

Total Charge-Transfer Cross Sections in Molecular Systems

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Abstract: Total charge-transfer cross sections of rare gas and molecular positive ions with atomic, diatomic, hydrocarbon, and fluorocarbon neutral targets are reported. The positive ions had an average energy of 50 eV so an electron-jump mechanism by nonorbiting collisions occurs. The most striking feature is that the total cross sections are pseudoresonant with respect to electronic energy levels in the product ion. The total cross sections are low for high vibrational excitation. These observations are reasonably related to low Franck-Condon factors for high vibrational states. Trends in reciprocal charge transfer and charge transfer of atomic *vs.* molecular ions having similar recombination energies suggest that Franck-Condon factors of the projectile ions are of minor importance for the total cross section. Thermal-ion charge transfer occurs mainly by orbiting collisions, and the existing data do not show the pseudoresonant effects observed here for higher energy ions.

Gas-phase charge-transfer reactions have been studied for a variety of atomic and molecular systems.^{2,3} Most previous studies have focused on two different aspects of charge-transfer reactions. One aspect is the kinetic energy dependence of the cross section.⁴ The second aspect is the determination of ion-impact breakdown curves or the dependence of the product ion mass spectrum on the amount of excitation energy deposited in the ion by charge transfer.^{5,6} Also, recent progress has been made in the observation and analysis of vibrational excitation in electronically excited ions produced by charge-transfer.⁷⁻⁹

This previous work has generally dwelt on the details of a particular reaction rather than on general comparisons between different reactions. We have tried to make such comparisons and to deduce general criteria which affect total charge-transfer reactions in diatomic and polyatomic systems. Atomic, diatomic, and a few polyatomic projectile ions have been used on atomic, diatomic, hydrocarbon, and fluorocarbon neutral targets.

At thermal-ion energies, Langevin orbiting collisions usually predominate¹⁰ and lead to complex formation from which one exit channel is charge transfer. When complex formation occurs the charge-transfer cross section probably depends on the reaction exothermicity but should not depend on the specific internal energy states of the individual reactants. At ion energies greater than about 10 eV the probability of orbiting collisions becomes small, the relative motion of the reactants becomes rectilinear, and charge transfer occurs by an electron-jump mechanism in a nonorbiting collision. The charge-transfer cross section then becomes dependent on the internal energy states of the reactants and resonance effects may be observed.¹¹

In our experiments the primary ion energy averaged about 50 eV. One previous study in this energy range indicated that no energy resonance effects on the total charge-transfer cross sections exist for polyatomic targets.¹² However, with improved experimental apparatus and more extensive investigation of molecular targets we find that the cross sections are pseudoresonant with respect to electronic energy levels. But the cross sections are also low for high vibrational excitation due to low Franck-Condon factors for higher vibrational states.

Experimental Section

The ion source of a Nuclide magnetic mass spectrometer, Model 12-90G, was modified for studying charge-transfer reactions in which little momentum is transferred.¹³ In brief, five grids were placed between the filament and the ion chamber; they are numbered from the filament. Electrons from the filament were accelerated by a potential between the filament and grid 3 to a desired energy. The ion source was sufficiently open so that the gas pressure in the grid region was similar to that in the ion chamber. Ionization occurs near grid 3. Grids 4 and 5 are 10 V negative with respect to the filament. They accelerate the positive ions into the ion chamber and prevent the electrons from entering the ion chamber. Only the primary positive-ion beam traverses the ion chamber and is monitored on the trap. The primary ions have forward momentum perpendicular to the exit direction from the ion chamber and are not detected through the mass-analysis section. Likewise, secondary ions formed by stripping or other mechanisms which involve large momentum exchange are efficiently discriminated from detection. However, secondary ions produced by charge transfer which involves little momentum exchange are efficiently collected and mass analyzed. The primary ions have a broad kinetic energy distribution asymmetric toward high energy with an average of about 50-60 eV.¹³

The efficiency of secondary ion collection can be affected by kinetic energy in the fragment ions. From the geometry of the ion source we calculate that detection efficiency will decrease for ions having more than 0.25 eV in the direction parallel to the primary ion beam and 0.30 eV in the plane perpendicular to the primary ion beam.¹³ A few experimental measurements of ion kinetic energy in the plane perpendicular to the primary ion beam were made by the retarding potential method.¹⁴ Some kinetic energy is observed in the products of reactions such as $\text{Ne}^+ + \text{O}_2 \rightarrow \text{O}^+$, but the kinetic energy is independent of the primary ion energy from about 35 to

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Table I. Total Charge-Transfer Cross Sections for Various Projectile Ions with Atoms and Diatomic Molecules ($\text{cm}^2 \times 10^{16}$)

Projectile	(RE), ^a eV	NO	O ₂	Xe	CO ₂	H ₂	CO	Kr	N ₂	Ar
NO ⁺	(9.4)	9.1	<0.2							
C ₂ H ₄ ⁺	(10.5)	2.3	Trace	1.1				<0.1		
C ₂ H ₂ ⁺	(11.4)	0.4	0.5	0.3	0.1	0.0	0.1	0.2	<0.5	Trace
O ₂ ⁺	(~12)	2.2	10.8	14.5	1.2	Trace	0.6	0.9	0.3	0.1
Xe ⁺	(12.5)	0.1	4.0	34.4	0.9		0.4	0.2	0.6	0.1
CO ₂ ⁺	(13.8)	0.7	0.4	9.0	17.3	Trace	1.7	4.8	0.6	0.2
H ₂ ⁺	(~14)	4.6	3.1	11.2	17.4	0.6	15.8	19.5	6.3	5.9
CO ⁺	(14.0)	5.6	0.7	5.3	26.7	0.2	28.5	28.9		0.6
Kr ⁺	(14.2)	0.2	0.3	0.3	12.6	Trace	12.1	27.2	0.3	0.7
N ₂ ⁺	(15.6)		3.6	3.7	1.6	2.2		1.5	30.8	10.0
Ar ⁺	(15.8)	2.6	1.5	0.8	1.6	0.9	1.4	0.4	6.4	25.0
Ne ⁺	(21.6)	1.2	0.5	1.2	1.1	Trace	0.7	0.7	0.5	0.5
He ⁺	(24.6)	1.1	1.7	8.5	2.4	Trace	1.0	1.7	2.9	2.4

^a Average values of ion recombination energy from ref 2.

85 eV. Slightly higher repeller fields are required to efficiently collect these ions with small amounts of kinetic energy. A repeller field of 6 V/cm proved optimum for collection of the product ions whether they had small amounts of kinetic energy or not. We feel that the reported cross sections are not significantly underestimated due to kinetic energy discrimination, although the Ne⁺ and He⁺ cross sections are most subject to this factor. Mass discrimination of the electron multiplier detector was corrected by Faraday cup measurements.

The use of this ion source for measuring charge-transfer cross sections has been described.¹⁵ A dual gas inlet system was used to produce mixtures with a 25-fold excess of projectile ion gas. The target gas was maintained at the same pressure in all experiments. Corrections for symmetric charge transfer within the target gas were made. The total pressure in the ion chamber was in the low 10⁻⁶-Torr region for asymmetric charge transfer, but for symmetric charge transfer it was 25 times lower to maintain the same target gas pressure.

All gases were lecture bottle grade from Matheson Co. or Air Products, Inc. except for *n*-C₄F₁₀ which was from Peninsular Chem Research.

Results

The phenomenological charge-transfer cross section is given by $Q = I_s/I_p dN$, where I_s and I_p are the measured secondary and primary ion currents, d is the effective distance traveled by the primary ions in the ion chamber, and N is the density of target molecules. In these experiments d and N are constant but unknown, so only relative cross sections are measured. The relative values are converted to an absolute scale by assigning the Ar⁺/Ar reaction a value of 25×10^{-16} cm². This value has been found by two sets of investigators for 50-eV Ar⁺ ions.^{16,17} Charge-transfer cross sections vary little in this energy range,² so the kinetic energy spread in our primary ions should not invalidate this normalization.

All cross sections were obtained under nearly identical ion-source conditions.¹² The electron energy could be varied independently from all other ion-source voltages. For the Kr⁺ + CH₄ reaction, the CH₄⁺/CH₃⁺ intensity ratio was plotted against the electron energy. The ratio decreased between electron energies from 15 to 50 eV and remained constant at higher electron energies. We interpret this to mean that the ratio of ²P_{3/2} to ²P_{1/2} states of Kr⁺ decreases with electron energy up to 50 eV and then presumably reaches the statistical ratio of 2:1. Therefore, for all the rare gas ions, 75-eV electrons were chosen to produce the

statistical distribution of ion states. For the molecular ions the following electron energies were selected to be lower than the appearance potential of any fragment ions: 23 eV for N₂; 19 eV for CO and CO₂; 17 eV for O₂, H₂, and C₂H₂; 13 eV for C₂H₄; and 12 eV for NO. Except for NO these electron energies are sufficient to produce excited electronic states of the parent ions.¹⁸⁻²¹ It is known²² that the 16.1-eV ⁴Π_u state of O₂⁺ is metastable for lifetimes long enough to be present in our ion beam. However, for 17-eV electrons its abundance will be low.²² Similarly, small yields of other metastable excited ions may be present in our ion beams. Their abundance cannot be evaluated quantitatively, but is probably small at the low electron energies used.

The results for total charge-transfer cross sections are shown in Tables I, II, and III. These total cross sections were obtained by summing the fragment-ion cross sections. We feel that most cross sections of less than 1 Å² are only of qualitative significance. The projectile ions are listed in order of increasing recombination energies. These generally correspond to ionization energies, but several molecular ions, notably H₂⁺, are exceptions.^{2,6} Thus the trend with recombination energy for any target molecule can be seen by reading down the column.

For the case of the five rare gas ions on methane, we can compare our cross sections on a relative basis with those of Hertel and Koski.²³ Hertel and Koski used a tandem mass spectrometer with perpendicular collection and measured the charge-transfer cross sections *vs.* ion kinetic energy. If we use their data to obtain total charge-transfer cross sections for 50-eV primary ions we find excellent agreement with our results.¹³ Thus we feel that our experimental method is valid and that it yields data comparable to those from more complex tandem mass spectrometers.

Discussion

1. Pseudoresonance Effects. The total charge-transfer cross sections for the target molecules in Tables

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Table II. Total Charge-Transfer Cross Sections for Various Projectile Ions with Hydrocarbons ($\text{cm}^2 \times 10^{16}$)

Projectile	RE, ^a eV	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	C ₂ H ₂	C ₂ H ₄	C ₃ H ₆
NO ⁺	(9.4)	0.5				0.5	1.4	
C ₂ H ₄ ⁺	(10.5)	Trace					12.9	
C ₂ H ₂ ⁺	(11.4)	0.8				23.4	9.4	
CH ₄ ⁺	(~12)	2.4						
O ₂ ⁺	(~12)	4.6				16.4	22.2	
Xe ⁺	(12.5)	8.9	34.0	43.2	35.5	3.1	13.3	37.0
CO ₂ ⁺	(13.8)	16.8				1.2	7.2	
H ₂ ⁺	(~14)	26.9				8.8	12.8	
CO ⁺	(14.0)	24.7				3.6		
Kr ⁺	(14.2)	30.6	10.0	30.5	21.2	0.9	16.6	27.8
N ₂ ⁺	(15.6)	14.2				9.8		
Ar ⁺	(15.8)	9.8	6.0	22.5	15.1	4.0	19.9	23.6
Ne ⁺	(21.6)	0.7	1.1	5.1	6.4	3.6	5.1	8.5
He ⁺	(24.6)	2.0	2.9	13.1	9.6	7.0	10.0	13.6

^a Average values of ion recombination energy from ref 2.

Table III. Total Charge-Transfer Cross Sections for Various Projectile Ions with Perfluoroalkanes ($\text{cm}^2 \times 10^{16}$)

Projectile	RE, ^a eV	CF ₄	C ₂ F ₆	C ₃ F ₈	n-C ₄ F ₁₀	c-C ₄ F ₈
C ₂ H ₂ ⁺	(11.4)	0.3				
O ₂ ⁺	(~12)	0.6	2.1	3.0		
Xe ⁺	(12.5)		2.0	5.3	11.8	11.1
CO ₂ ⁺	(13.8)	0.8	4.8	12.8		
H ₂ ⁺	(~14)	1.5	7.6	12.3		
CO ⁺	(14.0)	2.7	11.7	20.4		
Kr ⁺	(14.2)	10.0	13.8	17.2	25.8	21.5
N ₂ ⁺	(15.6)	11.6	19.1	32.6		
Ar ⁺	(15.8)	8.0	14.4	22.5	33.9	21.8
Ne ⁺	(21.6)	1.8	7.7	13.7	26.3	15.0
He ⁺	(24.6)	1.3	7.0	7.7	23.2	18.7

^a Average values of ion recombination energy from ref 2.

I-III show definite structure when compared to the recombination energy of the projectile ions. The cross sections are highest for both atomic and molecular projectile ions when their recombination energy (RE) approximates the ionization potential of the target. In addition, in some cases, such as O₂, the cross section increases for higher electronically excited states of the product ion. The significant point is that the cross sections generally decrease as the reaction exothermicity increases. To clarify these points we will discuss the target molecules in more detail.

CO, N₂, and CO₂ exhibit simple behavior. The ionization potentials are 14.0, 15.6, and 13.8 eV, respectively. In each case the charge-transfer cross sections are low for projectile ions with RE below these ionization potentials, reach a maximum at or slightly above this, and then decrease for higher RE's. For CO, highest cross sections occur with H₂⁺, CO⁺, and Kr⁺. The symmetric cross section is the highest, but this is not true for all targets (see CO₂ and Kr). For N₂, large cross sections occur for H₂⁺, N₂⁺, and Ar⁺. H₂⁺ actually has a range of recombination energies from about 12.5 to 16.5 eV⁶ so it can contribute to N₂⁺ formation, but its overall behavior is best represented by an average RE of 14 eV. CO₂ has large cross sections with CO₂⁺, H₂⁺, CO⁺, and Kr⁺; it is of interest that CO⁺ has a larger cross section than CO₂⁺.

For more exothermic reactions the cross sections decrease even though vibrational energy levels exist in the product ions for near-resonant matching with the projectile ion energies. The vibrational levels for CO⁺,¹⁸ N₂⁺,¹⁸ and CO₂⁺¹⁹ have been observed by photoelectron spectroscopy, as have several excited electronic states. These electronic states are at 16.6

and 19.7 eV for CO⁺; at 16.7 and 18.8 eV for N₂⁺; and at 17.3, 18.1, and 19.4 eV for CO₂⁺. Ne⁺ and He⁺ projectile ions could produce these states but would require high vibrational excitation to do so. The cross section for such processes seems low.

Argon has ionization energies of 15.8 and 15.9 eV and is therefore similar to N₂. However, Ar cannot be vibrationally excited. The charge-transfer cross sections for Ar and N₂ vs. RE are almost identical except that the symmetric reaction has the largest cross section in both cases. Likewise, Kr, with ionization energies of 14.0 and 14.7 eV shows similar behavior to CO and CO₂. These comparisons support the postulate that high vibrational excitation in molecular charge-transfer reactions has relatively low cross sections. Vibrational excitation certainly occurs, as indicated by extensive studies on ion-impact mass spectra.^{2,5} Our point is simply that the overall cross section is low.

O₂ and NO exhibit more complex behavior with respect to ion RE. O₂ has its largest cross sections with O₂⁺ and Xe⁺, which have RE's near the ionization potential of 12.1 eV for O₂. The cross section then decreases (H₂⁺ is again anomalous owing to its spread in RE), but seems to rise again for N₂⁺ and Ar⁺. The excited electronic states of O₂⁺ are at 16.1, 18.2, and 20.3 eV.¹⁸ It seems probable that the 16.1-eV state of O₂⁺ is being formed by charge transfer from N₂⁺ and Ar⁺. These would be slightly endothermic reactions, but we have generally observed this as in N₂⁺ + Ar. Kinetic energy conversion of a few vibrational quanta is probable and some metastable excited N₂⁺ is possible.

NO⁺ has electronic states at 9.3, 14.0, 15.7, 16.6,

17.2, 17.3, 18.3, and 18.9 eV.²⁰ The largest charge-transfer cross sections to NO occur for NO⁺ (RE = 9.3 eV), H₂⁺ and CO⁺ (RE = 14 eV), and Ar⁺ (RE = 15.8 eV). There is remarkable correlation between these cross sections and the formation of NO⁺ in low vibrational levels of its various electronic states.

The hydrocarbons listed in Table II show the same general features as found for the diatomic molecules. CH₄ has an ionization potential at 12.7 eV²¹ and shows large charge-transfer cross sections for ions with RE's of this order and somewhat higher. In this case the cross sections do increase for RE's 1–2 eV above the ground electronic energy level, but they eventually decrease for larger RE's which would give still higher vibrational excitations. The second CH₄⁺ electronic state is near 23 eV,²⁴ and it may be that the He⁺ cross section indicates this. The other alkanes were only studied with the rare gas ions, but they all show the same trend.

C₂H₄⁺ contains electronic states at 10.5, 12.4, 14.5, 15.7, and 18.9 eV.²¹ Most of the projectile ions show large cross sections with C₂H₄. This is consistent with the formation of one of the electronic states of C₂H₄⁺ in a low vibrational state. The other unsaturated compounds show similar behavior.

Little is known about the electronic states of the perfluoroalkanes shown in Table III. For CF₄, photoelectron spectroscopy has given ionization energies of 15.9, 17.2, and 18.5 eV.²⁵ However, no parent ion is observed in the mass spectrum and the lowest appearance potential by photoionization is 15.5 eV for CF₃⁺.²⁶ For the other perfluoro-*n*-alkanes the lowest photoionization appearance potentials occur for CF₃⁺ near 13.5 eV.²⁶ The charge-transfer cross sections have been discussed in connection with dissociative charge transfer.¹⁵ The cross sections show maxima for N₂⁺ and clearly decrease for ions of higher RE's. Note that the He⁺ cross sections are generally lower than the Ne⁺ cross sections, in contrast to the other molecules studied. The overall cross-section trends in the fluorocarbons agree with those found in other molecules and support the suggestion that high vibrational excitation is a low-cross-section process.

We have stressed the point that total charge-transfer cross sections show definite trends with the electronic energy levels of the target molecule and that population of highly excited vibrational levels in the product ion is improbable. In diatomic and in more complex molecules the large number of vibrational and rotational states associated with each electronic state will almost always allow near-resonant energy matching with the projectile ion energy. But this factor alone is not sufficient to provide a large cross section. We suggest that the Franck–Condon factors for the transition of the neutral target molecule to a vibrationally excited ion are of considerable importance. These factors will generally decrease for high vibrational excitation. We cannot analyze this suggestion quantitatively because the time of interaction for 50-eV ions is so long that considerably distorted Franck–Condon factors probably apply.²⁷ Qualitatively, the suggestion does explain

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the observed cross-section trends. One can regard the trends as pseudoresonant because they appear to be approximately resonant with electronic energy levels if vibrational levels are ignored.

Henglein and Muccini¹⁰ have reported several cross sections for symmetrical and unsymmetrical charge transfer in molecular systems. They operated an ion source in a single-stage mass spectrometer in the Cermak–Herman mode.²⁸ This is less direct than our method because they do not measure the primary-ion current. For asymmetric reactions they measure only the ratio σ_{BA}/σ_{AA} for the reactions B⁺ + A → B + A⁺ and A⁺ + A → A + A⁺. From their limited data they concluded that there is no resonance restriction for asymmetric charge transfer in molecular systems and that no correlation between the cross section and the ionization potential differences exists. This is the exact opposite of our conclusion. When our data are compared with theirs for the systems studied in common there is at least approximate agreement. The basic difference is that they did not systematically study the cross sections for a number of ions having different RE's with the same molecule. Thus they did not observe the trends that do exist. Also their experimental method is less direct than ours and only leads to cross-section ratios.

It is of interest to compare the cross sections for atomic and molecular ions having nearly the same RE. Ar⁺ and N₂⁺ probably satisfy this requirement most closely. For all targets except Ar the N₂⁺ cross section is larger. One might have predicted the opposite result, since N₂⁺ neutralization involves a Franck–Condon factor, although this factor should be large for N₂⁺. The Kr⁺ and CO⁺ also have nearly the same RE. This comparison is less valid because about one-third of the Kr⁺ is in the 14.7-eV state. In some cases the cross sections from these ions are largest for Kr⁺ as for CH₄, C₂H₄, C₂F₆, and CF₄ targets, but in other cases they are largest for CO⁺ as for C₃F₈, C₂H₂, and NO targets. It tentatively appears that the Franck–Condon factors in the projectile ion are not very important in the determination of the total charge-transfer cross section. The H₂⁺ reactions also lend some support to this postulate, since H₂⁺ projectile ions often have large cross sections while H₂ targets have very low cross sections. The low H₂ cross sections may also be due to competing H-atom-transfer reactions.

Finally, we compare cross sections for several reciprocal charge-transfer reactions which are approximately thermoneutral. We consider Ar⁺/N₂ and N₂⁺/Ar to be reciprocal reactions. Other examples are Kr⁺/CO with CO⁺/Kr and Xe⁺/O₂ with O₂⁺/Xe. In these three cases the cross section is always larger for the diatomic ion. This cannot be ascribed to energetics because, if anything, the diatomic ion reaction is slightly endothermic. For Kr⁺/CO₂ with CO₂⁺/Kr the Kr⁺ cross section is larger, but the CO₂⁺ reaction trend may be associated with better matching of the molecular RE with the ionization potential of the target, since molecular recombination energies are often spread over a small range. It is also consistent with the postulate that the Franck–Condon factors of the

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projectile ions are of minor importance for the total cross sections.

2. Comparison with Thermal Ion Data. Our data all refer to projectile ions having an average kinetic energy of about 50 eV. Extensive studies of thermal-ion charge transfer with atomic and diatomic projectile ions and diatomic targets have been carried out by Ferguson and coworkers²⁹ using a flowing-afterglow method and by Warneck³⁰ using photoionization mass spectrometry. Both workers conclude on the basis of their data that there is no correlation between the energy defect of the reaction and the charge-transfer cross section; *i.e.*, there are no pseudoresonance effects. As mentioned in the introduction, charge transfer may

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occur by complex formation at thermal ion energies and then resonance effects would not be expected. It is of interest, however, to examine this point in more detail by using a variety of projectile ions spanning a large RE range on the same target. Most thermal ion studies have compared the cross sections for the same ion on different targets.

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Theoretical Determination of the Reaction Path in the Prototype Electrocyclic Transformation between Cyclobutene and *cis*-Butadiene. Thermochemical Process^{1a}

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Abstract: A detailed study of the potential surfaces of the cyclobutene and *cis*-butadiene isomers is undertaken with the aim of determining the characteristics of the reaction (minimum energy) path followed by these systems in an electrocyclic transformation which is thermochemically induced. Nonempirical SCF and CI calculations using a large gaussian basis set are employed for this purpose and emphasis is placed upon the inherently nonlinear relationships which exist between the various geometrical quantities as they change from their respective equilibrium values in the two stable end products. As a result of this work it is demonstrated that a stepwise mechanism in which rotation of the methylene groups occurs only *after* the cyclobutene ring has been destroyed is much preferred to a linear procedure in which rotation and bond breaking occur simultaneously. Specifically, it is found that the energy barrier for CC stretch is approximately 1.1–1.2 eV, while that due to *pure* rotation at the optimum intermediate bond distance (4.49 bohrs) is only 0.85 eV; the total barrier for the reaction is thus found to be 0.6 eV above the experimental estimate for this quantity. In obtaining the various potential surfaces emphasis is placed upon the importance of configuration interaction in determining a reliable representation of the wave functions for various intermediate species, particularly for those corresponding to the disrotatory energy maximum and for structures in which the cyclobutene ring bond is partially destroyed. The stepwise mechanism found to be operative in this work indicates that the conrotatory mode is definitely preferred over the disrotatory, in agreement with experiment and with predictions emanating from the Woodward–Hoffmann rules; it is interesting, however, that in both cases quite symmetrical rotational potential curves are obtained. In addition it is found that for certain higher energy paths (involving different models for altering the various geometrical parameters) the disrotatory species is actually preferred, thereby clearly emphasizing the need for determining the *true* minimum-energy interconversion path in order to effect a reliable estimation of the relative stability of the two rotational modes.

The elucidation of the mechanism for electrocyclic reactions² is of great importance in theoretical chemistry because it illustrates the utility of the MO theory with regard to the understanding of dynamic processes, as well as for its more common applications in the area of static molecular properties. In the usual

case an electrocyclic reaction involves a simultaneous breaking of a CC bond and the rotation of a pair of CH₂ groups through 90°; such a transformation takes its stereospecific character from the relative direction in which this rotation occurs, and on the basis of what has been described as the principle of conservation of orbital symmetry,³ the stereospecific course of a large series of

(1) (a) Parts of this paper were presented at the Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, May 1970; (b) University of Nebraska; (c) Johannes Gutenberg Universität.

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), and references therein; R. B. Woodward and R. Hoffmann, "Die Erhaltung der Orbitalsymmetrie," Verlag Chemie GmbH, Weinheim, 1970.