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Probing Chemical Reactions in Momentum Space

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Abstract: A momentum space investigation of some reaction paths including C_{2v} dissociation of water as well as isomerization of HCN and CH_3CN, respectively, to HNC and CH_3NC is attempted. The tool for such an investigation is provided by the distinctive topography [Kulkarni, S. A.; Gadre, S. R.; Pathak, R. K. *Phys. Rev. A*, **1992**, *45*, 4399–4406] of molecular electron momentum densities (EMDs). The EMD as well as its Laplacian at $\vec{p} = \vec{0}$ are seen to follow the path of the reaction. The EMD topographies of reactants and products being different in the present case, a *transition region* instead of *transition state*, is observed in the momentum space perspective of these reactions. The most important conjecture (pending more exhaustive investigations) emanating from our study is that the information around $\vec{p} = \vec{0}$ serves as a criterion for following a chemical reaction in momentum space.

I. Introduction

Chemistry is a subject dealing with molecular structure and reactivity. Along a typical reaction path there exist numerous molecular structures that may be utilized for monitoring the progress of the reaction under study. Conventional methods employ gross quantities such as the total electronic energy for such an investigation. In this approach, one encounters concepts such as transition state, energy of activation, etc. Yet another powerful way for investigating chemical reactions is offered by the topographical analysis of the electron density, $\rho(\vec{r})$ along the reaction path as advocated by Bader et al.[1,2] In their methodology, critical points of the electron density are isolated and characterized for various molecular structures, and a systematic search for instabilities in these structures is then carried out. Such an analysis has been reported by Bader and co-workers[2,3] for some isomerization- and dissociation-type reactions. In particular, Bader et al.[2] have reported an investigation of $\rho(\vec{r})$ topography along a C_{2v} dissociative path of the water molecule. Catastrophes (instabilities) of two kinds (viz. fold and conflict) were observed by them for this case. For instance,[4] they noticed that the coalescence of a bond critical point (CP) of type (3, −1) with a ring CP of type (3, +1) gives rise to a fold-type catastrophe. This establishes a clearcut connection between the change of molecular structure and the observed catastrophe points. However, it may be noted that the electronic energies along the C_{2v} dissociative path chosen by them[2] are monotonic increasing indicating the absence of a transition state. On the other hand, isomerization reactions offer an example wherein one encounters a transition state from the energetic point of view. One of the extensively studied isomerization reactions viz., HCN → HNC, has been investigated by Pearson et al.[5] Here, the parameters R_{CN}, R_{MH}, and θ are employed to follow the reaction, where the former is the CN bond length, R_{MH} denotes the distance of the hydrogen atom from the CN center of mass (M), and θ stands for the angle between CN and MH vectors. Energetically, this reaction (for SCF calculations) shows a transition state at $\theta = 70.2°$. The use of topographical analysis[3] of electron densities for this reaction path brings out a singularity in the molecular structure within the range of $\theta = 72.1–72.4°$. The catastrophe observed on this reaction path has been classified as a conflict-type[3] one. Similar analysis has also been carried out for yet another isomerization reaction viz., $CH_3CN \rightarrow CH_3NC$ (firstly reported by Liskow et al.[6]), exhibiting a transition state at $\theta = 79.2°$. However, the instability in the molecular structure observed through the topography of electron density[3] was found in the vicinity of $\theta = 84°$. In summary, the instabilities in the molecular graph formed by electron densities indeed occur in the vicinity of the actual transition state on the reaction path. As a consequence, the positional electron density has been found to be a valuable tool for following the progress of a reaction.

Analogous to its $\vec{r}$-space definition, the electron density in the complementary space, viz., the electron momentum density (EMD), is defined as

$$\gamma(\vec{p}) = N \int |\phi(\vec{p},\vec{p}_2,\vec{p}_3 \dots \vec{p}_N)|^2 \, d\vec{p}_2 \dots d\vec{p}_N \qquad (1)$$

where $\phi(\vec{p},\vec{p}_2,\vec{p}_3 \dots \vec{p}_N)$ is a 3N-dimensional Fourier–Dirac transform of the N-electron wavefunction in position space given by

$$\phi(\vec{p}_1,\vec{p}_2, \dots \vec{p}_N) = (2\pi)^{-3N/2} \int \psi(\vec{r}_1,\vec{r}_2 \dots \vec{r}_N) \, e^{-i\sum_{j=1}^{N} \vec{p}_j\cdot\vec{r}_j} \, d\vec{r}_1 \, d\vec{r}_2 \dots d\vec{r}_N$$

(In eq 1 summation over electron spins is implicit.) The EMD has been[7] a subject of experimental and theoretical studies for the past several decades. The EMD is experimentally accessible[7,8] via the X-ray/γ-ray Compton scattering, positron annihilation as well as (e, 2e) techniques, followed by the reconstruction of three-dimensional EMD from this data. On the theoretical side, pioneering contributions to the studies of atomic and molecular

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(2) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *J. Chem. Phys.* **1979**, *70*, 4316–4329.

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(4) The critical points (CP) $\vec{p}$ of a three-dimensional scalar field are defined as those where $\vec{\nabla} f|\vec{p} = 0$. The nondegenerate CPs in the three-dimensional case are (3, +3) a minimum, (3, −3) a maximum, and (3, −1) as well as (3, +1) saddles. A classification of the CPs is given in terms of the eigenvalues λ_1, λ_2, λ_3 of the corresponding Hessian matrix $H_{ij} = \partial^2 f/\partial x_i \partial x_j|\vec{p}$. Here, the notation (r, σ) stands for the rank, r, and signature (excess of positive eigenvalues over the negative ones), σ. For a lucid introduction to topographical concepts, see: Stewart, I. *Sci. Am.* **1991**, *264*(*6*), 89–90 and for details of applications to atomic and molecular systems, see refs 1–3.

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EMDs were made in the 1930s and 1940s by Coulson and co-workers.[9] Among more recent investigations, those by Epstein,[10] Smith and co-workers,[11] and Tanner[12] are particularly noteworthy. However, unlike its positional counterpart, detailed topographical analyses of molecular EMDs have been conspicuous by their absence from the literature. Sagar et al.[11] have used the Laplacian of EMD for the analysis for atoms. More recently, MacDougall[14] has conjectured that the concentrations of EMD, i.e., $\nabla^2\gamma(\vec{p})$ could be employed for an understanding of high T_c superconductors. However, a first ever attempt to investigate the symmetry and topographical aspects of *molecular EMDs* has recently been made by Kulkarni et al.[13]

The highlight of the aforementioned study of Kulkarni et al.[13] is that the origin in the momentum space, viz., $\vec{p} = \vec{0}$, is necessarily a critical point, independent of the choice of the molecule as well as the nuclear coordinates. The information around $\vec{p} = \vec{0}$ is of immense chemical interest, since it pertains to the "valence region" due to the reciprocity[10] between the position and momentum space wave functions. These studies[13] further unravel a typical hierarchical structure in the EMD topography (that is governed solely by the criticality at $\vec{p} = \vec{0}$), which goes as follows: The existence of a minimum at $\vec{p} = \vec{0}$ allows exclusively CPs of (3, +1), (3, −1), and (3, −3)-types away from the origin. Similarly, if the EMD topology exhibits a (3, +1) saddle at the origin, CPs of the type (3, −1) and (3, −3) could at most be found at $\vec{p} \neq \vec{0}$; whereas for a (3, −1) at $\vec{p} = \vec{0}$, EMD topology show (3, −3) CPs elsewhere. Finally, a (3, −3) CP at $\vec{p} = \vec{0}$ is exclusive, i.e., it rules out the existence of any other CP in the entire EMD topology. Also, the type of criticality observed at $\vec{p} = \vec{0}$ is *never seen* elsewhere in the EMD topology.[13] Further, the eigenvalues[4] (λ_1,λ_2,λ_3) of the Hessian at $\vec{p} = \vec{0}$ have been employed[13] for defining and quantifying anisotropies in molecular EMDs.

In this light, the following questions are imminent: (i) Could a reaction be probed in the momentum space? (ii) What are the tools for such an investigation? (iii) Could the distinctive EMD topography be utilized for this purpose?

In the next section, we attempt an answer to these questions with a reference to the test cases of isomerization- and dissociation-type reactions discussed above.

II. Momentum Space Picture of Chemical Reactions

In this section, three case studies are taken up: C_{2v} dissociation of water as well as isomerization of HCN and CH_3CN. For this purpose, keeping in view the hierarchical structure of EMD (cf. section I) we employ the topography of EMD at $\vec{p} = \vec{0}$ as an investigative tool. The molecular wave functions for different geometries on the reaction path are generated at the restricted Hartree–Fock level by using program INDMOL,[15] and molecules are assumed to be nonvibrating.

II.1. C_{2v} Dissociation of H_2O. A minimum energy C_{2v} dissociative path of H_2O separating it to $O(^1D)$ and $H_2(^1\Sigma_g^+)$ has been extensively studied by Gangi and Bader.[16] This reaction path has also been studied by Bader et al.[2] using the topography of charge density. Here, we investigate the EMD topography for this reaction using the geometrical parameters reported by them[2] and employ a tz2p basis set (tz2p basis sets for H and O are contracted as [5s, 2p/3s, 2p] and [9s, 5p, 2d/5s, 3p, 2d], respectively). The geometrical as well as topographical parameters and the corresponding energies are presented in Table I. The intermediate geometries are obtained by linear interpolation. For the water molecule in its equilibrium geometry, the oxygen is at the origin with $C_2(y)$ axis passing through it and the hydrogens are in the y–z plane. It can be seen from Table I that water in its equilibrium geometry exhibits a minimum at $\vec{p} = \vec{0}$. This typical feature of criticality is retained until the two hydrogens are brought close to each other and ultimately separated from the oxygen atom (see the fifth and sixth row of Table I). A representative plot illustrating the reactant topography is presented in Figure 1, which corresponds to $R_H = 2.1$ and $R_{MO} = 2.39$ (where R_H is the distance between two hydrogen atoms and R_{MO} is the distance of oxygen from midpoint (M) of the H–H bond). Since this plot corresponds to a cross-section of a three-dimensional scalar field onto a two-dimensional one, we chose the p_x–p_z plane to monitor the change in topography. A first changeover in the critical structure of EMD (exhibiting (3, +1) CP at $\vec{p} = \vec{0}$) takes place in the region of $1.99 > R_H > 1.98$ and $2.525 > R_{MO} > 2.5125$. This criticality is retained over a small finite region and *not observed just at a point* on the reaction path. This change in topography from a minimum to a saddle in p_x–p_z plane is displayed in Figure 2 for $R_H = 1.92$ and $R_{MO} = 2.6$. Yet another change over in the nature of CP at $\vec{p} = \vec{0}$ (from 3, +1) to (3, −1) CP) is observed when $1.92 > R_H > 1.9$ and $2.625 > R_{MO} > 2.6$ (cf. Table I). This can be clearly seen from the Figure 3 which shows a planar maximum at $\vec{p} = \vec{0}$ with $R_H = 1.8$ and $R_{MO} = 2.75$. Thereafter, the nature of criticality at $\vec{p} = \vec{0}$ is retained until the dissociation of water.

Table I. Geometrical Parameters[a] on the C_{2v} Dissociative Path of Water Along with the Eigenvalues of the Hessian and EMD Value at $\vec{p} = \vec{0}$ Using tz2p Basis Set[c]

			eigenvalues at $\vec{p} = \vec{0}$				
R_H	R_{MO}	energy	λ_1	λ_2	λ_3	$\nabla^2\gamma(\vec{0})$[b]	$\gamma(\vec{0})$
2.88	1.11	−76.057	2.61	2.71	2.62	7.94	0.564
2.16	2.30	−75.872	0.72	4.25	2.04	7.01	0.856
2.10	2.39	−75.859	0.42	4.14	1.44	6.00	0.904
2.00	2.50	−74.848	0.07	3.84	0.69	4.60	0.960
1.99	2.5125	−75.847	0.03	3.80	0.61	4.44	0.967
1.98	2.525	−75.846	−0.01	3.76	0.53	4.28	0.973
1.92	2.6	−75.841	−0.25	3.49	0.07	3.31	1.010
1.90	2.625	−75.839	−0.32	3.34	−0.08	2.94	1.022
1.80	2.75	−75.834	−0.67	2.85	−0.72	1.46	1.078

[a] R_H corresponds to the distance between two hydrogen atoms, whereas R_{MO} is the distance from the midpoint of H–H bond to the oxygen nucleus. [b] The $\nabla^2\gamma(\vec{0})$ stands for $\nabla^2\gamma(\vec{p})|_{\vec{p}=\vec{0}}$. [c] All values are in au.

The most remarkable feature exhibited by the EMD in the course of this reaction is that its value at the origin, viz., $\gamma(\vec{0})$, is monotonic increasing and so is the total electronic energy of the structures on this reaction path. The Laplacian of any function conveys regions of concentration and depletions in the function. A higher positive-valued Laplacian of EMD at $\vec{p} = \vec{0}$ implies that there exists more charge in the valence region of wave function (in accordance with the Fourier transform relation) and such wave functions are known to be of better quality for the analysis of properties which critically depend on the long range spatial distribution of charge, e.g., dipole and quadrupole moments.[17,18] From another viewpoint,[19] such wave functions correspond to higher exterior electron density (density beyond the van der Waals'

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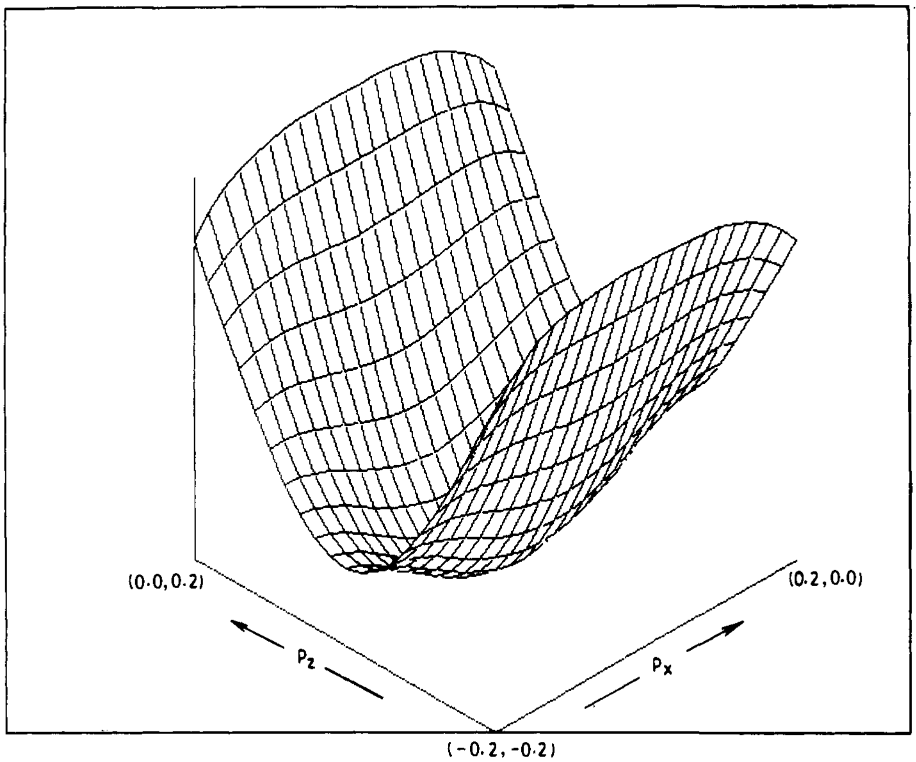

Figure 1. A three-dimensional grid plot of the EMD of H_2O molecule representing the topography of reactant, viz., a planar minimum in the p_x–p_z plane. See text (Section II.1) for details.

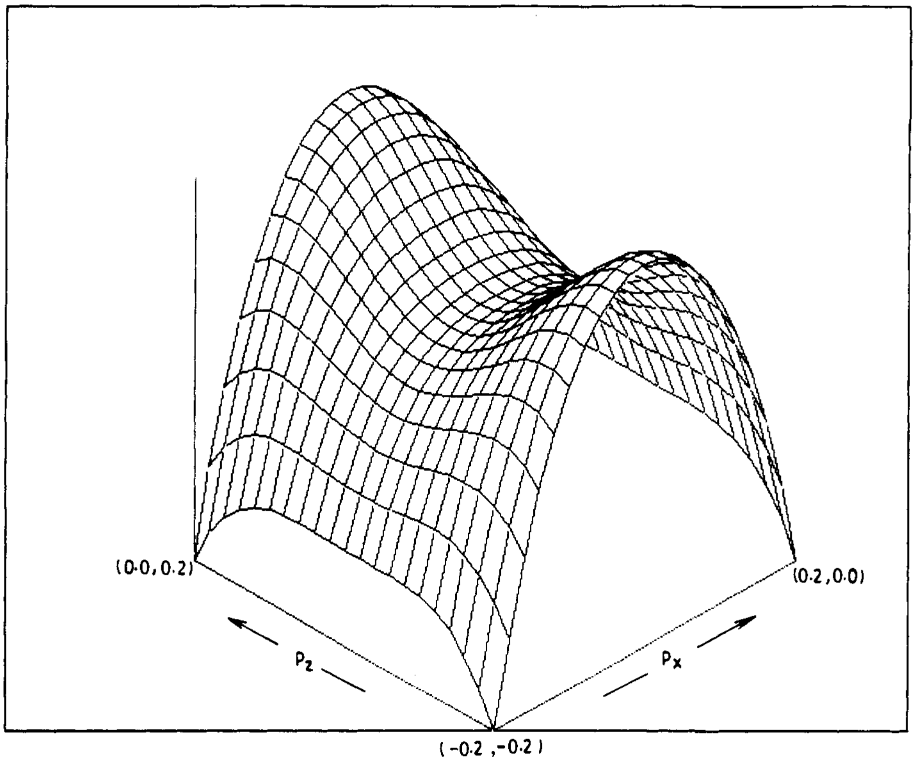

Figure 2. A three-dimensional grid plot of the EMD of H_2O molecule representing the topography of transition region, viz., a planar saddle in the p_x–p_z plane. See text (section II.1) for details.

surface) and hence are of better quality. This fact has been harnessed in an earlier study[13] using the Laplacian of EMD at the origin as an indicator of quality of the coordinate space wave function. Thus, extending the aforementioned facts, one may infer that a molecular structure is relatively stable if it has high positive Laplacian of EMD at $\vec{p} = \vec{0}$. In this study, we employ the Laplacian of the EMD as yet another parameter which can follow the reaction path and indicates the stability of structure. From Table I it is clear that the ground-state configuration of water has highest positive Laplacian and thereafter decreases monotonically, i.e., it is also seen to follow the reaction path.

In order to investigate the effect of basis set on EMD topography, similar work for this dissociation reaction is carried out using a double-ζ polarized (dzp) basis set. Here also, the parameters, viz., $\gamma(\vec{0})$ and $\nabla^2\gamma(\vec{0})$, show a similar trend to the one exhibited by the water molecule using tz2p basis. For all the

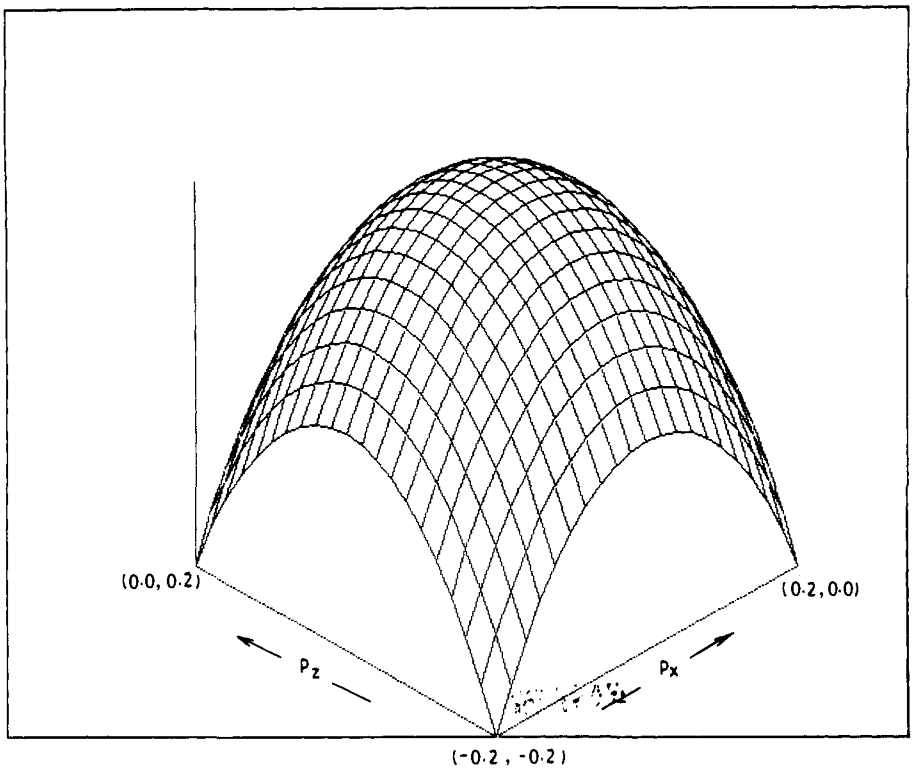

Figure 3. A three-dimensional grid plot of the EMD of H_2O molecule representing the topography of product region, viz., a planar maximum in the p_x–p_z plane. See text (section II.1) for details.

molecular structures studied, it should be noted that *the actual regions* on the reaction path spanned by both the basis sets, viz., tz2p and dzp for (3, +3), (3, +1), (3, −1) criticalities at $\vec{p} = \vec{0}$, are different. However, the general qualitative features of the topography are unaltered due to the change in basis set.[20]

Bawagan et al.[21] have suggested the use of correlated wave function for the analysis of orbital EMDs of valence orbitals. In this light, the effect of inclusion of correlation on EMD topography is also investigated for some representative molecules, viz., H_2O and HF in their equilibrium geometries. We have employed the natural orbitals[22] obtained from full CI calculations with 6-31G basis for this purpose. The eigenvalues of CP at $\vec{p} = \vec{0}$ for H_2O and HF are 1.08, 2.62, 1.86 and 0.38, 0.38, 1.23, respectively, whereas the corresponding SCF eigenvalues are 1.10, 2.62, 1.87 and 0.90, 0.90, 2.52. Thus, inclusion of correlation has no major effect on the *qualitative nature of EMD* topography. This conclusion is in agreement with the consensus reached in the literature regarding the accuracy of HF electron density, being yet another one-electron property.

II.2. Isomerization of HCN to HNC. For monitoring this reaction path, we have used the geometrical parameters reported by Pearson et al.[5] with triple-ζ polarized (tzp) basis set. In this reaction, the angle θ between the C–N and M–H vectors is used as a parameter. Intermediate geometries are obtained by fixing a θ and optimizing the R_{C-N} and R_{M-H} values. In order to follow this reaction, we treat HCN as a "reactant", whereas HNC is treated as a "product". For the ground-state HCN, the EMD shows (3, +1) type criticality at the origin. This nature of CP at $\vec{p} = \vec{0}$ is retained until 0 ~ 49° (cf. Table II). In a very narrow region of 49.21° > θ > 48.75°, the EMD topography switches over to a (3, −1) critical structure at $\vec{p} = \vec{0}$. Beyond θ = 49.21°, the EMD topology shows a *maximum* at $\vec{p} = \vec{0}$. The isomerized product of HCN, i.e., the HNC molecule, also shows a maximum at $\vec{p} = \vec{0}$. Thus, similar to the reaction path of dissociation of water, the intermediate criticality (i.e., the criticality of type different from reactant and product) is observed over a very narrow region on the potential energy surface as viewed in the momentum space. The reaction path is divided into three distinct regions: a region of isomerization with θ < 48.75° over which all molecular structures exhibit criticality at $\vec{p} = \vec{0}$ as that of ground-state HCN (i.e., (3, +1) CP). The molecular structures in yet another region with θ > 49.21° are seen to have a (3, −3) CP at $\vec{p} = \vec{0}$ corresponding to the product region. A critical examination of $\gamma(\vec{0})$ as well as $\nabla^2\gamma(\vec{0})$ values reveals that the $\gamma(\vec{0})$ is maximal at θ = 72.4° where $\nabla^2\gamma(\vec{0})$ is highly negative, though not maximally negative (cf. Table II). It is also known that[3] the topography of electron density shows instability in its structure in the range of 72.4° > θ > 72.1°. Thus, analogous to the C_{2v} dissociative path of water, $\gamma(\vec{0})$ and $\nabla^2\gamma(\vec{0})$ could be employed, as parameters for following the reaction path, for the present case as well.

Table II. Geometrical[a] as Well as Topographical Parameters in the Isomerization Reaction of HCN to HNC Using tzp Basis Set[c]

				eigenvalues[b] at $\vec{p} = \vec{0}$				
R_{C-N}	R_{M-H}	θ	energy	λ_1	λ_2	λ_3	$\nabla^2\gamma(\vec{0})$	$\gamma(\vec{0})$
2.148	3.164	0.0	−92.8995	−5.328	2.976	2.976	0.624	1.538
2.161	2.966	30.0	−92.8726	−8.869	2.256	1.926	−4.687	1.642
2.1850	2.678	48.75	−92.8391	−8.754	0.055	0.032	−8.667	1.809
2.1853	2.677	48.98	−92.8388	−8.778	0.014	−0.015	−8.779	1.813
2.1856	2.673	49.21	−92.8383	−8.801	−0.025	−0.031	−8.857	1.815
2.201	2.474	60.00	−92.8240	−9.651	−1.908	−1.332	−12.891	1.915
2.218	2.272	70.20	−92.8190	−9.821	−3.44	−2.099	−15.360	1.966
2.210	2.238	72.10	−92.8194	−9.761	−3.762	−2.250	−15.773	1.970
2.198	2.235	72.40	−92.8195	−9.740	−3.913	−2.364	−16.017	1.973
2.236	2.029	90.00	−92.8302	−9.331	−4.912	−2.204	−16.447	1.964
2.248	2.281	120.00	−92.8521	−10.122	−4.162	−1.378	−15.662	1.941
2.217	2.705	150.00	−92.8733	−9.597	−1.975	−1.014	−12.586	1.846
2.189	2.874	180.00	−92.8833	−8.460	−1.171	−1.171	−10.802	1.780

[a] R_{CN} is the C–N bond length; R_{M-H} is the distance of hydrogen from center of mass of C–N bond and θ is the angle in degrees between the C–N and M–H vectors. [b] Eigenvalues of the Hessian matrix at $\vec{p} = \vec{0}$. Note that $\nabla^2\gamma(\vec{0})$ stands for $\nabla^2\gamma(\vec{p})|_{\vec{p}=\vec{0}}$. [c] All values are in au.

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Table III. Geometrical[a] and Topographical Parameters in the Isomerization Reaction of CH_3CN to CH_3NC Using dz Basis Set[b]

		eigenvalues[c] at $\vec{p} = \vec{0}$				
θ	energy	λ_1	λ_2	λ_3	$\nabla^2\gamma(\vec{0})$	$\gamma(\vec{0})$
0.0	−131.8671	6.097	6.097	3.301	15.495	2.023
29.1	−131.7771	4.432	−1.245	3.738	6.925	2.085
39.2	−131.7751	3.485	−2.597	3.842	4.730	2.192
49.2	−131.7658	1.375	−4.203	3.645	0.817	2.315
59.2	−131.7549	−1.275	−6.026	3.177	−4.124	2.436
69.2	−131.7474	−3.645	−7.843	2.606	−8.882	2.541
79.2	−131.7450	−5.299	−9.203	2.096	−12.406	2.617
89.2	−131.7473	−5.946	−10.003	1.694	−14.255	2.664
99.2	−131.7530	−5.478	−10.394	1.347	−14.525	2.686
109.2	−131.7612	−4.207	−10.327	0.987	−13.547	2.685
119.2	−131.7714	−2.562	−9.752	0.561	−11.753	2.662
129.2	−131.7827	−0.947	−8.758	0.049	−9.656	2.619
180.0	−131.8410	−0.115	−0.115	−0.688	−0.918	2.412

[a] θ is the angle in degrees between C–N and C–M vectors where M is a center of mass of C–N bond. [b] Dz-basis is due to Snyder and Basch.[22] [c] Eigenvalues of the Hessian matrix at $\vec{p} = \vec{0}$. Note that $\nabla^2\gamma(\vec{0})$ stands for $\nabla\gamma(\vec{p})|\vec{p}=\vec{0}$. [d] All values are in au.

II.3. Isomerization of CH_3CN to CH_3NC. The last reaction considered in the present work for topographical analysis of EMD is yet another isomerization reaction: CH_3CN to CH_3NC. The geometrical parameters used for this reaction are those reported by Liskow et al.[6] using the double-ζ basis set due to Snyder and Basch.[23] It can be seen from Table III that ground-state CH_3CN has a minimum at $\vec{p} = \vec{0}$ in its EMD topology. On the other hand, the product of isomerization shows a maximum at the origin. Thus, in a passage from reactant to product, smooth transitions at various θ values are expected for criticality at $\vec{p} = \vec{0}$. First transition from (3, +3) to (3, +1) CP at $\vec{p} = \vec{0}$, occurs in the range of θ = 0 to 29.2°. The changed critical structure is retained over the range of 29.2° < θ < 59.2°. A critical structure of (3, −1) type is observed over a large region beyond 59.2°, even up to 129.2°. Thereafter, finally it attains a (3, −3) criticality at $\vec{p} = \vec{0}$ for ground-state CH_3NC. We have, however, not located the precise θ values for which these changes happen. If one monitors the reaction path via $\gamma(\vec{0})$ values, it shows a maximum around 99.2°. Similarly, the analysis of $\nabla^2\gamma(\vec{0})$ shows that it is maximally negative at θ = 99.2°. Thus in this reaction, both $\gamma(\vec{0})$ and $\nabla^2\gamma(\vec{0})$ show θ = 99.2° as the most unstable structure as viewed in the momentum space, which is beyond the actual transition state, in traversing from CH_3CN to CH_3NC.

III. Concluding Remarks

The distinctive topography of molecular EMDs culminating into the hierarchical structure[13] discussed in the Introduction has prompted us to embark upon a systematic investigation of reactions in momentum space. In the present study, the reaction pathways of C_{2v} dissociation of H_2O as well as isomerization of HCN and CH_3CN have been investigated in the momentum space. For this purpose, the value of EMD at $\vec{p} = \vec{0}$ as well as the corresponding eigenvalues of the Hessian matrix (and its trace, viz. $\nabla^2\gamma(\vec{0})$) have been employed. It has been observed that $\gamma(\vec{0})$ as well as $\nabla^2\gamma(\vec{0})$ exhibit a transition-state type behavior whenever the electronic energy shows a transition state. This is an interesting feature needing further detailed investigations before a generalization is made. The essential qualitative features of EMD topography are further observed to be independent of the choice of basis set (beyond dz quality) and inclusion of correlation.

For the reactions under study, the topographies at $\vec{p} = \vec{0}$ of the reactants and the corresponding product turned out to be of different type. In between these two extreme topographies, there exist smooth transitions naturally engendering fold-type catastrophes. These intermediate regions could be viewed as transition regions in $\vec{p}$-space. These regions for H_2O (on C_{2v} dissociative path) and HCN (on its isomerization path) were observed to be rather narrow. However, in the case of the methyl cyanide isomerization, the transition regions are more spread out. Here again, more case studies are warranted before carrying out appropriate generalizations. Thus, the answers to the questions (i) and (iii) posed in section I, regarding the feasibility of momentum space exploration of chemical reactions, appear to be in the affirmative.

The noteworthy feature of the present work is that the information around $\vec{p} = \vec{0}$ seems to be adequate for a momentum space analysis of a chemical reaction. This information could be in the form of $\gamma(\vec{0})$ or the entire set of eigenvalues at $\vec{p} = \vec{0}$ offering a probable answer to question (ii) in section I. The information around $\vec{p} = \vec{0}$ indeed refers to the "valence region" which is of supreme importance for understanding chemical reactions. For a corresponding study in position space, a search for various bond-, ring-, and cage-type critical points has to be carried out in three dimensions. On the other hand, in the momentum space, the information around a **single point** ($\vec{p} = \vec{0}$) could be used as a practical tool for probing chemical reactions. However, it may also be pointed out that the information at the origin though necessarily indispensible might not always prove to be sufficient for such an analysis. In view of this fact coupled with the aforementioned hierarchical structure, investigations on the EMD away from the origin are indeed worthwhile along a reaction path. Moreover, a detailed investigation incorporating correlation as well as vibrational effects to simulate a more realistic experimental situation needs to be conducted in the future.

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