Evidence for Long-lived Excited States of $[C_nH_2]^{2+}$ Carbocations

J. R. Appling, G. C. Shields and T. F. Moran†

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

The energetics, structures, stabilities and reactivities of $[C_nH_2]^{2+}$ ions have been investigated using computational methods and experimental mass spectrometric techniques. Spontaneous decompositions of $[C_nH_2]^{2+}$ into $[C_nH]^+ + H^+$ products, observed for ions with odd- n values, have been explained by invoking the formation of excited triplet states. Even- n $[C_nH_2]^{2+}$ ions possess triplet ground states with low-lying excited states, whereas odd- n ions have triplet states with energies several eV above ground singlet states. Radiationless transitions of vibrationally excited long-lived triplet state ions into singlet state continua are suggested as possible mechanisms for spontaneous deprotonation processes of odd- n $[C_nH_2]^{2+}$ ions. Evidence for these long-lived excited states has been obtained in bimolecular single electron transfer reactions.

INTRODUCTION

Ions of the type $[C_nH_2]^{2+}$ are responsible for reactions commonly observed in the doubly charged ($2E$) ion mass spectra of a wide variety of hydrocarbons including aromatics,¹⁻³ saturated aliphatics,⁴ alkynes,⁵ halogenated compounds,^{6,7} nitriles,⁸ amines^{9,10} and oxygen-containing compounds.¹¹ Within a given compound class, relative abundances of $[C_nH_2]^{2+}$ product ions of odd n are generally more intense than the corresponding even $(n-1)$ or $(n+1)$ product ions, which suggests an even-odd n effect in the stability and/or reactivity of $[C_nH_2]^{2+}$ ions. Stable doubly charged ions have also been observed in charge stripping experiments in which electrons are removed from singly charged ions during collisions with neutral target molecules. Minimum translational energy loss values measured¹² for $[C_nH_2]^+$ charge stripping reactions have been found to undergo an even-odd alternation in magnitude as n increases. Spontaneous proton eliminations have been observed by Rabrenović and Beynon¹³ for odd- n ions but not for $[C_nH_2]^{2+}$ ions with even n values. These deprotonation processes measured in Ref. 13 occurred within the microsecond time-'window' in a second field-free region of their mass spectrometer.

It is the purpose of the present investigation to examine $[C_nH_2]^{2+}$ ions using both self-consistent field molecular orbital (SCF-MO) methods as well as doubly charged ion mass spectrometric techniques in order to gain insight into the even-odd functional n behavior of these species. Our calculations show that odd- n $[C_nH_2]^{2+}$ ions possess excited triplet states several eV above ground singlet states, in contrast to the even- n series where ground states are triplets and excited singlet states have energies similar to ground triplet states. Triplet $\rightarrow$ singlet predissociation processes occurring for odd- n ions in the microsecond

time-scale rationalize spontaneous proton eliminations for odd- n $[C_nH_2]^{2+}$ ions observed by Rabrenović and Beynon.¹³ Experiments will be reported which demonstrate that electron impact ionization processes produce long-lived excited-state $[C_nH_2]^{2+}$ (odd- n) ions.

RESULTS AND DISCUSSION

Calculated structures of carbocations

In order to understand the fundamental basis of the aforementioned odd- n /even- n trends in $[C_nH_2]^{2+}$ formation, we have employed self-consistent field molecular orbital (SCF-MO) techniques to calculate the structures and energies of $[C_nH_2]^{2+}$ ions as a function of n , for $n=2-8$. Calculations were performed using the MINDO/3 method¹⁴⁻¹⁶ in which geometry-optimized structures were obtained by minimizing the energy with respect to all geometric variables using the Davidson-Fletcher-Powell method.¹⁷ Geometry-optimized minimum-energy structures have been determined for the lowest singlet (S_0) and triplet (T) states of $[C_nH_2]^{2+}$ ions, each of which has been found to be linear with hydrogen atoms at terminal positions. The ground electronic states for odd- n ions are singlets with the first excited triplet states more than 200 kJ higher in energy. In contrast, even- n $[C_nH_2]^{2+}$ ions possess triplet ground states with excited singlet states only 60 kJ higher in energy. The even- n triplet-singlet energy differences consistently decrease from 60 kJ in the case of $[C_2H_2]^{2+}$ to less than 1 kJ for $[C_8H_2]^{2+}$. Similarly, for odd- n ions, singlet-triplet energy differences decrease from 297 kJ for $[C_3H_2]^{2+}$ to 221 kJ for $[C_7H_2]^{2+}$. Both singlet and triplet state linear $[C_nH_2]^{2+}$ ions are calculated to be stable and require more than 3 eV of

† Author to whom correspondence should be addressed.

internal energy to dissociate by means of proton elimination.

Deprotonation of $[C_nH_2]^{2+}$ ions

Dissociation energies for the singlet and triplet states of $[C_2H_2]^{2+}$, shown as solid curves in Fig. 1 have been determined by keeping the respective geometry-optimized variables constant and computing the energy of each system as a function of C—H bond stretch. Stretching a C—H bond in $[C_2H_2]^{2+}$ increases the charge density on the departing hydrogen to +1 at long range. The energy for this deprotonation process goes through a maximum at 2.4 Å, which is 3.6 eV above the energy minimum and 3.7 eV above the dissociation asymptote. Dissociation energies have also been computed by stretching a C—H bond and allowing all other atoms in the doubly charged ion the opportunity to occupy minimum energy positions. Barriers to dissociation computed by either simple bond extension or bond extension/geometry optimization are within 0.01 eV of each other from the bottom of the potential energy well out to distances beyond 3 Å. The solid curves are shown connected to asymptotic energies of $[HC_2]^+ + H^+$ products which have been computed for separation bond distances of 1000 Å.

Deprotonation potential curves for lowest singlet (S_0) and triplet (T) states for higher members of the homologous $[C_nH_2]^{2+}$ ion series are presented as a function of C—H separation distance in Figs 2 and 3. The SCF-MO potential energy curves shown in Figs 2 and 3 illustrate that $[C_nH_2]^{2+}$ well-depths become larger as n increases from 3 to 8 and also indicate slight broadening of deprotonation barriers as n is increased. The SCF-MO potential energy corresponding to the C—H stretch was calculated in small

incremental values from $r = 0.7$ – 1.8 Å and fitted by a sixth-order polynomial expansion in r . The coefficients from this expansion were used¹⁸ to obtain the vibrational constants ω_e and $\omega_e x_e$, which were employed to calculate vibrational energies shown in Figs 2 and 3. These vibrational constants were obtained using the reduced mass of the separating proton $-[C_nH]^+$ pairs, following the usual spectroscopic methods used in the description of characteristic group frequencies which are outlined by Levine.¹⁹

Solid asymptotes represent energies of $HC_n^+ \cdots H^+$ systems calculated at separation distances of 1000 Å, where $[HC_n]^+$ fragments possess the configuration of geometry-optimized $[C_nH_2]^{2+}$. Dashed asymptotes represent energies obtained with a $HC_n^+ \cdots H^+$ separation distance fixed at 1000 Å combined with a geometry-optimized minimum-energy $[HC_n]^+$ structure. Deprotonation barriers have also been computed for singlet state ions in Figs 2 and 3 by stretching a $[HC_n \cdots H]^{2+}$ bond and allowing all other atoms in the doubly charged ion to move to positions of minimum energy. Energies for these systems computed by the geometry-optimized bond extension method are essentially equivalent to those calculated by the simple bond extension approach over distances from potential energy well minima to barrier maxima. At larger separation distances, the energies computed by these two methods tend to diverge and these energy shifts are illustrated in Fig. 4. Energies computed using the geometry-optimized minimum-energy bond extension method decrease smoothly for odd- n ions as well as $[C_6H_2]^{2+}$, whereas curves for $[C_2H_2]^{2+}$ and $[C_4H_2]^{2+}$ ions reflect more abrupt decreases with $C \cdots H$ bond extension at large separation distances. Corresponding atomic positional shifts from global energy minima that can occur as $C_\alpha \cdots H$ bonds are stretched in the respective $[H \cdots C_\alpha - C_\beta - C_\gamma - C_\delta - C_\epsilon - C_\zeta - C_\eta - H']^{2+}$

Figure 1. Potential energy hypersurfaces for deprotonation of $[HCCH]^{2+}$, computed for the lowest triplet and singlet states, are given as a function of $HCC^+ \cdots H^+$ distance.

Figure 2. Potential energy hypersurfaces for deprotonation of $[HC_3H]^{2+}$, $[HC_4H]^{2+}$ and $[HC_5H]^{2+}$ ions are given as a function of proton separation distance. Vibrational levels are represented by solid lines for ground state ions and by dashed lines for electronically excited ions. Triplet states are indicated by (T) and lowest energy singlet states are indicated by (S_0) .

ions are shown in Fig. 5. In general bond distance shifts are relatively small out to separating $C_\alpha \cdots H$ distances corresponding to the deprotonation barrier apex, with alternate compression and extension of adjacent C—C bonds. Every $[C_nH_2]^{2+}$ ion exhibits a small contraction of the C—H' bond as the $C_\alpha \cdots H$ bond is extended.

Role of the triplet state in deprotonation of $[C_nH_2]^{2+}$ ions

One of the most obvious features in Figs 1–3 is the relative energy alternation of singlet and triplet states as a function of $[C_nH_2]^{2+}$ carbon atom number. Energies of excited singlet states are very close to

Figure 3. Potential energy hypersurfaces for the deprotonation of $[HC_6H]^{2+}$, $[HC_7H]^{2+}$ and $[HC_8H]^{2+}$ ions are given as a function of proton separation distance. Vibrational levels are represented by solid lines for ground state ions and by dashed lines for electronically excited ions. Triplet states are indicated by (T) and lowest energy singlet states are indicated by (S_0) . Potential curves and vibrational levels for triplet (T) and singlet (S_0) states of $[HC_8H]^{2+}$ are indistinguishable and are given by the solid curve labelled S_0 .

Figure 4. Energy lowering of $[C_nH_2]^{2+}$ deprotonation curves computed using the geometry-optimized minimum-energy bond extension method, as compared to those computed by using the $C\cdots H$ bond extension approach (Figs 1–3). Energy differences (eV) are given as a function of separating $C-H$ bond distance (Å). Labelled curves illustrate energy differences for $[C_nH_2]^{2+}$ ions with $n = 2-7$.

those of triplet ground states for even- n ions and in the case of $[C_8H_2]^{2+}$ energies of the S_0 and T states virtually merge, as shown in Fig. 3. However, excited triplet state energies for odd- n ions are several eV higher than those of ground singlet states. Energetic triplet states may play an important role in

Figure 5. Bond distance shifts of geometry-optimized minimum-energy bond extension structures from the most stable minimum-energy geometry-optimized structures. Bond distance differences (Å) are given as a function of extended $C\cdots H$ bond distance. Numbers labeling each curve indicate n for each $[C_nH_2]^{2+}$ ion with structure $[H\cdots C_\alpha-C_\beta-C_\gamma-C_\delta-C_\epsilon-C_\zeta-H']^{2+}$.

spontaneous deprotonation processes observed by Rabenović and Beynon¹³ for odd- n $[C_nH_2]^{2+}$ ions. These workers¹³ found that decomposition of $[C_nH_2]^{2+}$ ions into $[C_nH]^+$ and H^+ occurred for odd- n ions a microsecond or so after formation, but that this deprotonation process did not take place for even- n $[C_nH_2]^{2+}$ ions. We propose that radiationless triplet-singlet transitions can be used to rationalize these experimental observations. It is not unreasonable to expect that both singlet and triplet $[C_nH_2]^{2+}$ ions can be formed in electron impact ionization/fragmentation of hydrocarbon molecules. Excited states so formed are expected to be relatively long-lived since triplet-singlet transitions are spin-forbidden, although it is possible for radiationless transitions to occur between the excited state and a lower state which possesses a dense manifold of isoenergetic levels.²⁰ In the case of odd- n $[C_nH_2]^{2+}$ ions, excited vibrational levels of the triplet states are isoenergetic with the ground singlet state continuum and predissociation processes²¹ are possible. Lifetimes for spontaneous predissociations of this type are typically in the microsecond time-range.²² Curtis and Boyd^{23,24} have shown recently that predissociation processes are responsible for unimolecular decompositions of doubly charged diatomic ions which occur on the microsecond time-scale. Predissociation processes occurring from vibrationally excited triplet levels by means of $T \rightarrow S_0$ curve crossings (case 1 of Herzberg²⁵) lead to $[HC_n]^+ + H^+$ products with several eV excess kinetic energy as a result of the relatively large energy differences between deprotonation barriers and dissociation asymptotes. A comparison between measured kinetic energies and those predicted from energy differences between SCF-MO barrier heights and dissociation asymptotes are given in Table 1. Product kinetic energies measured for deprotonation of $[C_nH_2]^{2+}$ ($n = 3, 5, 7$) ions are reasonably close to those estimated from respective potential energy curves. Although the concurrence of measured and computed kinetic energies supports the $T \rightarrow S_0$ predissociation mechanism, it does not prove the existence of excited precursor triplet states for odd- n $[C_nH_2]^{2+}$ ions.

Experimental evidence for long-lived excited states in bimolecular single electron transfer reactions

In order to obtain evidence concerning long-lived states of $[C_nH_2]^{2+}$ ions we have examined single electron transfer reactions with a view toward uncovering reaction channels that are sensitive to excitation energy present in the reactant ion. The predominant reaction channels involving single electron transfer reactions of keV $[C_nH_2]^{2+}$ ions are:

Reaction channel (1) forms $[C_nH_2]^+$ products which have the identical mass and approximately the same velocity as incident $[C_nH_2]^{2+}$ ions. These fast $[C_nH_2]^+$ products possess twice the energy-to-charge of the

Table 1. Energetics of $[HC_n \cdots H]^{2+}$ ion decomposition into $[HC_n]^+ + H^+$ products

$[C_nH_2]^{2+}(S_0)$ ion species n	$[HC_n \cdots H]^{2+}$ well-depth (eV)	Energy difference (eV) between $[HC_n \cdots H]^{2+}$ barrier height and $[HC_n]^+ + H^+$ dissociation asymptote ^a	Measured ^b average kinetic energy (eV) of $[HC_n]^+ + H^+$ products
2	3.58	3.72 (3.96)	—
3	4.74	3.19 (3.36)	2.99
4	5.31	2.65 (2.78)	—
5	6.02	2.28 (2.61)	2.46
6	6.39	1.97 (2.18)	—
7	6.90	1.68 (2.19)	2.08
8	7.10	2.00 (2.11)	—

^a Numbers given in parentheses refer to geometry-optimized $[HC_n]^+$ ion products.
^b Kinetic energies calculated using 50% peak width from Ref. 13. A rule indicates dissociations were not observed (see text).

reactant ions and can be monitored by the usual techniques of doubly charged ion mass spectrometry.⁵ Product $[C_nH]^+$ ions in reaction channel (2) result from reactions in which an electron is transferred over several Å initially forming $[C_nH_2]^+$ with sufficient internal energy to subsequently dissociate into $[C_nH]^+$ and H. In accord with previous observations,¹³ the narrow energy widths of product ion peaks from electron transfer reactions (1) and (2) are expected and found to be similar to that of the reactant ion peak. For the systems examined in this work we do not observe collision-induced dissociation to be an important mechanism leading to $[C_nH]^+$ ion formation. Such collision-induced dissociations would give rise to broad product ion peaks as a result of Coulombic repulsion between the separating $[C_nH]^+ + H^+$ pair, in contrast to our observations. Information on the relative importance of single electron transfer channels (1) and (2) has been obtained from measurement of product ion abundances. We have determined the ratio of dissociative to non-dissociative processes in collisions of $[C_nH_2]^{2+}$ incident ions. Ratios of these $[C_nH]^+/[C_nH_2]^+$ products from single electron transfer reactions of $[C_nH_2]^{2+}$ ions with various hydrocarbon targets are presented in Table 2. Generally non-dissociative single electron channels of $[C_nH_2]^{2+}$ ions, which form

$[C_nH_2]^+$ products of equal mass, predominate over the dissociative channels.

Energetics appropriate to channels (1) and (2) are illustrated in Fig. 6 where 'half-reactions' for the non-dissociative $[C_nH_2]^{2+} \rightarrow [C_nH_2]^+ + M \rightarrow M^+$ as well as dissociative $[C_nH_2]^{2+} \rightarrow [C_nH]^+ + H/M \rightarrow M^+$ reactions are presented for $n = 2-4$ where M refers to the respective target gases. Electron transfer processes occur in time periods which are short compared to nuclear motion and as a first approximation the Franck-Condon principle applies.²⁶ Descending vertical lines denote ionic recombination energies, i.e. energies liberated when a single electron combines with $[C_nH_2]^{2+}$ to form either $[C_nH_2]^+$ or $[C_nH]^+$ products. These recombination energies have been obtained from SCF-MO computations by determining the energy difference between $[C_nH_2]^{2+}$ and $[C_nH_{2,1}]^+$ ions which have been 'frozen' in the configuration of the geometry-optimized minimum-energy $[C_nH_2]^{2+}$ reactant ion. The solid curves in Fig. 6 illustrate the Franck-Condon ionization envelopes obtained from photoelectron spectra.²⁷⁻²⁹ Energetics for single electron transfer reactions for the $[C_nH_2]^{2+}$ ions ($n = 5-8$) are displayed in Fig. 7 where ionization energies for target gas molecules have been taken from Ref. 30 and recombination energies of $[C_nH_2]^{2+}$ ions have been determined from SCF-MO computations.

Reaction energetics for single electron transfer processes displayed in Figs 6 and 7 show that both ground and first excited states of $[C_nH_2]^{2+}$ ions liberate sufficient energy in the $[C_nH_2]^{2+} \rightarrow [C_nH_2]^+$ recombination 'half-reactions' to ionize the various target molecules listed in Table 2. Using techniques of doubly charged ion mass spectrometry we have observed that non-dissociative single electron transfers occur with high probability for all $[C_nH_2]^{2+}$ ions studied. The situation is not so straightforward for dissociative single electron transfer reactions since many of these processes require additional energy input which must be supplied by either translational energy of the colliding pair or internal excitation energy of the reactant ion. In particular, dissociative recombination energies of ground state $[C_5H_2]^{2+}(S_0)$ and $[C_7H_2]^{2+}(S_0)$ ions are less than target molecule

Table 2. Appearance energy differences and intensity ratios of $[C_nH_2]^+$ and $[C_nH]^+$ products from reactions

$[C_nH_2]^{2+} + M \begin{cases} \rightarrow [C_nH_2]^+ + M^+ \\ \rightarrow [C_nH]^+ + H + M^+ \end{cases}$			
Reactant $[C_nH_2]^{2+}$ ion n	Target species (M)	Difference (eV) between $[C_nH]^+$ and $[C_nH_2]^+$ appearance energies	$[C_nH]^+/[C_nH_2]^+$ product intensity ratio
2	Acetylene	0.0	0.0063
3	3-Chloropropene	0.0	0.27
4	1,4-Dichlorobutane	0.0	1.63
5	<i>tert</i> -2-Hexene	3.8	0.061
6	<i>tert</i> -2-Hexene	0.0	0.44
7	1-Heptene	2.6	0.19
8	1,7-Octadiene	0.0	0.13

Figure 6. Energetics of single electron transfer processes involving $[\text{HC}_n\text{H}]^{2+}$ ($n = 2-4$) ions. Energies liberated in the respective $[\text{HC}_n\text{H}]^{2+} \rightarrow [\text{HC}_n\text{H}]^+$ and $[\text{HC}_n\text{H}]^+ + \text{H}$ processes are given by vertical lines. Charge exchange products are indicated at the bottom of the figure. Ionizations of the various target gases are represented by the respective photoelectron spectra taken from Refs 27-29.

ionization energies, although triplet states of these ions possess more than enough internal energy to ionize target molecules and drive dissociative reactions. We have determined appearance energies of reaction products from charge transfer channels (1) and (2) for each $[\text{C}_n\text{H}_2]^{2+}$ ($n = 2-8$) system. As shown in Table 2, appearance energies of products from the dissociative channels (2) are identical to those from non-dissociative channels (1) for five of the systems studied. However, appearance energies of dissociative products are displaced from those of the non-dissociative products by 3.8 eV and 2.6 eV in the

$[\text{C}_5\text{H}_2]^{2+}$ and $[\text{C}_7\text{H}_2]^{2+}$ reactions, respectively. These energy differences are evidence that a significant population of $[\text{C}_5\text{H}_2]^{2+}$ and $[\text{C}_7\text{H}_2]^{2+}$ reactant ions in our beam are in long-lived internally excited states several eV above their respective ground S_0 states. These facts are consistent with T- S_0 state energy separations shown in Figs 2 and 3 for odd- n $[\text{C}_n\text{H}_2]^{2+}$ ions.

EXPERIMENTAL

Single electron transfer reactions of doubly charged ions were measured using a Hitachi RMU-7L double focusing mass spectrometer of Nier-Johnson geometry. A schematic and full description of this instrument has been given previously.³³ Reactant doubly charged ions were produced in a controlled electron impact ion source, and an ion acceleration voltage of 3200 V was used in this investigation. The first-field-free region, between the ion accelerating plates and 45° electrostatic sector, contained variable width collimating slits and a separate pumping system. Single electron transfer reactions of focused fully accelerated doubly charged $[\text{C}_n\text{H}_2]^{2+}$ ions occurred in this first field-free region to form forward scattered singly charged $[\text{C}_n\text{H}_2]^+$ product ions. Pressures in the collision region were sufficiently low to ensure that products resulted from single bimolecular collisions. In the case of very exothermic product channels it is possible for product $[\text{C}_n\text{H}_2]^+$ ions to be formed with excess internal energy and promptly dissociate into $[\text{C}_n\text{H}]^+$ ions. We have monitored these dissociative reaction channels by scanning the electrostatic sector from $2E$ to E , following the approach of Ref. 13. The compound under investigation was used to provide the ion source gas for reactant ion formation as well as target gas in the first field-free region. The compounds used in individual reactions are given in Table 1. We

Figure 7. Energetics of single electron transfer processes involving $[\text{HC}_5\text{H}]^{2+}$, $[\text{HC}_6\text{H}]^{2+}$, $[\text{HC}_7\text{H}]^{2+}$ and $[\text{HC}_8\text{H}]^{2+}$ ions. Energies liberated in the respective $[\text{HC}_n\text{H}]^{2+} \rightarrow [\text{HC}_n\text{H}]^+$ and $[\text{HC}_n\text{H}]^+ + \text{H}$ processes are given by vertical lines. Charge exchange products for each reaction are indicated at the bottom of the vertical lines. Ionization energies³⁰ of target gases used in the present study are represented by the shaded areas.

did not examine the influence of a range of target gases on different reaction channels involving individual $[C_nH_2]^{2+}$ ions. The compounds used in this investigation were high commercial grade and normal mass spectra showed them to be free of impurities.

Acknowledgement

Acknowledgement is made to the CONOCO Corporation for a fellowship award to JRA and to the National Science Foundation for funds which aided in the purchase of the mass spectrometer system.

REFERENCES

1. J. H. Beynon, A. Mathias and A. E. Williams, *Org. Mass Spectrom.* **5**, 303 (1971).
2. H. Sakurai, A. Tatematsu and H. Nakata, *Bull. Chem. Soc. Jpn.* **49**, 2800 (1976).
3. B. P. Mathur, E. M. Burgess, D. E. Bostwick and T. F. Moran, *Org. Mass Spectrom.* **16**, 92 (1981).
4. B. E. Jones, L. E. Abbey, H. L. Chatham, A. W. Hanner, L. A. Teleshefsky, E. M. Burgess and T. F. Moran, *Org. Mass Spectrom.* **17**, 10 (1982).
5. J. R. Appling, B. E. Jones, L. E. Abbey, D. E. Bostwick and T. F. Moran, *Org. Mass Spectrom.* **18**, 282 (1983).
6. H. Sakurai, A. Tatematsu and H. Nakata, *Shitsuryo Bunseki* **23**, 291 (1975).
7. A. W. Hanner, L. E. Abbey, D. E. Bostwick, E. M. Burgess and T. F. Moran, *Org. Mass Spectrom.* **17**, 19 (1982).
8. B. P. Mathur, L. E. Abbey, E. M. Burgess and T. F. Moran, *Org. Mass Spectrom.* **15**, 312 (1980).
9. T. Ast and J. H. Beynon, *Org. Mass Spectrom.* **7**, 503 (1973).
10. L. A. Teleshefsky, D. E. Bostwick, L. E. Abbey, E. M. Burgess and T. F. Moran, *Org. Mass Spectrom.* **17**, 627 (1982).
11. L. A. Teleshefsky, B. E. Jones, L. E. Abbey, D. E. Bostwick, E. M. Burgess and T. F. Moran, *Org. Mass Spectrom.* **17**, 481 (1982).
12. M. Rabrenović, C. J. Proctor, T. Ast, C. G. Herbert, A. G. Brenton and J. H. Beynon, *J. Phys. Chem.* **87**, 3305 (1983).
13. M. Rabrenović and J. H. Beynon, *Int. J. Mass Spectrom. Ion Proc.* **54**, 87 (1983).
14. R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**, 1285 (1975); **97**, 1294 (1975); **97**, 1302 (1975); **97**, 1307 (1975).
15. M. J. S. Dewar, D. H. Lo and C. A. Ramsden, *J. Am. Chem. Soc.* **97**, 1311 (1975).
16. M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.* **99**, 7432 (1977).
17. W. C. Davidon, *Comput. J.* **10**, 406 (1968); R. Fletcher, *ibid.* **8**, 33 (1965); R. Fletcher and M. J. D. Powell, *ibid.* **6**, 163 (1963).
18. M. Cobb, T. F. Moran, R. F. Borkman and R. Childs, *J. Chem. Phys.* **72**, 4463 (1980).
19. I. N. Levine, *Quantum Chemistry, Vol. II: Molecular Spectroscopy*, p. 265, Allyn and Bacon, Boston, Massachusetts, (1970).
20. K. F. Freed, *Acc. Chem. Res.* **11**, 74 (1978).
21. M. S. Child, *Molecular Spectroscopy*, Vol. 2, p. 466, Specialist Periodical Reports, The Chemical Society, London (1974).
22. A. Chutjian, *J. Chem. Phys.* **51**, 5414 (1969).
23. J. M. Curtis and R. K. Boyd, *J. Chem. Phys.* **80**, 1150 (1984).
24. J. M. Curtis and R. K. Boyd, *J. Chem. Phys.* **81**, 2991 (1984).
25. G. Herzberg, *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules*, 2nd ed., Van Nostrand, Princeton, New Jersey (1950).
26. T. F. Moran, in *Electron-Molecule Interactions and Their Applications*, Vol. 2, ed. by L. G. Christophorou, Academic Press, New York (1984).
27. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo (1981).
28. H. Schmidt and A. Schweig, *Angew. Chem. Int. Ed.* **12**, 307 (1973).
29. A. D. Baker, D. Betteridge, N. R. Kemp and R. E. Kirby, *Anal. Chem.* **43**, 375 (1971).
30. R. D. Levin and S. G. Lias, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., NSRDS-NBS* **71** (1982).