Control of Energy Deposition by Impact Parameter in Polyatomic Ion Collisions

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Abstract: Variation of the impact energy (E) in conjunction with the laboratory angle (θ) at which scattered ions are observed allows control of internal energy deposition in ion–neutral collisions. This is shown by the relative abundances of products formed with a particular energy loss for $Ar^{+\cdot}/Ar$ collisions and, for molecular projectiles, by the extent and type of fragmentation which follows collision. The relative abundances of the major ions of nitromethane which survive kilovolt-energy collisions were measured at various values of $E\theta$. These spectra represent the stability of the various ions present in the mass spectrum with respect to their depletion via a number of inelastic channels. In a more direct experiment, the extent to which product ion formation may be controlled by $E\theta$ was determined for several of the collision-induced dissociations which occur for the molecular ions of nitromethane and methanol. The methodology of angle-resolved mass spectrometry is demonstrated to allow facile selection of the quantity $E\theta$; thus, the internal energy deposition in a kilovolt-energy ion–neutral collision may be controlled and its average value approximately defined. It is therefore possible to enhance reactions which occur along a particular channel or to select ions of a particular internal energy for further investigation.

Introduction

It has recently been shown that the extent to which translational energy is partitioned into internal energy during a kilovolt-energy ion–molecule collision correlates with the laboratory scattering angle (θ) of the projectile.[1] This observation forms a ready basis for approximate selection of ion internal energies, formerly a difficult task in mass spectrometry.[2,3] Applications of this capability to ion structure characterization[4] and to other aspects of ionic chemistry[5] are presented elsewhere. Here the correlation between ion internal energy and scattering angle is extended to include the effects of variation of the projectile translational energy (E). Specifically, an attempt is made to investigate whether the reduced scattering angle,[6] defined as $\tau = E\theta$, can be used as a more fundamental measure of internal energy deposition than θ alone under the conditions employed here (kilovolt energies, small scattering angles). To a good approximation, τ is a function solely of the impact parameter in atomic systems.[7,8]

Previous investigations on atomic collisions support the idea that energy deposition depends upon the impact parameter and hence upon the reduced scattering angle.[9] This paper extends this enquiry to polyatomic systems, although some atomic collision data were also taken in testing the methodology. Two types of systems were studied: (1) inelastic collisions for $Ar^{+\cdot}/Ar$ where the final states are electronically excited and (2) inelastic collisions for organic ions, where the final products are fragment ions produced by unimolecular dissociation of the electronically excited projectile ion generated in the collision.

Relative cross sections were measured for the above types of reactions for processes of different endothermicities (Q). Thus, the relative abundances of the $Ar^{+\cdot}$ product ions associated with channels of Q = 13 and 32 eV[10] were of interest. For the organic systems, comparisons of ion abundance associated with collision-induced dissociations (CID) of varying endothermicities were made.

In addition to these direct measurements of channels of different Q as a function of kinetic energy (E) and scattering angle (θ), an indirect measure of energy deposition was possible for the organic systems. In this latter type of experiment, relative abundances were recorded for those ions which remain intact following collision. This represents in effect a postcollision mass spectrum at particular E and θ values.[11] These experiments thus present the results of integration over a number of individual inelastic channels, including both CID and charge exchange. However, it is the residual reactant ion abundance rather than the product ion abundance which is recorded. The two types of measurement provide complementary information.

Experimental Section

The technique of angle-resolved mass spectrometry as practiced here employs a Hitachi Perkin-Elmer RMH-2 double-focusing mass spectrometer. This has been modified to allow angular selection of the products of collisions between ions and the target gas which is introduced into a collision chamber located at the focal point between the electrostatic and magnetic sectors.[11] Variation of both ion kinetic energy and scattering angle is readily accomplished and thus this experimental arrangement is well suited for measurements in which the quantity $E\theta$ is of interest. Ion kinetic energy was measured using a precision resistive divider network and a six-place differential voltmeter (Keithley 662) to an uncertainty of less than 1 part in 10^5. Angular resolution in the plane of analysis was ±0.1°. Resolution is calculated by convoluting the ion beam profile with the instrument geometry.[11] An electron ionizing energy of 70 eV and a total emission current of 1 mA were used. The gas pressure in the collision cell, measured by a capacitance manometer, was typically 10–15 mTorr. This pressure range was found to optimize the efficiency of collision-induced dissociations. Argon was employed as collision gas in all experiments.

Results and Discussion

Energy-loss spectra for $Ar^{+\cdot}$ scattered from an argon target are shown in Figure 1. Two types of processes are represented: first, elastic collisions, where there is no change in the internal energies of the collision partners; second, inelastic collisions, where part of the translational energy of the $Ar^{+\cdot}$ ion is partitioned into electronic excitation energy. It is this second type of collision that is of chemical interest, especially for comparison with the molecular systems which are discussed below. At constant values of $E\theta$ the energy-loss spectra (Figure 1) are similar, indicating that the extent of electronic excitation remains nearly constant, even though both E and θ are varied over a large range. At higher values of $E\theta$, more energetic collisions are being sampled and the abundance of elastically scattered ions decreases relative to those scattered inelastically. The deeply inelastic channel (Q = 32 eV) also increases relative to the process with smaller energy loss (Q = 13 eV). The data shown and the trends noted are representative of a larger data set which covers the energy 1010–8000 eV and a range of laboratory scattering angles from 0.15 to 1.3°. These phe-

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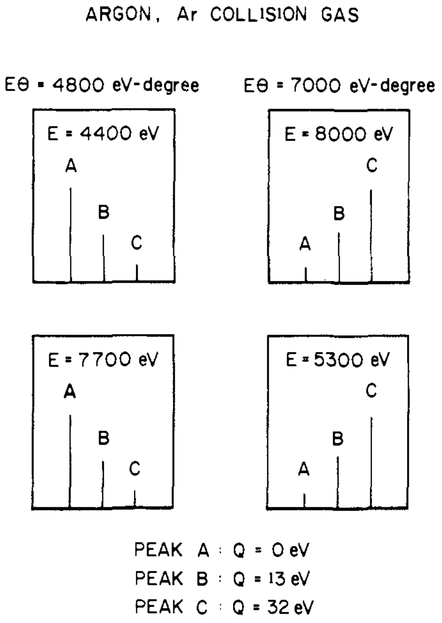

Figure 1. Relative abundance vs. energy loss for argon ions incident on an argon target for various values of $E\theta$.

nomena verify the control of $E\theta$ over energy deposition indicating that the reaction may be directed through selection of the impact parameter, that is, $E\theta$. This feature provides great flexibility in that either the kinetic energy or the scattering angle can be adjusted so as to maximize the occurrence of a reaction which occurs via a particular channel.

The results discussed thus far are analogous to those obtained for $Ar^{+\cdot}/Ar$ and other atomic systems in which absolute cross sections were determined.[12] They therefore constitute a validation of the experimental method and allow its application in testing the behavior of molecular systems. As is the case for the simpler systems, the effect of reduced scattering angle on final state distribution is of interest for polyatomic species.

Variation of the parameter $E\theta$ was found to produce striking effects which could be followed by recording mass spectra of residual reactant ions or by recording individual collision-induced dissociations. The mass spectra of residual reactant ions following collision with neutral species disclose information on the relative ability of these ions to survive kilovolt-energy collisions. Spectra of this type, for the major ions of nitromethane produced by electron impact upon nitromethane, are shown in Figure 2. The figure covers data for a range of impact parameters ($E\theta$ varies from 1000 to 5000 eV·deg) and demonstrates differential ion removal by fragmentation and charge exchange for collisions of varying strength. For example, the relatively unstable nitromethane molecular ion only survives the weak collisions which are sampled at low values of $E\theta$. Conversely, the most intense ion in each of these spectra is the stable closed shell nitroso ion, NO^+. The resonance-stabilized NO_2^+ ion is predictably more intense than CH_3^+ and $CH_3NO_2^{+\cdot}$. However, at the highest values of $E\theta$, all major ions of nitromethane decrease relative to NO^+.

In the third type of experiment the products of collision-induced dissociations of a polyatomic ion were monitored as a function of laboratory scattering angle and ion translational energy. The data found in Figure 3 represent the changes in relative importance of the three collision-induced dissociation reactions:

$$CH_3NO_2^{+\cdot} \rightarrow NO_2^+ + CH_3^\cdot \qquad (1)$$

$$CH_3NO_2^{+\cdot} \rightarrow NO^+ + CH_3O^\cdot \qquad (2)$$

$$NO_2^+ \rightarrow NO^+ + O \qquad (3)$$

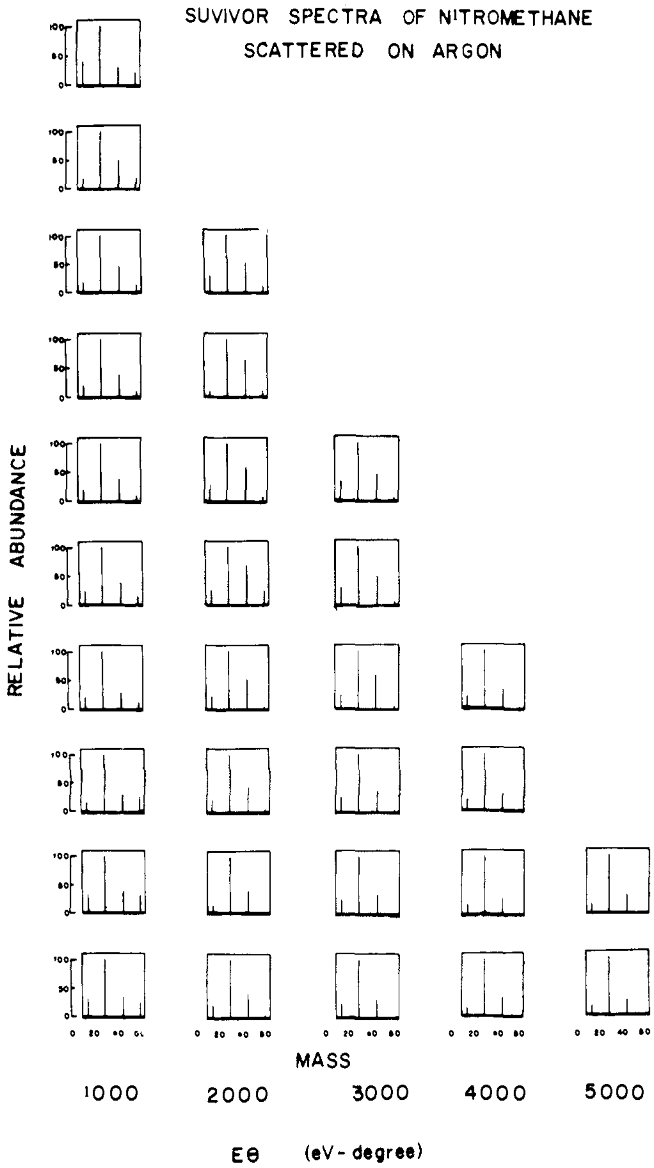

Figure 2. Spectra of ions from nitromethane which survive collision with an argon target at various values of $E\theta$. From low to high mass the ions are CH_3^+, NO^+, NO_2^+, and $CH_3NO_2^{+\cdot}$, respectively.

The least endothermic of these reactions (1) dominates at low values of $E\theta$, while at larger values of $E\theta$ sufficient energy is deposited in the nitromethane molecular ion so that the two-step dissociation (2) to the very stable NO^+ ion becomes the major pathway for fragmentation. An increase in the production of NO^+ from NO_2^+ is also observed as energy deposition (i.e., $E\theta$) is incremented.

A compact representation of the effects of varying internal energy upon the fragmentation behavior of a particular ion is available in the form of a breakdown curve. Plots of collision-induced fragment ion intensity vs. scattering angle can be used to display data similar to that contained in breakdown curves obtained by quasi-equilibrium theory calculations[13] or charge-exchange experiments.[14] These curves, in essence, show the mass spectrum of a molecule as a function of its internal energy.[15] Recent studies have demonstrated that variation of the scattering angle at constant ion energy provides curves which are related to breakdown curves.[5] The same results can be obtained by a systematic variation in both scattering angle and accelerating potential as shown for the molecular ion of nitromethane (Figure 4).

Data taken for values of $E\theta$ for E = 3.5 and 5.5 keV are superimposed onto the 7.5-keV data. The similarity existing

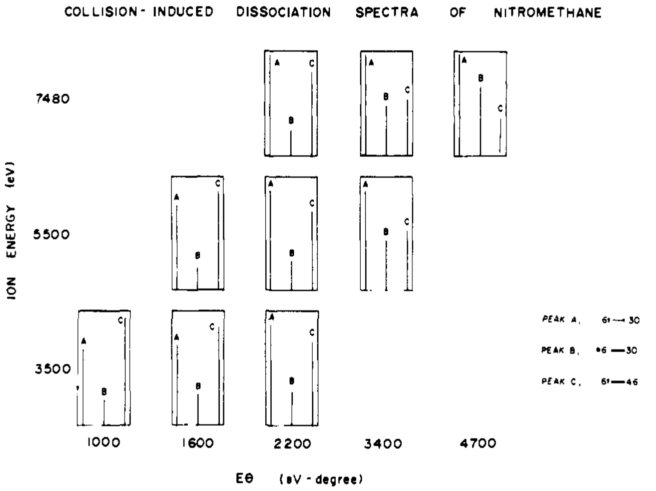

Figure 3. The relative abundance of selected collision-induced dissociation reactions of ions from nitromethane at various values of $E\theta$.

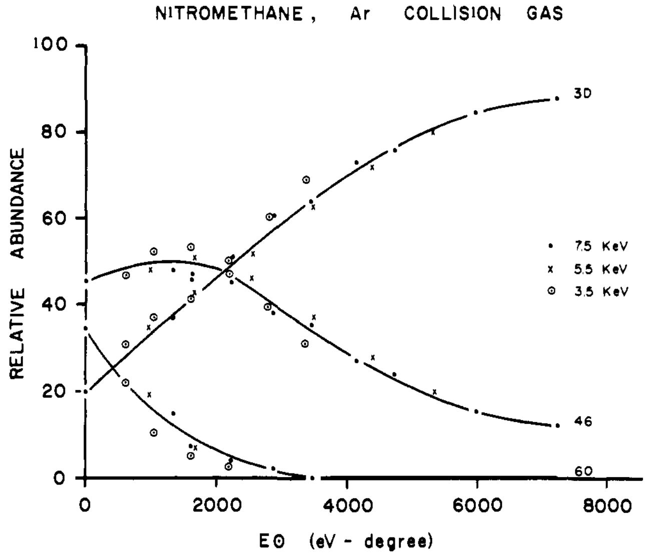

Figure 4. The normalized collision-induced dissociations of the nitromethane molecular ion plotted as a function of $E\theta$, by analogy with a breakdown curve.

between the three sets of data provides both a measure of the experimental error and further support for the hypothesis that energy deposition may be controlled by either E or θ but that the absolute amount of excitation is a function of the product $E\theta$. The internal energy deposition/scattering angle relationship has a form which depends upon the interaction potential for the collision pair.[9] For the systems and conditions used here, a screened coulomb potential applies and the internal energy deposition varies[17] as θ^2.

The control of $E\theta$ over energy deposition is further shown in data obtained for collision-induced dissociations of various ions of methanol. These dissociations and the apparent masses at which the products are observed are given in Table I. The relative abundances of these ions were measured for five sets of values of $E\theta$, each at a different accelerating potential (Figure 5). At constant $E\theta$ the spectra remain identical, but when $E\theta$ is increased the two-step (higher energy) dissociation ($32^+ \to 29^+$) increases in importance relative to the one-step dissociation ($32^+ \to 31^+$). These results provide further verification of the control of $E\theta$ over internal energy deposition.

Conclusion

It is evident from this study that high ion translational energies are not required to induce extensive fragmentation upon collision. Rather, the extent of fragmentation is dependent upon several variables, in particular on both the accelerating voltage and scattering angle. Thus the use of high accelerating voltages can be circumvented by sampling products at greater scattering angles.

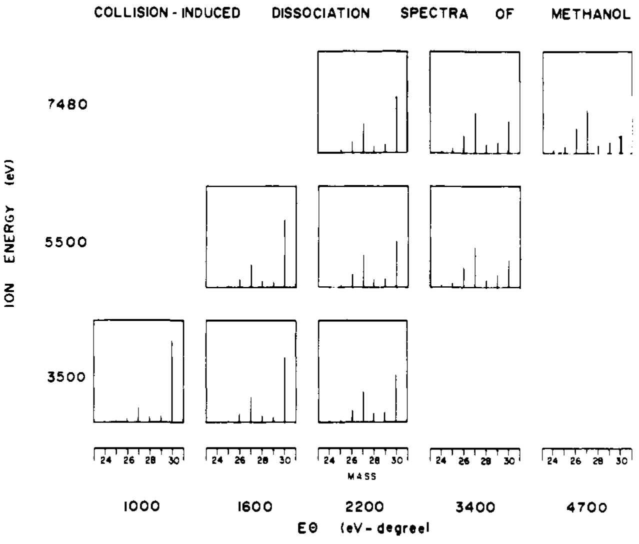

Figure 5. The relative abundance of selected collision-induced dissociation reactions of ions of methanol vs. mass at various values of $E\theta$. The reactions are listed in Table I.

Table I

reaction ($m_1^+ \to m_2^+$)	apparent mass, m^* ($m^* = m_2^2/m_1$)	reaction ($m_1^+ \to m_2^+$)	apparent mass, m^* ($m^* = m_2^2/m_1$)
$32^+ \to 31^+$	30.0	$32^+ \to 29^+$	26.3
$31^+ \to 30^+$	29.0		
$32^+ \to 30^+$	28.1	$31^+ \to 28^+$	25.3
$31^+ \to 29^+$	27.1	$32^+ \to 28^+$	24.5

As collisional activation becomes an increasingly important facet of analytical mass spectrometry,[16] the need to extend the concepts developed in atomic collision theory to molecular systems is evident. Control over energy deposition in polyatomic ion-neutral collisions, as demonstrated here, provides qualitative estimates of ionic stability and the energetics of collision-induced dissociations. More importantly, the ability to observe ion-molecule reaction products at a selected impact parameter should provide detailed insights into the phenomenon of collisional activation for molecular systems, just as it has done for atom-atom collisions.

It is important to recognize that, in spite of the simplifications made in developing segments of this paper, the correlation between impact parameter and scattering angle in atomic systems is not simply transferred to molecular systems. In the latter there are many impact parameters which, while of equal magnitude, are chemically dissimilar; that is, they represent scattering on different potential energy surfaces. As such they can lead to nonequivalent energy depositions and scattering angles. For example, consider an amino alcohol impacting upon an atomic target where either the N or the O terminus might closely approach the target. Even though the impact parameters for these collisions could be identical, the resulting excitations would be distinct, due, for example, to lone-pair excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. The consequence of these considerations is a blurring of the scattering angle/internal excitation relationship.

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References and Notes

(1) J. A. Laramée, P. H. Hemberger, and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.*, **33**, 231 (1980).
(2) E. Lindholm, *Adv. Chem. Ser.*, **No. 58**, 1 (1966).
(3) T. Baer, A. S. Werner, B. P. Tsai, and S. F. Lin, *J. Chem. Phys.*, **61**, 5468 (1974).
(4) D. M. Fedor and R. G. Cooks, *Anal. Chem.*, **52**, 679 (1980).
(5) J. A. Laramée, P. H. Hemberger, and R. G. Cooks, *J. Am. Chem. Soc.*, **101**, 6460 (1979).
(6) F. T. Smith, R. P. Marchi, and K. G. Dedrick, *Phys. Rev.*, **150**, 79 (1966).
(7) Chr. M. Lehmann and G. Liebfried, *Z. Phys.*, **172**, 465 (1962).
(8) F. T. Smith, R. P. Marchi, W. Aberth, D. C. Lorents, and O. Heinz, *Phys. Rev.*, **161**,31 (1967).
(9) (a) J. T. Park in "Collision Spectroscopy", R. G. Cooks, Ed., Plenum Press, New York, 1978; (b) M. S. Child, "Molecular Collision Theory", Academic Press, New York, 1974.
(10) M. Barat, J. Baudon, M. Abignoli, and J. C. Houver, *J. Phys. B*, **3**, 230 (1970).
(11) J. A. Laramée, J. J. Carmody, and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.*, **31**, 333 (1979).
(12) J. Baudon, M. Barat, and M. Abignoli, *J. Phys. B*, **3**, 207 (1970).
(13) M. Vestal and G. Lerner, "Fundamental Studies Relating to the Radiation Chemistry of Small Organic Molecules", Office of Aerospace Research, USAF, ARC67-01114, 1067.
(14) B. Andlauer and Ch. Ottinger, *J. Chem. Phys.*, **55**, 1471 (1971).
(15) K. Levsen, "Fundamental Aspects of Organic Mass Spectrometry", Verlag Chemie, New York, 1978.
(16) (a) F. W. McLafferty, "High Performance Mass Spectrometry: Chemical Applications", ACS Symposium Series 70, American Chemical Society, Washington, D.C.; (b) K. Levsen and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, **15**, 509 (1976); (c) T. L. Kruger, J. F. Litton, R. W. Kondrat, and R. G. Cooks, *Anal. Chem.*, **48**, 2113 (1976).
(17) P. H. Hemberger, A. R. Hubik, J. A. Laramée, and R. G. Cooks, in preparation.

Effect of the Methyl Group Rotation on the Rate of Intramolecular Proton Exchange in α-Methyl-β-hydroxyacrolein

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Abstract: Ab initio SCF calculations were used to determine the potential-energy profile for the intramolecular proton exchange in α-methyl-β-hydroxyacrolein for various orientations of the methyl group. The proton transfer was found to occur only when the methyl group orientation causes the transfer profile to be symmetric. Thus rotation and transfer were seen to be strongly coupled, in agreement with experimental evidence. An analytical two-dimensional potential representing the coupled motion was fitted to the SCF energies obtained. From the eigenstates of the potential the splitting of the two nondegenerate A levels and that of the lowest degenerate E levels were calculated and found in reasonable agreement with those estimated from experimental data.

Introduction

A mechanism involving tunnelling has been suggested to explain the very large value of the rate constant for the acid-base neutralization reaction in condensed phases of water and methyl alcohol.[1,2] The tunnelling occurs when the proton moves from the donor to the acceptor site in a double minimum potential energy profile. Theoretical studies of the motion of the proton in this potential[3-5] indicate that in symmetric profiles the rate of proton exchange is several orders of magnitude larger than that predicted from the semiclassical WKB approach which can be successfully used in asymmetric profiles and unbonded systems. Even though the calculated results in the cases of ice, liquid water, and methyl alcohol[5] were consistent with the accepted experimental values, questions remain on the applicability of the calculation to condensed phases.

Interpretation of the microwave spectrum of the molecule of β-hydroxyacrolein[6] suggests the existence of a long-amplitude nonharmonic oscillation due to the intramolecular hydrogen bonded proton exchange. In this case, the interaction between the proton exchange and the surrounding molecules is reduced to a minimum.

Experimentally[7] and theoretically[8,9] the geometry of minimum energy for the molecule corresponds to the asymmetric conformation with the proton covalently bound to either one of the oxygens. The energy for the geometrically optimized symmetric intermediate is calculated to be 11.6 kcal/mol above the minima.[9] The reaction coordinate for the interconversion of the two equivalent minimum energy conformations is a symmetric double minimum energy potential. Theoretical calculations for the proton exchange in this case[9] resulted in a tunnelling frequency that was within the range of values deduced from the interpretation of the microwave spectrum.

Substituted β-hydroxyacrolein molecules may provide an opportunity to study the role of the symmetry of the profile in proton-exchange mechanisms. α-Methyl-β-hydroxyacrolein is the simplest of these substituted molecules for which reliable theoretical calculations are feasible.

In this molecule, the double-minimum potential for the proton exchange will be symmetric only when one of the C–H bonds of the methyl group is in a plane that is perpendicular to the plane containing all the carbon and oxygen atoms of the molecule. Departure from this geometry by rotation of the methyl group will result in an asymmetric double minimum profile. This asymmetry may reduce or completely eliminate tunnelling. As a result tunnelling will only occur at selected conformations of the methyl group, in which case a very strong coupling between the two motions will result. This coupling has been suggested by Sanders[10,11] from a study of the microwave spectrum of the molecule.

Calculations

Ab initio, self-consistent-field calculations with an extended basis set known as 4-31G[12,13] were performed to determine the energy of the five significant geometries of the molecule of α-methyl-β-hydroxyacrolein. These five geometries are represented by structures I–V in Figures 1 and 2. For each of the five geometries the bond lengths and the bond angles were varied until the minimum energy was achieved. These bond lengths and angles are shown in Tables I and II. The numbers

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