

necessary. Reproducibility was within  $\pm 10\%$ .

In the emission, monitoring, and photolysis experiments, sample solutions were filtered immediately before use through a 0.22- $\mu\text{m}$  Millipore filter and transferred to a 1  $\times$  1-cm spectrofluorimeter cell. The solutions were deaerated by argon purging for 20 min. The temperature of the solution in the cell was controlled to 0.1  $^{\circ}\text{C}$  by circulating thermostated water.

Luminescence data of solid  $\text{W}(\text{CO})_5\text{L}$  were recorded with use of a triangular cell with the front face at 45 $^{\circ}$  to the exciting light. Conventional absorption spectra were obtained by means of Cary Model 14R and Hewlett-Packard 8450A recording spectrophotometers. Infrared spectra were recorded in isoctane with a Perkin-Elmer Model 281 spectrometer.

Elemental analyses were performed by Analytical Facility, California Institute of Technology.

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**Registry No.**  $\text{W}(\text{CO})_5$ (pyridine), 14586-49-3;  $\text{W}(\text{CO})_5$ (piperidine), 31082-68-5;  $\text{W}(\text{CO})_5$ (4-acetylpyridine), 60166-30-5;  $\text{W}(\text{CO})_5$ (4-benzoylpyridine), 60166-31-6;  $\text{W}(\text{CO})_5$ (4-cyanopyridine), 60166-32-7;  $\text{W}(\text{CO})_5$ (4-formylpyridine), 60166-33-8;  $\text{W}(\text{CO})_6$ , 14040-11-0;  $\text{W}(\text{CO})_5$ (THF), 36477-75-5.

## Excitation Energies in Trimethylenemethane Derivatives

Sheila B. Auster, Russell M. Pitzer,\* and Matthew S. Platz

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received October 7, 1981

**Abstract:** Calculations of triplet-to-singlet and other excitation energies have been carried out on two derivatives of trimethylenemethane (TMM), I modified to contain a five-membered ring and II also including two methyl groups, using (9s5p/4s), [4s3p/2s] Gaussian basis sets. The triplet-singlet energy for II is computed to be 11.7 kcal/mol, only 3.2 kcal/mol lower than that of TMM itself. Additional calculations were carried out in order to make comparisons and, as an aid in understanding the effects of the substituents, with results consistent with previous ideas and models of radical stabilization.

Trimethylenemethane (TMM) and its derivatives have been studied for several reasons. In 1948 it was pointed out that the central carbon atom in TMM (unsynthesized at that time) has the highest bond order possible for a trigonal carbon atom,<sup>1</sup> and thus TMM is a benchmark in Coulson's free valence system.<sup>2</sup> The nonclassical bonding of TMM, its predicted triplet ground state, and its small size add to its theoretical interest and have made it a common textbook example in discussions of molecular orbital (MO) theory.<sup>3,4</sup> Published theoretical studies of TMM have run the gamut from qualitative MO treatments<sup>5</sup> to extensive calculations with configuration interaction wave functions.<sup>6,7</sup>

TMM and TMM derivatives have been postulated as intermediates in a number of reactions involving methylenecyclopropanes<sup>8-10</sup> in which the mechanism required a low-lying singlet state with a low barrier to rotation about the methylene-ring bond. No direct observations of TMM were made, however, until Dowd<sup>11</sup> reported its synthesis and ESR spectrum in 1966. Subsequently there has been a considerable amount of further work on TMM,<sup>12,13</sup> complexes of  $\text{Fe}(\text{CO})_3$  and TMM derivatives,<sup>14-16</sup> and

reactions of methylenecyclopropanes.<sup>17</sup>

Perhaps the most interesting question regarding TMM and its derivatives at present concerns the excitation energy from the ground (triplet) state to the excited (singlet) state. The best theoretical calculation to date of the energy difference from the lowest energy ground-state geometry (planar  $D_{3h}$   $^3A_2'$ ) to the lowest energy excited-state geometry (nonplanar  $C_{2v}$   $^1B_1$ ) is 14 kcal/mol.<sup>7</sup> The experimental measurement that is available for comparison is the activation energy for the disappearance of the TMM ESR spectrum, 7.0 kcal/mol.<sup>18</sup> It is not entirely clear how this value is related to the excitation energy.<sup>19,20</sup> For the alkyl-substituted TMM (II), however, a 3.5 kcal/mol value for the upper limit of the excitation energy has been obtained<sup>21</sup> by the analysis of kinetic data from matrix olefin condensation reactions. Since the comparison of the 14 kcal/mol and 3.5 kcal/mol values is hampered by the fact that they are obtained for different molecules, we felt that it was important to calculate the excitation energy for the TMM derivative (II) itself.

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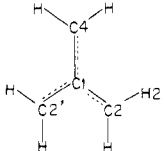
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(20) Aside from the intrinsic difficulties in precise comparisons of activation energies with energy surface features, Berson (ref 19) and Davidson and T. Borden (as quoted in ref 7) have suggested that the activation energy in this case may correspond to a surface crossing rather than an excitation energy. Unpublished calculations by E. R. Davidson, K. Tanaka, and W. T. Borden have not, however, shown such a low-energy crossing.

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Table I. Optimized Geometries for Trimethylenemethane

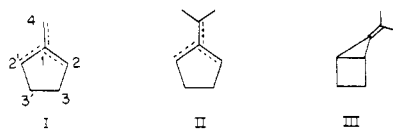


state	C1-C2, A	C1-C4, A	H-C4-H, deg	C2-C1-C2', deg	C1-C2-H2, deg	H-C2-H, deg
<sup>3</sup> B <sub>2</sub>	1.409	1.409	117.5	120	121.25	117.5
<sup>1</sup> A <sub>1</sub>	1.477	1.340	117	117	120.75	118.5
<sup>3</sup> B <sub>1</sub>	1.382	1.496	119	121.5	122	117.25
<sup>1</sup> B <sub>1</sub>	1.382	1.501	119	121.5	122	117.25
<sup>1</sup> B <sub>2</sub>	1.380	1.509	119	121.5	122	117.25

Reviews of TMM work, both experimental and theoretical, have been written by Dowd,<sup>22</sup> Weiss,<sup>23</sup> Berson,<sup>19</sup> and Borden and Davidson.<sup>24,25</sup>

### Theoretical Methods

We have used open-shell restricted Hartree-Fock wave functions (for states of the  $b_1 a_1$  <sup>3</sup>B, <sup>1</sup>B type) and two-configuration self-consistent-field wave functions (for states of the  $a_2, b_2$  <sup>1</sup>A type) to calculate the energies of the ground and low-lying excited electronic states of 2-methylene-1,3-cyclopentadiyl (I) and 2-(1-methylethylidene)-1,3-cyclopentadiyl (II) along with comparison calculations on TMM and a model fragment of I and II. The basis set used was of (9s5p/4s) primitive size, contracted to [4s3p/2s].<sup>26</sup>



Wave functions of this type, although they are far from being as accurate as those that can be obtained for TMM, do give essentially the same value for the TMM <sup>1</sup>B<sub>1</sub> excitation energy as the more accurate wave functions and yet are practical to obtain for the TMM derivatives. The corresponding TMM <sup>1</sup>B<sub>1</sub> excitation energy is 15.1 kcal/mol and is changed only to 14.9 kcal/mol on adding d functions, to 17.6 kcal/mol on correlating the  $\pi$  orbitals, and then back to 14.3 kcal/mol on correlating the  $\sigma$  orbitals as well.<sup>7</sup>

### TMM Results and Standardization

Some of the characteristics of the electronic states of TMM are as follows: At  $D_{3h}$  geometries, the open-shell part of the TMM electron configuration is  $(e'')^2$ , which gives rise to three electronic states of which the lowest two are <sup>3</sup>A<sub>2</sub>' and <sup>1</sup>E'. The Jahn-Teller theorem applies to the <sup>1</sup>E' state and requires that the removal of the 3-fold axis, which lowers the symmetry to  $C_{2v}$ , split the degeneracy of the energy levels with one level lowered and the other raised.<sup>27</sup> The  $D_{3h}$   $e''$  orbitals become  $b_1$  and  $a_2$  orbitals in  $C_{2v}$ , and the two  $C_{2v}$  states are  $b_1 a_2$  <sup>1</sup>B<sub>2</sub> and  $b_1 a_2$  <sup>1</sup>A<sub>1</sub>; in this <sup>1</sup>A<sub>1</sub> state, mixing of the two configurations is required for a proper representation.

The <sup>1</sup>B<sub>2</sub> state has been found to have a small barrier to rotation about the C-C bond along the 2-fold axis,<sup>28</sup> and the minimum energy geometry is found to have this CH<sub>2</sub> group perpendicular to the rest of the molecule. This rotation changes the  $b_1$  orbital to  $b_2$  and the <sup>1</sup>B<sub>2</sub> state to <sup>1</sup>B<sub>1</sub>. To reduce the symmetry to  $C_{2v}$  most simply, the 3-fold axis is removed by either changing the

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Table II. Population Analysis

state	radical population <sup>a</sup>		$\pi$ overlap population <sup>b</sup>	
	C2	C4	C1-C2	C1-C4
TMM				
<sup>1</sup> B <sub>2</sub>	0.51	1.01	0.33	-0.14
<sup>1</sup> B <sub>1</sub>	0.50	1.00	0.31	-0.15
<sup>3</sup> B <sub>1</sub>	0.50	0.99	0.31	-0.14
<sup>1</sup> A <sub>1</sub>	0.95	0.15	-0.06	0.56
<sup>3</sup> B <sub>2</sub>	0.67	0.67	0.22	0.22
I				
<sup>1</sup> B <sub>2</sub>	0.50	1.01	0.27	-0.15
<sup>1</sup> B <sub>1</sub>	0.50	0.99	0.32	-0.20
<sup>3</sup> B <sub>1</sub>	0.50	0.99	0.32	-0.18
<sup>1</sup> A <sub>1</sub>	0.90	0.19	-0.04	0.55
<sup>3</sup> B <sub>2</sub>	0.63	0.72	0.25	0.17
II				
<sup>1</sup> B <sub>2</sub>	0.50	0.97	0.28	-0.18
<sup>1</sup> B <sub>1</sub>	0.49	0.95	0.28	-0.07
<sup>3</sup> B <sub>1</sub>	0.49	0.94	0.27	-0.05
<sup>1</sup> A <sub>1</sub>	0.92	0.78	-0.09	0.59
<sup>3</sup> B <sub>2</sub>	0.64	0.67	0.23	0.21
TMM Fragment				
<sup>1</sup> B <sub>2</sub>	0.51	1.00	0.33	-0.13
<sup>1</sup> B <sub>1</sub>	0.50	0.99	0.32	-0.18
<sup>3</sup> B <sub>1</sub>	0.51	0.98	0.31	-0.17
<sup>1</sup> A <sub>1</sub>	0.94	0.17	-0.07	0.57
<sup>3</sup> B <sub>2</sub>	0.65	0.71	0.23	0.19

<sup>a</sup> "Radical population" is the population of the open shell MO's. For singlet states this is difficult to define for configuration interaction wavefunctions. <sup>b</sup> For the B<sub>1</sub> states " $\pi$ " refers to the orbitals analogous to the  $\pi$  orbitals for the other states.

Table III. Geometrical Parameters for I<sup>a</sup>

state	C1-C4	C1-C2	C2-C3	C2-C1-C2', deg
<sup>1</sup> B <sub>2</sub>	1.494	1.382	1.520	110.13
<sup>1</sup> B <sub>1</sub> , <sup>3</sup> B <sub>1</sub>	1.483	1.382	1.520	110.13
<sup>1</sup> A <sub>1</sub>	1.345	1.465	1.520	104.29
<sup>3</sup> B <sub>2</sub>	1.419	1.401	1.520	109.05

<sup>a</sup> Bond distances in Å.

angles between the C-C bonds or by changing the C-C bond lengths so that they are unequal. The latter has been found to be the important change. If the C-C bond along the 2-fold axis is lengthened and the other two are shortened, the <sup>1</sup>B<sub>2</sub> state is lowered and the <sup>1</sup>A<sub>1</sub> state is raised, and vice versa. The <sup>1</sup>A<sub>1</sub> state is the state that is capable of forming an additional bond and going to methylenecyclopropane, but since both <sup>1</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> are part of the same Jahn-Teller energy surface, they are easily interconverted through non- $C_{2v}$  geometries.<sup>27</sup>

Our calibration calculations on TMM were carried out with fixed C-H bond lengths of 1.07 Å, but all other geometrical parameters were optimized for each of the states. The geometry results are given in Table I, and the energies at those geometries are included in Table IV. For the ground state  $((e'')^2$  <sup>3</sup>A<sub>2</sub>' in  $D_{3h}$  notation,  $b_1 a_2$  <sup>3</sup>B<sub>2</sub> in  $C_{2v}$  notation) the optimum C-C bond length was found to be 1.409 Å, and the calculated excitation energies at this geometry were 21.8 kcal/mol for <sup>1</sup>B<sub>2</sub> and 17.4 kcal/mol for <sup>1</sup>A<sub>1</sub>. The difference of 4.4 kcal/mol, although considerably less than the value for a STO-3G basis,<sup>25</sup> indicates the inaccuracy of our wave functions in treating these two states, which would be degenerate if enough configuration interaction terms were included.<sup>27</sup> Since previous results show that configuration interaction terms make little change in the <sup>1</sup>B<sub>1</sub> (and presumably <sup>1</sup>B<sub>2</sub>) excitation energy, we may estimate that all of our <sup>1</sup>A<sub>1</sub> excitation energies will be too low by approximately this value of 4.4 kcal/mol.

### Results on TMM Derivatives

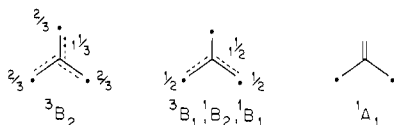
An initial set of calculations was carried out on the derivatives I and II and the TMM fragment by using a common set of

Table IV. Energies of TMM and Derivatives

state	TMM <sup>a</sup>	I <sup>a</sup>	I <sup>b</sup>	I <sup>c</sup>	II <sup>a</sup>	II <sup>c</sup>	TMM frag <sup>a</sup>
Energies Relative to <sup>3</sup> B <sub>2</sub> , kcal/mol							
<sup>1</sup> B <sub>2</sub>	16.9	16.4	23.9	21.2	16.3	17.5	16.7
<sup>1</sup> B <sub>1</sub>	14.9	14.3	15.5	18.6	11.7	14.9	14.6
<sup>3</sup> B <sub>1</sub>	13.7	13.1		17.4	10.3	13.7	13.4
<sup>1</sup> A <sub>1</sub>	10.5 <sup>d</sup>	9.1 <sup>d</sup>	18.7	17.6	11.0 <sup>d</sup>	19.5	9.5 <sup>d</sup>
Total Energies, hartrees							
<sup>3</sup> B <sub>2</sub>	-154.832942	-231.715821	-229.04382		-309.751238		-154.816864

<sup>a</sup> This work. <sup>b</sup> Reference 30. <sup>c</sup> Borden and Davidson model from ref 27. <sup>d</sup> Subject to 4.4 kcal/mol estimated correction. See text.

geometrical parameters. Population analysis results confirmed earlier qualitative descriptions<sup>25</sup> of all of the states in terms both of the location of the electrons in singly occupied MO's and of the following bond orders: <sup>3</sup>B<sub>2</sub> (2<sup>2</sup>/<sub>3</sub> electron on C2, C2', C4; C1-C2, C1-C2', C1-C4: 4<sup>1</sup>/<sub>3</sub> bonds); <sup>1</sup>B<sub>1</sub>, <sup>1</sup>B<sub>2</sub>, <sup>3</sup>B<sub>1</sub> (1<sup>1</sup>/<sub>2</sub> electron on C2, C2'; 1 electron on C4; C1-C2, C1-C2': 3<sup>1</sup>/<sub>2</sub> bonds; C1-C4: 1 bond); <sup>1</sup>A<sub>1</sub> (1 electron on C2, C2'; C1-C2, C1-C2': 1 bond; C1-C4: 2 bonds).



For better allowance for the effects of the substituents, some geometry optimization was carried out on I. Optimization calculations on II were too expensive, so its geometrical parameters were taken to be the same as for I; TMM fragments with these parameters were studied as well.

We chose to carry out our partial optimization in terms of these variables: (1) the C1-C4 bond length, (2) the C1-C2 bond length, (3) the C2-C3 bond length, and (4) the C2-C1-C2' bond angle, which were varied, and (5) the H2-C2-C1 bond angle and (6) the angle between C3-C3' and the projection of C3-H3 in the plane of the ring, which were held fixed. After we optimized the energy of each state with respect to variables 1-4, we made a final optimization of each state's energy in which the entire apical portion of the molecule (C1, C4, H's on C4) was moved with respect to the remainder of the molecule, corresponding to a different choice of variables.<sup>29</sup>

The bond lengths changed during optimization in the manner expected from the qualitative description of the bond orders in each state. Population analysis results are given in Table II, the bond lengths and angles in Table III, and the excitation energies in Table IV. In comparing excitation energies, it should be noted that the <sup>3</sup>B<sub>2</sub> and <sup>3</sup>B<sub>1</sub> energies represent two values on the same energy surface, as do <sup>1</sup>B<sub>2</sub> and <sup>1</sup>B<sub>1</sub>.

## Discussion

It is clear from the calculated excitation energies that the alkyl substituents added in changing TMM to I and I to II have definite, but quite limited, effects. If the crude 4.4 kcal/mol correction is added to all of the <sup>1</sup>A<sub>1</sub> energies, then the lowest singlet excitation energy is the 11.7 kcal/mol value for II, reduced 3.2 kcal/mol from the TMM value, but still quite a bit larger than any published experimental estimates.

Table IV includes the results of Dixon, Dunning, Eades, and Kleier.<sup>30</sup> These authors used the PRDDO method,<sup>31</sup> which uses integral approximations with minimum basis wave functions, to carry out a more extensive geometry optimization of I. They then used STO-3G minimum basis wave functions, with some configuration interaction among the  $\pi$  MO's, to evaluate energies. Their geometrical parameters and excitation energies are quite like ours, although the latter are higher, as has already been seen

(29) At the suggestion of D. A. Dixon who encountered this difficulty in PRDDO calculations.<sup>30</sup>

(30) D. A. Dixon, T. H. Dunning, R. A. Eades, and D. A. Kleier, *J. Am. Chem. Soc.*, **103**, 2878 (1981).

(31) T. A. Halgren, D. A. Kleier, J. H. Hall, L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100**, 6595 (1978).

Table V. Excitation Energies<sup>a</sup> from Substituent Effect Models

state	I <sup>b</sup>	I <sup>c</sup>	II <sup>b</sup>	II <sup>c</sup>
<sup>1</sup> B <sub>2</sub>	17.6	16.7	15.7	14.8
<sup>1</sup> B <sub>1</sub>	15.5	14.6	13.7	12.7
<sup>3</sup> B <sub>1</sub>	14.3	13.4	12.5	11.5
<sup>1</sup> A <sub>1</sub>	7.6	9.5	11.3	13.2

<sup>a</sup> In kcal/mol relative to <sup>3</sup>B<sub>2</sub>. Models based on TMM fragment energies from this work and stabilization factor from ref 27.

<sup>b</sup> Stabilization factor applied to all substituents. <sup>c</sup> Stabilization factor only applied to methyl groups.

for TMM when configuration interaction is only included for the  $\pi$  MO's.

Also in Table IV are the results of a model developed by Borden and Davidson<sup>27</sup> by carrying out STO-3G configuration interaction calculations on a number of substituted TMM's, not, however, including I or II. Their results were consistent with the well-known stabilization of radicals by alkyl substitution, and they found that they could obtain a good fit to their results simply by assuming a stabilization factor of 2.8 kcal/mol per odd electron for methyl substitution at radical centers. In calculating the values in Table IV, which represent this model, we assumed that the two-carbon linkage completing the five-membered ring was equivalent to two separate methyl groups. Since Borden and Davidson did not include a configuration interaction treatment of the nonplanar states directly in their work, we also assumed that the internal rotation barriers about the C1-C4 bond are given well by the Hartree-Fock values so that we could obtain energies for the B<sub>1</sub> states. The excitation energies calculated with this model are generally in the same order as ours, but are higher by a few kcal/mol.

Forming I from TMM involves a distortion of the molecule as well as the addition of the C<sub>2</sub>H<sub>4</sub> ring-closing linkage and, in particular, the decrease of the angle C2-C1-C2' from 120° to 110° or lower. In order to separate this effect from the substituent effect, we carried out calculations on the TMM fragment in which the geometrical parameters of I were used for TMM (last column of Table IV). About half of the change in excitation energies is seen to be due to this geometry change, and the rest is then ascribable to the alkyl substitution made in closing the ring.

In order to refine the Borden and Davidson model for our systems and to check on our assumption that the ring completion has the same radical stabilization effect as two methyl groups, we used our TMM fragment energies together with the 2.8 kcal/mol per odd electron factor to calculate the excitation energies of I and II. This was done in two ways: (1) by considering that the ring-closing linkage was equivalent to two methyl groups and (2) by ignoring it. The results, in Table V, show that for I it is better to ignore the effects of the ring-closing linkage, while for II it is better for some states to consider the linkage to be equivalent to two methyl groups, while for other states it is better not to do so. Thus in general it seems that the ring-closing linkage is less effective than methyl groups in stabilizing radical centers.

## Conclusions

We have carried out better than double- $\zeta$  quality calculations on the low-lying electronic excitations of two TMM derivatives. The energy of the ground state to first excited-state transition, <sup>3</sup>B<sub>2</sub> to <sup>1</sup>B<sub>1</sub>, is lowest for II. This value is computed to be 11.7

kcal/mol, somewhat lower than the TMM value but not greatly so. On the basis of the comparisons with more accurate wave functions in the TMM case, a crude estimate of the accuracy of our calculated excitation energies is  $\pm 3$  kcal/mol. In addition, the variation principle for total energies (Table IV) provides a rough guide for comparisons with other calculations.

The pattern of substituent effects on the TMM excitation energies is found to be reasonably consistent with models for alkyl

stabilization of radical centers.

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## Probing of Chemical Bonding through Two-Photon Spectroscopy of Substituted Benzenes

Richard P. Rava and Lionel Goodman\*

Contribution from the Department of Chemistry, Rutgers-The State University of New Jersey, New Brunswick, New Jersey 08903. Received January 11, 1982

**Abstract:** The  ${}^1L_b$  two-photon spectra of second-row substituted benzenes, F, OH, and  $\text{NH}_2$ , are examined. The spectrum of phenol, which is reported for the first time, shows a mixture of Franck-Condon (FC) (allowed) and vibronic coupling (forbidden) character, in contrast to fluorobenzene and aniline which show very weak and very strong FC character, respectively. Perturbation theory treatment of the problem indicates that the degree of allowedness in the spectrum (though all are formally allowed by symmetry) is measured by resonance interaction of the substituent with the ring. This results from introduction of charge-transfer character into the intermediate and final state wave functions in the two-photon tensor. The potential field effect of the substituent (i.e., the inductive effect) is found to play only a minor role in inducing two-photon intensity unlike one-photon spectra where this effect dominates. The two-photon intensities are thus a direct measure of the resonance strength of chemical bonds.

### I. Introduction

It has taken nearly two decades for the regularities in molecular two-photon (TP) spectra to begin to become clear since Abella's initial observation of the TP spectrum in atomic cesium.<sup>1</sup> The large differences between normal optical, i.e., one-photon (OP), and TP spectra show the power of TP spectroscopy for studying molecular excited states. For example, TP spectra of linear polyenes demonstrate the existence of a previously unobserved (OP forbidden) low-lying state which might account for the photochemistry of these molecules.<sup>2</sup> And despite the many OP studies of the spectrum of benzene, definitive assignment of the 2600-Å absorption to the  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  transition was only finally made by TP spectroscopy.<sup>3,4</sup> The benzene spectrum indicates that the accepted norms of OP spectroscopy are not carried over to TP absorption. An example is found in the effect of deuterium perturbations, which is insignificant except for frequency shifts in OP absorption, but reveals new heretofore unobserved modes in the TP spectra.<sup>5</sup> The TP spectrum also allows studies such as Doppler-free rotational spectra (which has indicated that the benzene  ${}^1B_{2u}$  excited state is not planar<sup>6</sup>) and on the changes of the normal coordinates on going to the excited state.<sup>7,8</sup> These studies are either difficult or impossible in OP absorption but are made possible because of the nature of TP transitions.

In this paper we exploit the dependence of the TP substituted benzene  ${}^1L_b \leftarrow {}^1A^9$  transition tensor on resonance contributions

to study valence interactions for the second-row substituents, F, OH, and  $\text{NH}_2$ . There have been many studies of substituent effects on benzene spectra, but as we will show in this example, TP spectroscopy provides a powerful approach for examining the resonance contribution to chemical bonding.

### II. Basic Ideas

The TP selection rules derive from the three basic terms in the TP transition amplitude:<sup>10,11</sup> (i) a (symmetric) scalar term which requires transitions between states of identical symmetry; (ii) a symmetric tensor term which follows selection rules appropriate for electric quadrupole transitions; (iii) an antisymmetric tensor term which obeys selection rules appropriate for magnetic dipole transitions but is zero in a one laser experiment which employs photons of identical frequency and polarization (i.e., as in our experiments). This should be compared to the OP transition amplitude which follows selection rules appropriate for electric dipole transitions. Only transitions between states of the same parity are allowed in TP spectroscopy, compared to the opposite in OP. Thus, from the  $A_{1g}$  ground state of benzene, a TP transition to the near-ultraviolet  $B_{2u}$  state is parity forbidden. Only by mixing g-parity electronic states into  $B_{2u}$  can the TP transition show allowed character.

We will employ states in a perturbation scheme as zeroth-order levels (rather than orbitals or configurations) and show that the TP spectral intensities of substituted benzenes can be understood in terms of resonance interactions of the substituent,<sup>12</sup> i.e., the tendency for an electron of the substituent group to enter into conjugation with the benzene  $\pi$  electrons.<sup>13</sup> In the case of sec-

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