

Interactions of Be and Mg Atoms with C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>V. Balaji<sup>†</sup> and K. D. Jordan\*

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Ab initio calculations are employed to study the C<sub>2v</sub> interactions of Be(1<sup>1</sup>S), Be(1<sup>3</sup>P), Mg(1<sup>1</sup>S), and Mg(1<sup>3</sup>P) with acetylene and ethylene molecules. Previous studies, in which the geometries of the hydrocarbons were "frozen" at their isolated molecule values, indicated that the interactions involving the Be(1<sup>1</sup>S) species were repulsive. The present calculations show that distortions of the hydrocarbons are important for the interaction of both the <sup>1</sup>S and <sup>3</sup>P atoms and that there are deep minima on both the <sup>3</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> potential energy surfaces. The <sup>1</sup>A<sub>1</sub> minima are found to be due to avoided crossings between the lowest two <sup>1</sup>A<sub>1</sub> states.

## Introduction

The interactions of metal atoms and small metal clusters with molecules are currently of considerable experimental and theoretical interest. In recent years matrix isolation spectroscopy<sup>1-6</sup> and supersonic jets combined with laser spectroscopic methods<sup>7-10</sup> have developed into very important tools for the study of the complexes between molecules and metal atoms or clusters. On the theoretical side the advances of the past few years have made it possible to accurately determine the geometries and vibrational frequencies of small polyatomic molecules and to study the interaction of these molecules with metal atoms as well as small metal aggregates.<sup>10-20</sup>

Catalytic reactions involving acetylene and ethylene are important both in their own right and as models for more complex unsaturated hydrocarbons. Thus, it is not surprising that the interactions of these species with metal atoms have been the subject of several theoretical studies. One of the earliest ab initio studies was that of Swope and Schaefer,<sup>18</sup> who examined the Be-C<sub>2</sub>H<sub>2</sub> and Be-C<sub>2</sub>H<sub>4</sub> systems. Although this pioneering work provided much insight into the nature of the interaction of Be with acetylene and ethylene, these calculations were carried out with rigid structures for the hydrocarbons; that is, the hydrocarbons were not allowed to distort when the Be atom approached. More recently, theoretical calculations on the Be-C<sub>2</sub>H<sub>2</sub> and Mg-C<sub>2</sub>H<sub>2</sub> systems have been carried out by Witko and Bonacic-Koutecky,<sup>19</sup> who also assumed rigid hydrocarbon structures.

Theoretical calculations<sup>21</sup> have shown that the π\* orbitals of acetylene and ethylene are strongly stabilized upon distortion of the hydrocarbons, with C<sub>2</sub>H<sub>4</sub><sup>-</sup> having both syn and anti structures and C<sub>2</sub>H<sub>2</sub><sup>-</sup> both cis and trans structures. This suggests that geometry distortions and charge transfer from the metal atom to the low-lying π\* orbitals are likely to be significant in the interactions of metal atoms with these hydrocarbons.

In this study we consider the C<sub>2v</sub> interaction of Be(1<sup>1</sup>S), Be(1<sup>3</sup>P), Be<sup>+</sup>(1<sup>2</sup>S), and Be<sup>+</sup>(1<sup>2</sup>P) as well as the corresponding Mg species with acetylene and ethylene molecules. The geometries are completely optimized within the constraint of C<sub>2v</sub> symmetry. In a very recent study, published while we were preparing this manuscript, Gosavi et al.<sup>20</sup> considered the role of the distortion of C<sub>2</sub>H<sub>4</sub> when interacting with Be(3<sup>3</sup>P). These authors reached conclusions similar to ours concerning the importance of the distortion of the ethylene moiety in the <sup>3</sup>B<sub>2</sub> BeC<sub>2</sub>H<sub>4</sub> complex. They did not consider the singlet potential energy surface. Nor did they consider the BeC<sub>2</sub>H<sub>2</sub>, MgC<sub>2</sub>H<sub>2</sub>, or MgC<sub>2</sub>H<sub>4</sub> species.

The calculations in the present study were performed with the GAUSSIAN 82 program.<sup>22</sup> The geometries were determined in the self-consistent field (SCF) Hartree-Fock (HF) procedure using analytical gradients and the 6-31G\* (6d) basis sets.<sup>23</sup> The closed-shell and open-shell species were treated in the spin-restricted and spin-unrestricted Hartree-Fock approximations, respectively. To establish that the C<sub>2v</sub> complexes are actually po-

TABLE I: Orbital and State Symmetries of the Metal Atoms and Hydrocarbons in the C<sub>2v</sub> Point Group

Be <sup>+</sup> ( <sup>2</sup> S)	1s <sup>2</sup> 2s	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub>	<sup>2</sup> A <sub>1</sub>
Be( <sup>1</sup> S)	1s <sup>2</sup> 2s <sup>2</sup>	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup>	<sup>1</sup> A <sub>1</sub>
Be( <sup>3</sup> P)	1s <sup>2</sup> 2s2p	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> 3a <sub>1</sub>	<sup>3</sup> A <sub>1</sub>
		1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> 1b <sub>1</sub>	<sup>3</sup> B <sub>1</sub>
		1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> 1b <sub>2</sub>	<sup>3</sup> B <sub>2</sub>
Mg <sup>+</sup> ( <sup>2</sup> S)	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub>	<sup>2</sup> A <sub>1</sub>
Mg( <sup>1</sup> S)	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup>	<sup>1</sup> A <sub>1</sub>
Mg( <sup>3</sup> P)	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s3p	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub>	<sup>3</sup> B <sub>2</sub>
		1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub>	<sup>3</sup> A <sub>1</sub>
		1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 2b <sub>1</sub>	<sup>3</sup> B <sub>1</sub>
C <sub>2</sub> H <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup>	<sup>1</sup> A <sub>1</sub>
C <sub>2</sub> H <sub>4</sub> ( <sup>1</sup> A <sub>g</sub> )		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	<sup>1</sup> A <sub>1</sub>
		4a <sub>1</sub> <sup>2</sup>	
Be + C <sub>2</sub> H <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	<sup>1</sup> A <sub>1</sub>
		1b <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup>	
		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	<sup>3</sup> A <sub>1</sub>
		1b <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> 7a <sub>1</sub>	
		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	<sup>3</sup> B <sub>2</sub>
		1b <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> 3b <sub>2</sub>	
		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	<sup>3</sup> B <sub>1</sub>
		1b <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> 3b <sub>1</sub>	
Be + C <sub>2</sub> H <sub>4</sub> ( <sup>1</sup> A <sub>g</sub> )		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	<sup>1</sup> A <sub>1</sub>
		4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> <sup>2</sup>	
		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	<sup>3</sup> A <sub>1</sub>
		4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> 7a <sub>1</sub>	
		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	<sup>3</sup> B <sub>2</sub>
		4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> 3b <sub>2</sub>	
		1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup>	<sup>3</sup> B <sub>1</sub>
		4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup> 6a <sub>1</sub> 2b <sub>1</sub>	

tential minima, the harmonic vibrational frequencies of the BeC<sub>2</sub>H<sub>2</sub> and BeC<sub>2</sub>H<sub>4</sub> species were determined at the HF level of

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TABLE II: Hartree-Fock Optimized Geometries<sup>a</sup>

geometrical parameter <sup>b</sup>	Be		Mg		Be <sup>+</sup>		Mg <sup>+</sup>	
	<sup>1</sup> A <sub>1</sub>	<sup>3</sup> B <sub>2</sub>	<sup>1</sup> A <sub>1</sub>	<sup>3</sup> B <sub>2</sub>	<sup>2</sup> A <sub>1</sub>	<sup>2</sup> B <sub>2</sub>	<sup>2</sup> A <sub>1</sub>	<sup>2</sup> B <sub>2</sub>
<b>C<sub>2</sub>H<sub>2</sub></b>								
M-X, Å	1.393	1.662	1.838	2.115	1.947	1.555	2.573	1.997
C-C, Å	1.373	1.258	1.374	1.273	1.198	1.269	1.194	1.285
C-H, Å	1.076	1.072	1.085	1.077	1.069	1.074	1.064	1.077
α, deg	52.8	31.0	57.8	39.5	4.00	30.0	5.00	39.2
<b>C<sub>2</sub>H<sub>4</sub></b>								
M-X, Å	1.388	1.715	1.860	2.161	2.033	1.611	2.637	2.084
C-C, Å	1.645	1.420	1.624	1.439	1.345	1.444	1.336	1.506
C-H, Å	1.082	1.078	1.084	1.079	1.079	1.079	1.078	1.078
β, deg	110.4	115.5	108.4	114.7	117.0	116.2	116.8	115.2
γ, deg	46.8	20.1	49.4	25.5	5.00	25.3	5.10	29.4

<sup>a</sup>The 6-31G\* Hartree-Fock geometries of the free molecules are as follows. C<sub>2</sub>H<sub>2</sub>: R<sub>CC</sub> = 1.186 Å and R<sub>CH</sub> = 1.057 Å. C<sub>2</sub>H<sub>4</sub>: R<sub>CC</sub> = 1.317 Å and R<sub>CH</sub> = 1.076 Å, β = 116.4°. <sup>b</sup>X denotes the center of the CC bond and MX the distance from the metal atom to X. α gives the degree of bending of the HCC groups away from linear. β is the HCH angle. γ gives the degree of bending of the CH<sub>2</sub> groups out of the plane. The angle is measured between the C-C bond and the plane of the CH<sub>2</sub> group.

theory. The importance of electron correlation effects in determining the stabilities and relative energies of singlet and triplet complexes was examined by carrying out full fourth-order many-body perturbation theory calculations at the HF geometries. Only the valence electrons were correlated in the perturbation theory calculations. The second-, third-, and fourth-order results are designated by MP2, MP3, and MP4(SDTQ), respectively.

### Results and Discussion

The orbital occupations of the metal atoms, the hydrocarbons, and the metal atom-hydrocarbon complexes in C<sub>2v</sub> symmetry are given in Table I. The electronic configurations given for the complexes are those appropriate for the noninteracting metal-hydrocarbon systems. As will be seen, the interactions in the complexes are such that the orbital occupations may differ from those given in Table I.

Swope and Schaefer<sup>18</sup> found that the <sup>2</sup>A<sub>1</sub> Be<sup>+</sup>-C<sub>2</sub>H<sub>2</sub> and Be<sup>+</sup>-C<sub>2</sub>H<sub>4</sub> systems are strongly bound, with most of the binding arising from the classical electrostatic interaction. They also reported that the C<sub>2v</sub> interactions of Be(<sup>1</sup>S) with the acetylene or ethylene molecules are repulsive when the hydrocarbons are held rigid. The <sup>3</sup>B<sub>2</sub> potential energy surfaces, on the other hand, were found to be quite attractive. This was rationalized in terms of donation of charge from the b<sub>2</sub>-type p orbital of Be into the π\* LUMO of the hydrocarbon. The other two C<sub>2v</sub> surfaces, <sup>3</sup>A<sub>1</sub> and <sup>3</sup>B<sub>1</sub>, derived from the interaction with Be(<sup>3</sup>P), were reported to be repulsive or to have only very shallow minima.

Our calculations show that distortions of the hydrocarbons are very important in the neutral (as well as in the <sup>2</sup>B<sub>2</sub> cationic) complexes and, moreover, that when such distortions are allowed deep minima are also found in the lowest <sup>1</sup>A<sub>1</sub>, <sup>3</sup>A<sub>1</sub>, and <sup>3</sup>B<sub>1</sub> potential energy surfaces. The <sup>3</sup>A<sub>1</sub> and <sup>3</sup>B<sub>1</sub> states at their minima are found to have the following electronic configurations:

BeC<sub>2</sub>H<sub>2</sub>: ...5a<sub>1</sub><sup>2</sup>3b<sub>2</sub>1b<sub>1</sub>6a<sub>1</sub>1a<sub>2</sub> (<sup>3</sup>A<sub>1</sub>) and

...5a<sub>1</sub><sup>2</sup>3b<sub>2</sub><sup>2</sup>1b<sub>1</sub>6a<sub>1</sub> (<sup>3</sup>B<sub>1</sub>)

and

BeC<sub>2</sub>H<sub>4</sub>: ...4a<sub>1</sub><sup>2</sup>3b<sub>2</sub><sup>2</sup>5a<sub>1</sub>6a<sub>1</sub> (<sup>3</sup>A<sub>1</sub>) and ...4a<sub>1</sub><sup>2</sup>3b<sub>2</sub><sup>2</sup>2b<sub>1</sub>5a<sub>1</sub> (<sup>3</sup>B<sub>1</sub>)

Relative to the configurations given in Table I and considered by Swope and Schaefer, three of these states involve double ex-

TABLE III: Hartree-Fock Total Energies, Dissociation Energies, Dipole Moments, and Atomic Charges of the Complexes

	disso- cn energy, <sup>a</sup> eV	dissoc energy, <sup>a</sup> eV	dipole moment, <sup>b</sup> D	net atomic charges, e		
				metal	C	H
<b>BeC<sub>2</sub>H<sub>2</sub></b>						
<sup>1</sup> A <sub>1</sub>	-91.4092	0.67	2.20 (4.09)	0.01	-0.17	0.16
<sup>3</sup> B <sub>2</sub>	-91.4038	2.13	-2.10 (-0.90)	0.05	-0.26	0.24
<sup>2</sup> A <sub>1</sub>	-91.1586	1.77				
<sup>2</sup> B <sub>2</sub>	-91.1468	5.47				
<b>MgC<sub>2</sub>H<sub>2</sub></b>						
<sup>1</sup> A <sub>1</sub>	-276.3292	-2.29	6.10 (8.10)	0.35	-0.31	0.14
<sup>3</sup> B <sub>2</sub>	-276.3842	1.02	-0.14 (0.92)	0.26	-0.33	0.20
<sup>2</sup> A <sub>1</sub>	-276.1987	0.77				
<sup>2</sup> B <sub>2</sub>	-276.1419	3.50				
<b>BeC<sub>2</sub>H<sub>4</sub></b>						
<sup>1</sup> A <sub>1</sub>	-92.5805	-0.49	2.23 (3.53)	0.22	-0.42	0.16
<sup>3</sup> B <sub>2</sub>	-92.6037	1.75	-1.49 (-0.92)	0.11	-0.45	0.20
<sup>2</sup> A <sub>1</sub>	-92.3735	1.81				
<sup>2</sup> B <sub>2</sub>	-92.3464	5.08				
<b>MgC<sub>2</sub>H<sub>4</sub></b>						
<sup>1</sup> A <sub>1</sub>	-277.5054	-3.32	5.26 (6.63)	0.47	-0.54	0.15
<sup>3</sup> B <sub>2</sub>	-277.5858	0.68	0.20 (0.88)	0.28	-0.50	0.18
<sup>2</sup> A <sub>1</sub>	-277.4140	0.80				
<sup>2</sup> B <sub>2</sub>	-277.3498	3.37				

<sup>a</sup>The dissociation energies are computed by subtracting the energies of the complexes from those of the appropriate dissociation products.

<sup>b</sup>The total dipole moments are given first, followed by parentheses by the "corrected" values obtained by subtracting the dipole moments of the hydrocarbons (distorted so as to have the geometries in the complexes) from those of the complexes. The sign of the dipole moment is chosen so that a positive value is consistent with the plus end of the dipole pointing toward the metal atom and the minus end toward the hydrocarbon moiety. This need not be consistent with the charge distribution obtained from the Mulliken population analysis.

citations into the 3b<sub>2</sub> orbital, while the fourth, <sup>3</sup>A<sub>1</sub> BeC<sub>2</sub>H<sub>2</sub>, involves a 1b<sub>1</sub>7a<sub>1</sub> → 3b<sub>2</sub>1a<sub>2</sub> excitation.<sup>24</sup> The stability of these configurations derives from the low energy of the 3b<sub>2</sub> π\* orbital in the distorted complexes. These <sup>3</sup>A<sub>1</sub> and <sup>3</sup>B<sub>1</sub> species lie within a few kcal/mol of the Be(<sup>3</sup>P) + hydrocarbon asymptotes, indicating that there are barriers (at least in C<sub>2v</sub> symmetry) to dissociation for these states. Because the <sup>3</sup>A<sub>1</sub> and <sup>3</sup>B<sub>1</sub> complexes lie relatively high in energy and because a single-reference-based procedure is probably not adequate for their description, we will not deal with these further in this study. Rather, the subsequent discussion of the neutral complexes will be limited to the <sup>3</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> states.

**Neutral Acetylene Complexes.** The optimized geometries of the <sup>1</sup>A<sub>1</sub> and <sup>1</sup>B<sub>2</sub> complexes of Be and Mg with C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> and those of the <sup>1</sup>A<sub>1</sub> and <sup>1</sup>B<sub>2</sub> cations of these systems are

(24) Gosavi et al. (ref 20) considered <sup>3</sup>B<sub>1</sub> and <sup>3</sup>A<sub>1</sub> states for the BeC<sub>2</sub>H<sub>4</sub> system with orbital occupations being those given in Table I, and thus they concluded that the <sup>3</sup>B<sub>1</sub> state is only weakly attractive and the <sup>3</sup>A<sub>1</sub> state is repulsive.

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TABLE IV: Dissociation Energies (eV) of the Neutral Complexes<sup>a</sup>

complex	approximation			
	HF	MP2	MP3	MP4(SDTQ)
BeC <sub>2</sub> H <sub>2</sub>				
<sup>1</sup> A <sub>1</sub>	0.67	0.99	0.82	0.74
<sup>3</sup> B <sub>2</sub>	2.13	2.58	2.67	2.67
MgC <sub>2</sub> H <sub>2</sub>				
<sup>1</sup> A <sub>1</sub>	-2.29	-1.76	-1.98	-1.84
<sup>3</sup> B <sub>2</sub>	1.02	1.35	1.41	1.44
BeC <sub>2</sub> H <sub>4</sub>				
<sup>1</sup> A <sub>1</sub>	-0.49	0.06	-0.19	-0.25
<sup>3</sup> B <sub>2</sub>	1.75	2.90	2.31	2.30
MgC <sub>2</sub> H <sub>4</sub>				
<sup>1</sup> A <sub>1</sub>	-3.32	-2.54	-2.80	-2.69
<sup>3</sup> B <sub>2</sub>	0.68	1.10	1.10	1.12

<sup>a</sup>The dissociation energies are computed by subtracting the energies of the complexes from those of the appropriate dissociation products. A negative dissociation energy means that the complex lies energetically above its dissociation limit.

TABLE V: Singlet (<sup>1</sup>A<sub>1</sub>)-Triplet (<sup>3</sup>B<sub>2</sub>) Energy Separations (eV)<sup>a</sup>

complex	approximation			
	HF	MP2	MP3	MP4(SDTQ)
BeC <sub>2</sub> H <sub>2</sub>	0.15	0.68	0.69	0.74
MgC <sub>2</sub> H <sub>2</sub>	-1.50	-0.75	-0.83	-0.68
BeC <sub>2</sub> H <sub>4</sub>	-0.63	0.06	0.03	-0.12
MgC <sub>2</sub> H <sub>4</sub>	-2.19	-1.28	-1.36	-1.21

<sup>a</sup>A plus sign indicates that the <sup>1</sup>A<sub>1</sub> state is more stable than the <sup>3</sup>B<sub>2</sub>.

summarized in Table II. The corresponding HF energies, dipole moments, and total atomic charges as determined from a Mulliken population analysis are given in Table III.

Our HF calculations show the <sup>3</sup>B<sub>2</sub> states of BeC<sub>2</sub>H<sub>2</sub> and MgC<sub>2</sub>H<sub>2</sub> to be bound with respect to their M(<sup>3</sup>P) + C<sub>2</sub>H<sub>2</sub> dissociation limits by 2.13 and 1.02 eV, respectively. Our binding energy for the <sup>3</sup>B<sub>2</sub> BeC<sub>2</sub>H<sub>2</sub> complex is about 2.5 times greater than that reported by Swope and Schaefer. This increased stability is largely a result of the "relaxation" of the geometry of the hydrocarbon portion of the complex. Our BeC<sub>2</sub>H<sub>2</sub> results also differ from those reported previously in that we find that the <sup>1</sup>A<sub>1</sub> complex is bound by 0.67 eV with respect to the Be(<sup>1</sup>S) + C<sub>2</sub>H<sub>2</sub> asymptote. Although the <sup>1</sup>A<sub>1</sub> state of MgC<sub>2</sub>H<sub>2</sub> also possesses a minimum, it lies considerably (≈2.3 eV) above the Mg(<sup>1</sup>S) + C<sub>2</sub>H<sub>2</sub> dissociation limit.

The binding energies of the neutral complexes and the singlet-triplet separations at various levels of theory are reported in Tables IV and V, respectively. From Table IV it is seen that for BeC<sub>2</sub>H<sub>2</sub> electron correlation has little effect on the stability of the <sup>1</sup>A<sub>1</sub> complex while it stabilizes the <sup>3</sup>B<sub>2</sub> complex (relative to the Be(<sup>3</sup>P) + C<sub>2</sub>H<sub>2</sub> asymptote) by about 0.5 eV. At the highest level of theory, MP4(SDTQ), the <sup>1</sup>A<sub>1</sub> species is 0.74 eV more stable than the <sup>3</sup>B<sub>2</sub> species, leading us to conclude that the BeC<sub>2</sub>H<sub>2</sub> molecule has a singlet ground state. We also observe that, in the MP4(SDTQ) approximation, the minimum in the <sup>3</sup>B<sub>2</sub> surface lies at the same energy as the Be(<sup>1</sup>S) + C<sub>2</sub>H<sub>2</sub> asymptote.

Electron correlation stabilizes both the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> complexes (relative to the respective asymptotes) of MgC<sub>2</sub>H<sub>2</sub> by about 0.4 eV. At the MP4 level of theory, the <sup>3</sup>B<sub>2</sub> complex is more stable than the <sup>1</sup>A<sub>1</sub> complex by about 0.7 eV. It should be emphasized that the <sup>3</sup>B<sub>2</sub> MgC<sub>2</sub>H<sub>2</sub> species lies energetically above the Mg(<sup>1</sup>S) + C<sub>2</sub>H<sub>2</sub>(X<sup>1</sup>Σ<sup>+</sup>) asymptote.

**Neutral Ethylene Complexes.** Swope and Schaefer reported that Be(<sup>3</sup>P) interacts more strongly with ethylene than with acetylene. However, we find that when distortions of the hydrocarbons are permitted, the interactions of the <sup>1</sup>S and <sup>3</sup>P states of Be and Mg with ethylene are less attractive than those with acetylene. The minima in the <sup>3</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> potential energy surfaces of both BeC<sub>2</sub>H<sub>4</sub> and MgC<sub>2</sub>H<sub>4</sub> lie above the respective M(<sup>1</sup>S) + C<sub>2</sub>H<sub>4</sub> asymptotes. This implies that the <sup>1</sup>A<sub>1</sub> interaction potentials are repulsive at large metal atom-C<sub>2</sub>H<sub>4</sub> distances and have barriers at intermediate distances. (As will be shown below, this is also

the case for the <sup>1</sup>A<sub>1</sub> acetylene complexes.) For BeC<sub>2</sub>H<sub>4</sub> the MP4(SDTQ) calculations predict that the <sup>1</sup>A<sub>1</sub> ground state is slightly (≈0.1 eV) more stable than the <sup>3</sup>B<sub>2</sub> species and that the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> minima lie respectively 0.25 and 0.37 eV above the Be(<sup>1</sup>S) + C<sub>2</sub>H<sub>4</sub> asymptote. For MgC<sub>2</sub>H<sub>4</sub> the <sup>3</sup>B<sub>2</sub> species is about 1.2 eV more stable than the <sup>1</sup>A<sub>1</sub> complex.

**Cations.** The ethylenic and acetylenic portions of the <sup>2</sup>A<sub>1</sub> cation complexes are only slightly distorted from the structures of the isolated neutral molecules. In the <sup>2</sup>B<sub>2</sub> complexes, however, the hydrocarbon moieties are strongly distorted. The CCH angles in the <sup>2</sup>B<sub>2</sub> BeC<sub>2</sub>H<sub>2</sub><sup>+</sup> and MgC<sub>2</sub>H<sub>2</sub><sup>+</sup> complexes are bent from linear by 30° and 39°, respectively, and the CH<sub>2</sub> groups of <sup>2</sup>B<sub>2</sub> BeC<sub>2</sub>H<sub>4</sub><sup>+</sup> and MgC<sub>2</sub>H<sub>4</sub><sup>+</sup> are distorted out of the plane by 25° and 29°, respectively. In addition, the CC bonds are significantly longer in the <sup>2</sup>B<sub>2</sub> cation complexes than in the free molecules. Both the extent of elongation of the C-C bonds and the angular distortions of the hydrocarbons are similar in the <sup>2</sup>B<sub>2</sub> cations and the corresponding neutral <sup>3</sup>B<sub>2</sub> complexes. The ethylenic portions of the <sup>2</sup>A<sub>1</sub> and <sup>2</sup>B<sub>2</sub> states of BeC<sub>2</sub>H<sub>4</sub><sup>+</sup> and MgC<sub>2</sub>H<sub>4</sub><sup>+</sup> species have structures quite close to those of the corresponding states resulting from the interaction of Cu(<sup>2</sup>S) and Cu(<sup>2</sup>P) with C<sub>2</sub>H<sub>4</sub>.<sup>15</sup>

As noted by Swope and Schaefer, the stability of the <sup>2</sup>A<sub>1</sub> complexes is due almost entirely to electrostatic interactions. The binding in the <sup>2</sup>B<sub>2</sub> complexes derives both from electrostatic interactions and from "chemical bonding" involving the singly occupied b<sub>2</sub> orbital. Although the <sup>2</sup>P cation states of Be and Mg lie about 4 eV above the <sup>2</sup>S ground states, the energy separation between the <sup>2</sup>A<sub>1</sub> and <sup>2</sup>B<sub>2</sub> complexes is much smaller. Indeed, the two cation states are separated by only 0.32 and 0.74 eV in BeC<sub>2</sub>H<sub>2</sub><sup>+</sup> and BeC<sub>2</sub>H<sub>4</sub><sup>+</sup>, respectively. The <sup>2</sup>A<sub>1</sub>/<sup>2</sup>B<sub>2</sub> splittings are appreciably larger in the Mg complexes.

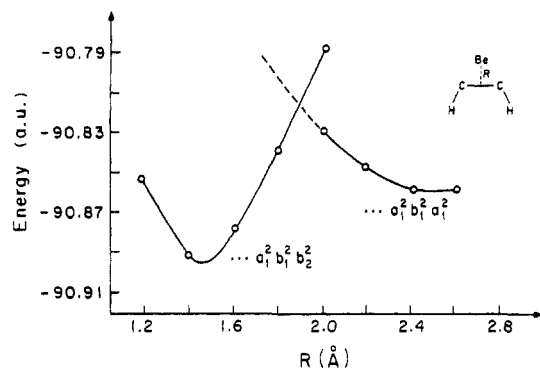
**General Discussion.** For all four systems (BeC<sub>2</sub>H<sub>2</sub>, BeC<sub>2</sub>H<sub>4</sub>, MgC<sub>2</sub>H<sub>2</sub>, and MgC<sub>2</sub>H<sub>4</sub>), the <sup>3</sup>B<sub>2</sub> species have appreciably shorter CC bonds, smaller bending distortions, and larger metal-CC distances than the <sup>1</sup>A<sub>1</sub> species. Moreover, the geometries of the <sup>3</sup>B<sub>2</sub> complexes are quite similar to those of the <sup>2</sup>B<sub>2</sub> cations, the main difference being that the metal-hydrocarbon distances are about 0.1 Å shorter in the cations.

Examination of the wave functions of the <sup>1</sup>A<sub>1</sub> complexes reveals that their electronic configurations differ from the "expected" configurations by a a<sub>1</sub><sup>2</sup> → b<sub>2</sub><sup>2</sup> excitation. This situation is analogous to that for the interaction of Be with H<sub>2</sub> in C<sub>2v</sub> symmetry: At long Be-H<sub>2</sub> distances, the lowest energy <sup>1</sup>A<sub>1</sub> BeH<sub>2</sub> configuration is 1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>3a<sub>1</sub><sup>2</sup>, while at short distances it is 1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>.<sup>25</sup> As a result the Be + H<sub>2</sub> → HBeH insertion process has a sizable barrier.<sup>25</sup>

To examine further the crossing problem in the Be(<sup>1</sup>S) + C<sub>2</sub>H<sub>2</sub> system, a series of SCF calculations (using the 3-21G basis set<sup>26</sup>) were performed for a range of Be-C<sub>2</sub>H<sub>2</sub> distances. In these calculations the Be-C<sub>2</sub>H<sub>2</sub> distance was stepped along a grid, with all other degrees of freedom being optimized at each Be-C<sub>2</sub>H<sub>2</sub> distance. Both <sup>1</sup>A<sub>1</sub> configurations were considered. This was accomplished by starting one set of calculations at long distance and stepping toward shorter Be-C<sub>2</sub>H<sub>2</sub> distances, and in the other by starting at short Be-C<sub>2</sub>H<sub>2</sub> distance and stepping to longer distances. For each point the starting "guess" orbitals were taken to be those from the previous point. Following this procedure, it was possible to obtain both solutions near R = 2.0 Å, but at distances somewhat shorter than this only the ...5a<sub>1</sub><sup>2</sup>3b<sub>2</sub><sup>2</sup> solution was obtained. (With an SCF program utilizing symmetry-adapted orbitals and allowing specification of occupation numbers according to the symmetry types, it would be possible to obtain both solutions at all values of R). The resulting potential energy curves are shown in Figure 1. As expected, the ...5a<sub>1</sub><sup>2</sup>6a<sub>1</sub><sup>2</sup> configuration is repulsive and the ...5a<sub>1</sub><sup>2</sup>3b<sub>2</sub><sup>2</sup> configuration has a deep minimum at short Be-C<sub>2</sub>H<sub>2</sub> distances. In an adiabatic picture these two configurations will undergo an avoided crossing, and the lowest

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**Figure 1.**  $^1A_1$  potential energy surfaces for the interaction of Be with acetylene.

$^1A_1$  adiabatic potential energy surface for the Be +  $C_2H_2$  system will have a barrier, occurring near  $R = 1.9$  Å and about 0.8 eV in height, separating the ground-state reactants from the complex. If the geometry of the acetylene moiety is frozen to that of the free molecule, then the  $\dots 5a_1^2 6a_1^2 / \dots 5a_1^2 3b_2^2$  curve crossing occurs at a very high energy relative to the dissociation limits. Although the above discussion has focused on the Be +  $C_2H_2$  system, similar avoided crossings occur in the  $^1A_1$  potential energy surfaces of the Be +  $C_2H_4$ , Mg +  $C_2H_2$ , and Mg +  $C_2H_4$  systems.

The minima in the  $^1A_1$  and  $^3B_2$  surfaces of the  $MC_2H_2$  and  $MC_2H_4$  complexes derive from the relatively low energy of the  $3b_2$  orbital of the distorted hydrocarbons. However, there remains the question as to the origin of the differences in the stability of the various complexes and the nature of bonding in the complexes. Since the energies of the LUMO's of  $C_2H_2$  and  $C_2H_4$  drop quickly with distortion (CCH bending in the former case and out-of-plane distortion in the latter) of the complexes, one might expect the complexes to have appreciable ionic character. The greater stability of the acetylenic vs the ethylenic complexes is consistent with the greater stabilization of the  $HCCH^-$  upon cis bending than of  $C_2H_4^-$  upon syn distortion.<sup>21,27</sup>

The  $^1A_1$  states of the metal complexes have fairly large dipole moments, being somewhat greater than 2 D for the Be complexes and over 5 D for the Mg complexes. However, since the dipole moment of the distorted hydrocarbons themselves are appreciable, it is useful to "correct" the dipole moments of the complexes by subtracting the dipole moments of the bent hydrocarbons. The corrected dipole moments for the  $^1A_1$   $BeC_2H_2$  and  $MgC_2H_2$  species are 4.09 and 8.10 D, respectively, and those of the  $^1A_1$   $BeC_2H_4$  and  $MgC_2H_4$  species are 3.53 and 6.63 D, respectively. These results indicate that there is indeed considerable ionic character ( $M^{2+}C_2H_2^{2-}$  and  $M^{2+}C_2H_4^{2-}$ ) in the  $^1A_1$  complexes. The larger dipole moments (consistent with greater  $M^{2+}$ hydrocarbon $^{2-}$  character) of the Mg  $^1A_1$  complexes compared with those of the Be complexes have two causes: (1) the Mg-hydrocarbon distances are longer than the Be-hydrocarbon distances, and (2) the  $b_2$  orbital is more localized on the hydrocarbon in the Mg complexes.

The total dipole moment of  $^3B_2$   $MgC_2H_4$  is 0.20 D, while those of the other three  $^3B_2$  complexes are negative. The "corrected" dipole moments are also -0.9 and 0.9 D for  $^3B_2$   $BeC_2H_2$  and  $MgC_2H_2$ , respectively. The corresponding values for  $^3B_2$   $BeC_2H_4$  and  $MgC_2H_4$  are -0.9 and 0.9 D. An analogous situation was found for the  $^3B_2$  complexes of  $BeH_2$  and  $MgH_2$ , for which the dipole moments were found to be small and oriented  $Be^{2+}H_2^{2-}$  and  $Mg^{2+}H_2^{2-}$ , respectively.<sup>25</sup> The relatively small values of the corrected dipole moments of the  $^3B_2$  states suggest that these systems represent classic examples of donation/back-donation bonding, with charge being donated from the  $b_2(p)$  orbital of the metal into the vacant  $\pi^*(3b_2)$  orbital of the hydrocarbon and from the occupied  $4a_1$  orbital of the hydrocarbon into the partially filled  $2s$  orbital of the metal atom. Examination of the SCF MO's reveals strong mixings of these types. The Mulliken population analysis gives a net positive charge on the metal atom in all the

**TABLE VI: Normal-Mode Vibrational Frequencies ( $cm^{-1}$ )**

species	vibrational symmetries and frequencies			
	$A_1$	$A_2$	$B_1$	$B_2$
<b>BeC<sub>2</sub>H<sub>2</sub></b>				
$^1A_1$	1010.7	1142.4	809.2	1004.0
	1136.9			1308.3
	1528.7			3350.1
	3371.4			
$^3B_2$	796.6	831.5	703.6	268.1
	964.3			812.5
	1892.4			3391.7
	3347.5			
<b>BeC<sub>2</sub>H<sub>4</sub></b>				
$^1A_1$	668.9	405.7	729.8	964.8
	1051.9	1257.1	878.5	1130.7
	1152.3	3301.1	3321.4	1563.9
	1593.4			3246.4
	3259.5			
$^3B_2$	728.2	780.2	600.3	204.2
	1010.4	1330.9	858.5	871.2
	1273.4	3370.6	3394.2	1571.8
	1645.2			3292.5
	3304.3			

complexes, including  $^3B_2$   $BeC_2H_2$  and  $BeC_2H_4$ , for which the dipole moments would seem to indicate that the metal atoms are negatively charged. However, it is well-known that the Mulliken population analysis frequently does not give accurate charge distributions. In addition, charge distributions deduced from dipole moments can deviate considerably from the "true" distributions, particularly when there are highly polarizable groups, such as  $Be^{(3)P}$ , in the molecule.

Both the "corrected" dipole moments and the Mulliken population analyses for the  $^3B_2$  Mg complexes are consistent with a net  $Mg^{2+}$ hydrocarbon $^{2-}$  character. The greater distortions of the hydrocarbon moieties in the  $^3B_2$  Mg-hydrocarbon complexes than in the corresponding Be complexes are also consistent with greater metal  $\rightarrow \pi^*$  donation in the former.

The geometries of the hydrocarbon portions of the complexes are particularly sensitive to the occupation and charge distribution of the  $b_2$  orbitals. For instance, the hydrocarbons are much more distorted in the  $^1A_1$  complexes in which the  $b_2$  orbital is doubly occupied (in the single-configuration picture) than in the  $^3B_2$  complexes in which it is only singly occupied. Also, the Mg complexes are somewhat more distorted than the Be complexes, consistent with the greater localization of the  $b_2$  orbitals on the hydrocarbons in the Mg species. The similar structures of the  $^3B_2$  neutral complexes and of the  $^2B_2$  states of the cationic complexes are due to the similar degree of metal  $\rightarrow$  hydrocarbon ( $\pi^*$ ) donation in the neutral and cationic species. The hydrocarbon ( $a_1$ )  $\rightarrow$  metal ( $s$ ) donation apparently plays a relatively small role in determining the structures of the hydrocarbon portion of the complexes.

The geometry optimizations were performed in  $C_{2v}$  symmetry which leaves open the possibility that some of the complexes may be unstable toward distortions to lower symmetry. To check this possibility, the normal-mode vibrational frequencies were calculated for the  $^3B_2$  and  $^1A_1$  complexes of Be with  $C_2H_2$  and  $C_2H_4$ , and the resulting frequencies are tabulated in Table VI. In all cases the vibrational frequencies are positive, indicating that the complexes are stable to distortions. The  $^3B_2$  complexes have a low-frequency  $b_2$  bending mode (204 and 268  $cm^{-1}$  for  $BeC_2H_4$  and  $BeC_2H_2$ , respectively) with a sizable component due to Be "wagging" motion. For the  $^1A_1$  species, the modes with appreciable Be involvement are much higher in frequency.

## Conclusions

The present investigation shows that it is essential to allow for the distortions of molecules such as ethylene and acetylene when considering their interaction with ground or electronically excited Be and Mg atoms. The lowest  $^3B_2$  and  $^1A_1$  states of the  $MC_2H_2$  and  $MC_2H_4$ , where M = Be or Mg, are found to have minima corresponding to highly distorted complexes. The  $BeC_2H_2$  and

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BeC<sub>2</sub>H<sub>4</sub> complexes are found to have <sup>1</sup>A<sub>1</sub> ground states, while the MgC<sub>2</sub>H<sub>2</sub> and MgC<sub>2</sub>H<sub>4</sub> complexes have <sup>3</sup>B<sub>2</sub> ground states. The minima in the <sup>1</sup>A<sub>1</sub> potential energy surfaces are due to an avoided crossing and concomitant change in electronic configuration at intermediate metal-hydrocarbon distances.

The potential energy surfaces derived from the interaction of Be(<sup>1</sup>P) and Mg(<sup>1</sup>P) with ethylene and acetylene were not examined in this study. However, in analogy to the Be(<sup>1</sup>P) + H<sub>2</sub> and Mg(<sup>1</sup>P) + H<sub>2</sub> systems,<sup>25</sup> we expect the <sup>1</sup>B<sub>2</sub> surfaces to be very attractive for the interaction of Be(<sup>1</sup>P) or Mg(<sup>1</sup>P) with C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> and that there are likely to be crossings between the <sup>1</sup>B<sub>2</sub> and <sup>1</sup>A<sub>1</sub> potential energy surfaces, near the potential barriers of the latter. Such crossings could play an important role in the quenching dynamics of the <sup>1</sup>P metal atoms by the hydrocarbons.<sup>28</sup>

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Several of the properties considered here such as the relative energies of the singlet and triplet states of the complexes could be strongly altered if the metal atoms were replaced by small metal clusters. Theoretical studies of the interaction of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> with two or more Be or Mg atoms are currently under way in our laboratory.

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**Registry No.** Be, 7440-41-7; Mg, 7439-95-4; C<sub>2</sub>H<sub>2</sub>, 74-86-2; C<sub>2</sub>H<sub>4</sub>, 74-85-1; BeC<sub>2</sub>H<sub>2</sub>, 92219-99-3; MgC<sub>2</sub>H<sub>2</sub>, 112816-30-5; BeC<sub>2</sub>H<sub>4</sub>, 112816-28-1; MgC<sub>2</sub>H<sub>4</sub>, 112816-29-2.

## Unimolecular Reaction Rate Theory for Highly Flexible Transition States. Use of Conventional Coordinates

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An alternative method for implementing RRKM theory for unimolecular reactions with highly flexible transition states is described using conventional coordinates. The number of available states for motion in the transition state  $N_{EJ}$  is determined via an appropriate average over the absolute space orientations and body-fixed momenta of the two fragments. The results of calculations of  $N_{EJ}$  for the C<sub>2</sub>H<sub>6</sub> → 2CH<sub>3</sub> reaction (or alternatively for the corresponding recombination reaction) obtained from the present expression are shown to be equivalent numerically to those obtained previously by Wardlaw and Marcus.

### I. Introduction

In recent years there has been an increase in the degree of molecular state selection available in experimental studies of unimolecular reactions.<sup>1</sup> Concurrent with this increase in state resolution has been an increased need for the theoretical determination of energy and angular momentum resolved unimolecular dissociation or isomerization rate constants  $k_{EJ}$  for realistic potential energy surfaces. Previous calculations of  $k_{EJ}$  have included those involving fully classical methods (both trajectory calculations and variationally implemented RRKM theory),<sup>2</sup> the statistical adiabatic channel model,<sup>3</sup> and a partially quantum partially classical variationally implemented RRKM theory.<sup>4</sup> The present paper focuses on an alternative method for implementing the latter.

In RRKM theory the specific rate constant,  $k_{EJ}$ , for the dissociation or isomerization at a given energy  $E$  and total angular momentum quantum number  $J$  is given by<sup>5</sup>

$$k_{EJ} = \frac{N_{EJ}}{h\rho_{EJ}} \quad (1)$$

where  $\rho_{EJ}$  is the density of states for the reactant at the given  $E$  and  $J$ . The quantity  $N_{EJ}$  is the number of available states for motion in the transition state, which is to be determined variationally, i.e., by finding a potential hypersurface for which  $N_{EJ}$  is minimized. In most practical applications the full hypersurface is not varied but rather some coordinate  $R$ , which describes the progress of the reaction. The value of  $R$  that gives a minimum in  $N_{EJ}$ , labeled  $R^\ddagger$ , is a function of  $E$  and  $J$ .

In a recent series of articles,<sup>4</sup> Wardlaw and Marcus have shown how Monte Carlo integration techniques may be used to facilitate the calculation of  $N_{EJ}$ 's. The basis of this method is the introduction of an approximate separation of variables into the conserved modes, i.e., modes which do not change their nature in the

transition from reactant to products, and the transitional modes, i.e., modes which do have a considerable such change. The

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