.; Lanz, K.; Tross, R.; Jürgen, D.; Hess, B. A., Jr.; Schaad, L. *J. Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 74.
 (15) Maier, G.; Jürgen, D.; Tross, R.; Reisenauer, H. P.; Hess, B. A., Jr.; Schaad, L. *J. Chem. Phys.* **1994**, *189*, 367.
 (16) Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664 and references therein.
 (17) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526.
 (18) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400.

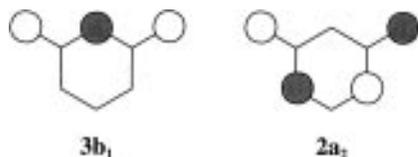
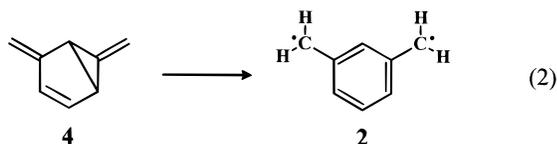


Figure 1. Schematic representation of the Hückel non-bonding MO's in *m*-xylylene.

Pollack *et al.*,¹⁹ who found that they could not deprotonate the 3-methylbenzyl cation in the gas phase.

Detailed studies of the reactivity of **2** have been carried out by Goodman and Berson.²⁰ It was found that **2**, prepared from the bis-methylene hydrocarbon **4** (eq 2),^{21,22} can be trapped by conjugated dienes to form vinyl indanes and *m*-cyclophenes.^{21–23} Product distributions obtained from trapping deuterium labeled reagents indicated a symmetric intermediate;²² however, the spin state of the reacting species could not be determined.



The reactivity of several derivatives of **2** has also been studied. Gajewski *et al.*²⁴ have examined the reactions of alkylated *m*-xylylenes in solution. They found that the tetramethyl derivative of **2** undergoes rapid dimerization at room temperature, and that the formation of the dimer was inhibited by the presence of oxygen. In addition, a cyclopropyl-substituted *m*-xylylene was studied. It was found that the cyclopropyl group remained intact during the dimerization, suggesting that the reacting species was a triplet biradical. Similar experiments carried out previously²⁵ with cyclopropyl-substituted TMM found that some of the product ring-opened, which was interpreted to mean that a singlet biradical was generated. Perhaps the oldest and most famous derivative of *m*-xylylene is Schlenk's hydrocarbon, **3**.²⁶ This ground-state triplet biradical is well characterized.^{27,28} A summary of the properties of other *m*-xylylenes, including naphtho and oxo derivatives, is provided elsewhere.²⁹

Semiempirical methods^{7,30–32} and *ab initio* molecular orbital calculations^{5,6} have been carried out to examine the electronic structure of **2**. The most instructive of these is the multi-configurational SCF study by Kato *et al.*,⁶ in which a clear description of the electronic structure of **2** is provided. The two Hückel non-bonding molecular orbitals (NBMO's) for *m*-xylylene are shown in Figure 1. The $3b_1$ orbital resembles that for a pentadienyl system, while the $2a_2$ orbital resembles a

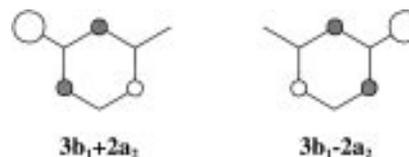


Figure 2. Schematic representation of the GVB orbitals of *m*-xylylene, constructed from the linear combinations of the non-bonding molecular orbitals.

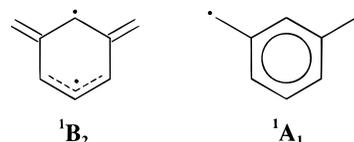


Figure 3. Schematic description of the bonding in the singlet states of *m*-xylylene.

heptatrienyl system. Three low-lying electronic states, one triplet and two singlets, can be formed by placing two electrons in the two NBMO's. The 3B_2 and 1B_2 states are formed by placing one electron in each of the orbitals, and are open shell states. The wave functions for these states are shown in eqs 3 and 4, respectively.

$$^3B_2 = \left| \frac{\dots 3b_1 2a_2 (\alpha\beta + \beta\alpha)}{\sqrt{2}} \right\rangle, \dots 3b_1 2a_2 (\alpha\alpha), \dots 3b_1 2a_2 (\beta\beta) \quad (3)$$

$$^1B_2 = \left| \frac{\dots 3b_1 2a_2 (\alpha\beta - \beta\alpha)}{\sqrt{2}} \right\rangle \quad (4)$$

A closed-shell 1A_1 state is formed by using a two-configuration wave function, as shown in eq 5,

$$^1A_1 = c_1^2 |\dots 3b_1^2\rangle - c_2^2 |\dots 2a_2^2\rangle = \left| \frac{(c_1 3b_1 + c_2 2a_2)(c_1 3b_1 - c_2 2a_2)(\alpha\beta - \beta\alpha)}{\sqrt{2}} \right\rangle \quad (5)$$

The weighted sums and differences of the $3b_1$ and $2a_2$ orbitals shown in eq 5 are the generalized valence bond (GVB) orbitals of *m*-xylylene. The GVB orbitals are best represented as benzylic orbitals, as shown in Figure 2. As discussed by Kato *et al.*,⁶ electron repulsion within the singlet states will distort the NBMO's from the pure Hückel orbitals. Thus, the bonding in the singlet states of *m*-xylylene will be more localized than that in the triplet. A schematic picture of the bonding in the 1B_2 and 1A_1 states is shown in Figure 3.

The calculations that have been carried out on *m*-xylylene have focused for the most part on the relative energies of the three electronic states. *Ab initio* calculations that include π correlation⁵ predict the 3B_2 state to be the lowest energy state, with the 1A_1 and 1B_2 states lying *ca.* 10 and 23 kcal/mol (0.4 and 1 eV) higher in energy, respectively.

Here we report the 351-nm photoelectron spectrum of the negative ion of *m*-xylylene, $2^{\cdot-}$. Electron detachment to form three electronic states of **2** is observed. The relative energies of the three states are obtained, and are in good agreement with theoretical predictions. Experimental vibrational frequencies are obtained for the 3B_2 and 1A_1 states of *m*-xylylene, and are readily assigned by comparison with the frequencies of *m*-xylene and with the aid of *ab initio* calculations.

(19) Pollack, S. K.; Raine, B. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6308.

(20) Berson, J. A. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1988; Vol. II, Chapter 10.

(21) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867.

(22) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409.

(23) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5424.

(24) Gajewski, J. J.; Paul, G. C.; Chang, M. J.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150.

(25) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563.

(26) Schlenk, W.; Brauns, M. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 661, 716.

(27) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Eng.* **1970**, *9*, 906.

(28) Luckhurst, G. R.; Pedulli, G. F.; Tiecco, M. *J. Chem. Soc. B* **1971**, 329.

(29) Platz, M. In *Diradicals*; Borden, W. T., Ed.; John Wiley & Sons: New York, 1982; p 195.

(30) Baudet, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 191.

(31) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.

(32) Döhnert, D.; Koutecky, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789.

Experimental Section

The experiments described in this paper were carried out using a negative ion photoelectron spectrometer and procedures described in detail elsewhere,^{33,34} and only a brief description is provided here. The apparatus consists of three major parts: ion production, mass analysis and photodetachment, and electron energy analysis.

Ions are prepared in *ca.* 0.5 Torr of helium in a liquid nitrogen-cooled flowing afterglow ion source. Primary ions, in this case, $O^{\bullet -}$, are produced by a microwave electrical discharge in a small amount of oxygen seeded in the helium buffer gas. Typical $O^{\bullet -}$ currents are 1.5–2 nA. *m*-Xylylene ions, $2^{\bullet -}$, are generated by allowing the $O^{\bullet -}$ to react with *m*-xylene, added just after the microwave source. Bruins *et al.*³⁵ reported that an $[M - 2H]^{\bullet -}$ ion is the major product in the reaction of *m*-xylene with $O^{\bullet -}$, and, moreover, that labeling studies show that one hydrogen is removed from each methyl group to give the *m*-xylylene structure.

Ions prepared in the flowing afterglow are thermalized by collisions with the helium buffer gas. Liquid nitrogen is passed through a stainless steel jacket around the flowing afterglow in order to cool the ions to below room temperature. Ions formed under these conditions typically have temperatures of 175–185 K, based on the intensities of hot bands in the photoelectron spectra. The ions are gently extracted from the flowing afterglow through a 1-mm orifice in a small nosecone into a differentially pumped region where they are accelerated to 735 eV, focused, and mass-selected using a Wien velocity filter ($M/\Delta M \approx 40$). Deprotonated *m*-xylene has been reported in a study of the reaction of $O^{\bullet -}$ with *m*-xylene,³⁵ and the resolution of our mass filter is not sufficient to completely resolve the $[M - 2H]^{\bullet -}$ and $[M - H]^{\bullet -}$ ions. However, clean spectra of $2^{\bullet -}$, with negligible contribution from the $[M - H]^{\bullet -}$ ion, could be obtained by using very low flows of *m*-xylene precursor in order to minimize the possibility of secondary reactions that might lead to $[M - H]^{\bullet -}$ ions, and by selecting the low-*m/z* side of the *m/z* 104–105 peak. Under these conditions, approximately 5 pA of $2^{\bullet -}$ could be prepared.

After mass selection, the ions are decelerated to 40 eV and enter into the laser interaction region, where they are crossed with the 351-nm output of an argon ion laser at the center of an external buildup cavity that has been described previously.³³ The laser power inside the cavity is ~ 50 W. The kinetic energies of photodetached electrons are measured using a hemispherical electrostatic analyzer, with a resolution of ~ 8 meV. The absolute energy scale is calibrated using the $^3P_2 + e^- \leftarrow ^2P_{3/2}$ peak in the spectrum of $O^{\bullet -}$ (EA(O) = 1.461 12 eV).³⁶ A small energy scale compression factor, γ , is determined by comparing the measured fine structure peak positions with the known³⁷ term energies in the tungsten atom. The extent of the scale compression is less than 1%. Electron binding energy is determined by subtracting the electron kinetic energy from the laser photon energy, 3.531 19 eV.

Materials. All reagents were obtained from commercial suppliers and were used as received. *m*-Xylene (98%) was obtained from Aldrich. Gas purities were He 99.995% and O_2 99%.

Results

The photoelectron spectrum of $2^{\bullet -}$, prepared in a liquid nitrogen cooled flowing afterglow from the reaction of $O^{\bullet -}$ with *m*-xylene,³⁵ is shown in Figure 4. Three electronic states of **2** are observed in the spectrum, and as will be discussed below, these are assigned to the 3B_2 , 1A_1 , and 1B_2 states of *m*-xylylene.

The region of the lowest energy state is shown in Figure 5. As this corresponds to electron detachment to give the ground state of *m*-xylylene, this set of peaks is ascribed to the formation

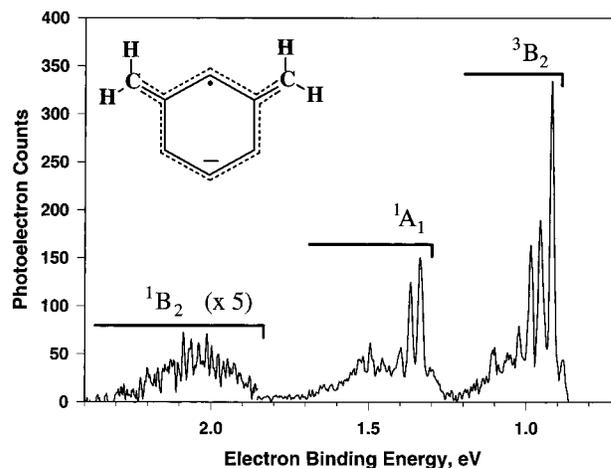


Figure 4. The 351-nm photoelectron spectrum of the *m*-xylylene negative ion, $2^{\bullet -}$.

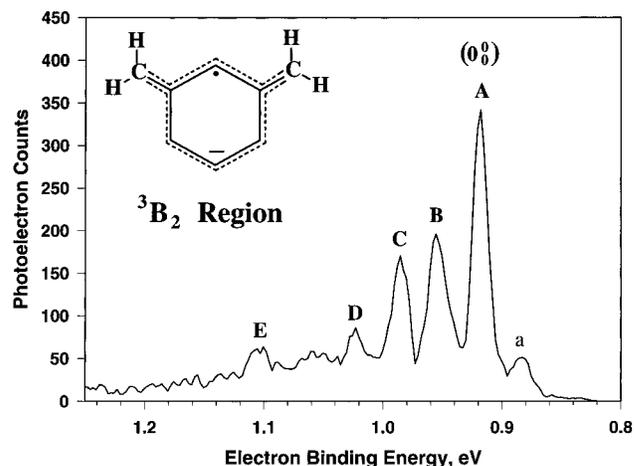


Figure 5. The 3B_2 region of the photoelectron spectrum of $2^{\bullet -}$. Positions and assignments of labeled peaks are provided in Table 1.

of the 3B_2 state.³ The origin of this feature is an intense peak at an electron binding energy of 0.919 ± 0.008 eV, the electron affinity of *m*-xylylene. Three neutral vibrations of the biradical are active in this region, at 290 ± 20 , 540 ± 20 , and 1500 ± 40 cm^{-1} , which correspond to peaks B, C, and E, respectively. Peak D is a combination band, corresponding to excitation of one quanta of each of the two low-frequency modes. A weak hot band (peak a) is also observed, giving an anion vibrational frequency of 275 ± 20 cm^{-1} . Based upon analysis of the neutral spectrum, this frequency corresponds to the α -carbon bending vibration in the anion. The relative positions of all the observed peaks are listed in the left half of Table 1.

The two excited states observed in the spectrum correspond to the formation of singlet states, because the lowest energy triplet state of **2** is 2.8 eV higher in energy than the ground state.¹⁸ Detachment to give the first excited state (Figure 6) is weaker than that for the ground state, but still has well-resolved features. This is assigned to formation of the 1A_1 state on the basis of angular distribution measurements (*vide infra*). The origin of this band is 0.415 ± 0.008 eV (9.6 ± 0.2 kcal/mol) higher than that for the ground state. Three vibrations are observed in this region, at 265 ± 20 , 1000 ± 40 , and 1260 ± 40 cm^{-1} , which correspond to peaks B, D, and E in Figure 6. A 275- cm^{-1} hot band is also detected, and is labeled as peak a. The relative positions of the observed peaks for this state are listed in the right half of Table 1.

The third observed state is a very weak state, *ca.* 20 \times weaker than the ground state transition, and exhibits no resolvable

(33) Ervin, K. M.; Lineberger, W. C. In *Advances in Gas Phase Ion Chemistry*; Adams, N. G., Babcock, L. M., Eds.; JAI Press: Greenwich, 1992; Vol. 1; p 121.

(34) Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

(35) Bruins, A. P.; Ferrer-Correia, A. J.; Harrison, A. G.; Jennings, K. R.; Mitchum, R. K. *Adv. Mass. Spectrom.* **1978**, *7*, 355.

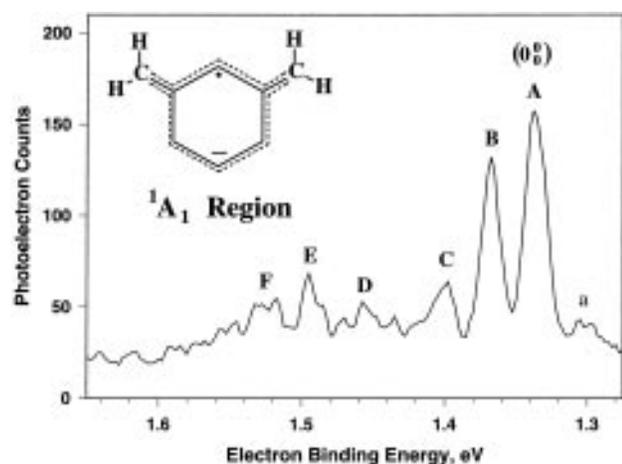
(36) Neumark, D. M.; Lykke, K. R.; Andersen, T.; Lineberger, W. C. *Phys. Rev. A* **1985**, *32*, 1890.

(37) Moore, C. E. *Atomic Energy Levels*; US GPO Circular No. 467: Washington, 1952.

Table 1. Peak Positions and Assignments for the Photoelectron Spectrum of 2^{-}

peak ^a	3B_2		1A_1	
	distance from origin, cm ⁻¹	assign ^b	distance from origin, cm ⁻¹	assign ^b
a	275	1 ₁ ⁰	275	1 ₁ ⁰
A	0	0 ₀ ⁰	0	0 ₀ ⁰
B	290	1 ₀ ¹	265	1 ₀ ¹
C	540	2 ₀ ¹	535	1 ₀ ²
D	850	1 ₀₋₀ ¹	1000	3 ₀ ¹
E	1500	4 ₀ ¹	1260	4 ₀ ¹
F			1515	1 ₀ ⁴

^a Peaks labeled in Figures 5 (3B_2) and 6 (1A_1). ^b Vibrational assignments are as follows: 1, α -carbon bending; 2, ring deformation; 3, ring breathing; 4, CH₂ bending. See text for details.

**Figure 6.** The 1A_1 region of the photoelectron spectrum of 2^{-} . Positions and assignments of labeled peaks are provided in Table 1.

features. The angular distribution results described below indicate that this state has an electronic structure similar to that of 3B_2 . Therefore, this transition is assigned to the 1B_2 state. The vertical detachment energy for this state is obtained from the most intense part of the band, and is at a binding energy of 2.04 eV.

Angular Distribution Measurements. The angular dependence of the photoelectron signal is given by eq 6, where θ is the angle between the electric field vector of the laser and the electron collection direction, σ_{tot} is the total photodetachment cross section, and β is the anisotropy parameter³⁸⁻⁴⁰ ($-1 \leq \beta \leq 2$),

$$I(\theta) = \left[\frac{\sigma_{\text{tot}}}{4\pi} \right] \left[1 + \frac{\beta(3 \cos^2 \theta - 1)}{2} \right] \quad (6)$$

The spectra in Figures 4-6 were obtained with the laser electric field oriented at 54.7° ("the magic angle") with respect to the detector. When this is the case, the signal is independent of the anisotropy parameter. The photoelectron spectrum of 2^{-} was also measured with laser polarizations of 0° and 90°. The anisotropy parameter can be calculated from the photodetachment yields at these two orientations via the relationship

$$\beta = \frac{I_0 - I_{90}}{0.5I_0 + I_{90}} \quad (7)$$

where I_0 and I_{90} are the photodetachment signals at 0° and 90°.

(38) Cooper, J.; Zare, R. N. *J. Chem. Phys.* **1968**, *48*, 942.

(39) Cooper, J.; Zare, R. N. *J. Chem. Phys.* **1968**, *49*, 4252.

(40) Hall, J. L.; Siegel, M. W. *J. Chem. Phys.* **1968**, *48*, 943.

The value of β depends on the nature of the orbital from which the electron is detached and the electron kinetic energy.⁴¹ For atomic ions, detachment from an s orbital results in a p-wave ($l = 1$) continuum electron, and $\beta = +2$, independent of electron kinetic energy. Detachment of an electron from a p orbital results in a mixture of s- and d-wave continuum electron states, giving an energy-dependent value for β . At threshold, s-wave ($l = 0$) detachment dominates, giving $\beta = 0$ and an isotropic photoelectron angular distribution. At energies ~ 1 eV above threshold, d-wave detachment becomes more important and β approaches -1 . Detachment from molecular anions is more complicated, but it has been found that, in general, β is positive for detachment from σ (s-like) orbitals and negative for detachment from π (p-like) orbitals in the electron energy range corresponding to the data reported here. The important point is that the photoelectron angular distribution provides a signature for the orbital from which the electron was detached.

The measured anisotropy parameters for the states labeled 3B_2 , 1A_1 , and 1B_2 in Figure 4 are -0.53 ± 0.10 , 0.0 ± 0.10 , and -0.5 ± 0.2 , respectively. The values of β measured for detachment to give the ground state and the second excited state are similar, and basically what would be expected for detachment of a benzylic anion (351-nm photodetachment of benzyl anion results in $\beta = -0.42$ ^{42,43}). The anisotropy parameter for the first excited state indicates nearly isotropic detachment, and is significantly different from that of the other two states. We interpret these results to mean that the ground state and second excited state result from detachment from the same orbital, while the first excited state arises from electron detachment from a different orbital. This indicates that the second excited state has an electronic structure similar to the ground state, and is therefore assigned to be the open-shell 1B_2 state. The first excited state has an electronic structure that is significantly different from the ground state, consistent with what would be expected for the closed-shell 1A_1 state.

Discussion

The triplet ground state and two singlet states of *m*-xylylene are observed in the photoelectron spectrum of 2^{-} . While the triplet state has been observed previously, the present study constitutes the first direct detection of the singlet states. In the sections below, we discuss the important features of each of the bands, including the results of the Franck-Condon analysis. However, first we address the nature and structure of the *m*-xylylene negative ion.

The *m*-Xylylene Ion. As noted above, the *m*-xylylene negative ion required for this study was prepared from the reaction of $O^{\bullet -}$ with *m*-xylene. Bruins *et al.*³⁵ reported that deuterium-labeling studies indicate that one hydrogen is removed from each methyl group in this reaction. Although 1,1- H_2^+ abstraction to form a phenyl carbene negative ion is a possibility for this system, we did not see signals in the photoelectron spectrum that can be attributed to any $[M - 2H]^{\bullet -}$ ions other than 2^{-} , consistent with the reported results. Features that arise due to isomeric impurities can usually be distinguished by changing source conditions slightly, thereby changing the fraction of each ion.⁴³ The relative intensities of the three features in Figure 4 are independent of the source conditions, which suggests that they arise from detachment from only one isomer of the anion.

(41) Hanstorp, D.; Bengtsson, C.; Larson, D. *J. Phys. Rev. A* **1989**, *40*, 670.

(42) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.

(43) Gunion, R. F.; Karney, W.; Wenthold, P. G.; Borden, W. T.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 5074.

Table 2. Experimentally Determined Quantities

quantity	state		
	³ B ₂	¹ A ₁	¹ B ₂
term energy, ^a kcal/mol	0.0	9.6 ± 0.2	≤21.5
vib freq, ^b cm ⁻¹ (ΔQ_i) ^c			
α -carbon bending	290 (0.360) ^c	265 (0.423) ^c	
ring deformation	540 (0.213) ^c		
ring breathing ^d		1000 (0.117) ^c	
CH ₂ bending ^d	1500 (0.093) ^c	1260 (0.097) ^c	

^a Energy relative to the ground state. ^b Determined from average peak spacings; see Table 1. Estimated uncertainty is ± 20 cm⁻¹ unless otherwise noted. ^c The value in parentheses is the normal coordinate displacement in units of amu^{1/2} Å. ^d Estimated uncertainty is ± 40 cm⁻¹.

intensities of the observed transitions can be accurately reproduced using a Franck-Condon fitting routine described elsewhere.^{33,50} The Franck-Condon factors obtained from such a fit are the “normal coordinate displacements”, ΔQ_i , the elements of the Duschinsky **K** matrix.⁵¹ The vibrational frequencies and corresponding Franck-Condon factors obtained by fitting the photoelectron spectrum are listed in the top half of Table 2. The largest normal coordinate displacements are observed for the low-frequency modes, indicating a moderate difference in the geometries between the ion and the neutral in these coordinates.

The ¹A₁ State. The first excited state observed in the photoelectron spectrum of 2⁻ is assigned to the closed-shell ¹A₁ state of *m*-xylylene. From the position of the origin peak, it is found that this state is 9.6 ± 0.2 kcal/mol higher in energy than the ³B₂ state, in excellent agreement with theoretical predictions.⁵⁻⁷

Three vibrations are observed for the ¹A₁ state, at 265 ± 20, 1000 ± 40, and 1260 ± 40 cm⁻¹. The mode at 265 cm⁻¹ is the α -carbon bending vibration in the ¹A₁ state. The 1000-cm⁻¹ vibration does not correspond to any observed in the ³B₂ region, but agrees well with the symmetric “ring-breathing” mode of *m*-xylene, 998 cm⁻¹.⁴⁸ Migirdicyan and Baudet¹⁸ report 988 cm⁻¹ for this mode in the ³B₂ state, and so a value of 1000 cm⁻¹ for the ¹A₁ state seems quite plausible. The 1260-cm⁻¹ mode is assigned to bending of the methylene group. The spectroscopic assignments for the observed peaks for this state

(50) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1988**, *92*, 5405.

(51) Duschinsky, F. *Acta Physicochim. URSS* **1937**, *7*, 551.

are given in Table 1. The vibrational frequencies for this state and the corresponding optimized Franck-Condon factors are summarized in the bottom half of Table 2. The Franck-Condon factor for the α -carbon bending mode in this state is similar in magnitude to that for the ³B₂ state, which indicates that the CCC bond angles are similar. This is consistent with the calculated geometries for these states.⁶

The ¹B₂ State. The ¹B₂ feature does not contain any resolvable peaks. The maximum of this band is the vertical detachment energy (VDE), the energy required to form the neutral at the same geometry of the ion. The VDE for this state is at a binding energy of 2.04 eV. The energy of the *adiabatic* transition is less than this value. Detectable signal for the ¹B₂ is first observed at a binding energy of ~1.85 eV, which indicates that the ¹B₂ state lies ≤ 21.5 kcal/mol above the ³B₂ state. *Ab initio* calculations that include π correlation⁵ predict this state to be 23–24 kcal/mol higher in energy than the ³B₂ state, consistent with the present result.

Conclusions

Photoelectron spectroscopy of negative ions continues to be a powerful means for the study of biradicals. In this study of the *m*-xylylene, well-resolved spectra are obtained despite the fact that the system contains eight carbon atoms and has active vibrational modes below 300 cm⁻¹. Three electronic states of *m*-xylylene are observed in the spectrum, and the measured physical properties, such as relative energies and vibrational frequencies, are in good agreement with theoretical predictions. The ¹A₁ and ¹B₂ states are found to be 9.6 ± 0.2 and ≤ 21.5 kcal/mol, respectively, higher than the triplet ground state. Detachment of the *m*-xylylene ion leads to activation of α -carbon bending modes in both the ³B₂ and ¹A₁ states. Ring deformation, ring breathing, and CH₂ bending vibrations are also observed. The results presented here suggest that negative ion photoelectron spectroscopy will be amenable to the study of even more complex systems, and these types of studies are currently being planned.

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE 93-18639 and PHY 95-12150) and the Air Force Office of Scientific Research (AASERT). We thank Professor Wes Borden and Dr. David Hrovat for providing us with the results of their *ab initio* calculations.

JA9623830