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Solvation of clyclopentadienyl and substituted clyclopentadienyl radicals in small clusters. III. Pre-reactive clusters

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The hydrogen abstraction reaction between cyclopentadienyl radicals [Xcpd, X=H, CH_3(m), F, CN] and substituted methanes (CH_4, C_2H_6, CH_3CH_2OH, CH_3Cl, CH_2F_2, CHF_3, and CH_3OH) is studied for the isolated one-to-one van der Waals clusters created in a supersonic expansion. Three different types of fluorescence excitation spectra are characterized for these cluster systems: (1) sharp spectra are observed for some clusters, suggesting no cluster chemistry for either the ground or excited electronic states of Xcpd—CNcpd/CH_3Cl, CH_2F_2, CHF_3, CH_3OH; (2) broad spectra are observed suggesting initiation of cluster chemistry on the excited state cluster potential energy surface—CNcpd–CH_4, Fcpd–CHF_2Cl, CHF_3; and (3) only a greatly reduced bare radical signal is observed, but no cluster emission can be detected—cpd, mcpd/all substituted methanes, Fcpd–CH_2F_2, CH_3Cl, CH_3CH_2OH, CH_3OH, C_2H_6, and CNcpd/C_2H_6, CH_3CH_2OH. These results, taken together, suggest that the Xcpd radicals undergo an excited electronic state electrophilic hydrogen abstraction reaction with substituted methanes. The radical reactivities are in the order mcpd~cpd>Fcpd>CNcpd and the substituted methane reactivities are in the order C_2H_6>C_2H_5OH>CH_4>CH_3Cl~CH_3OH>CH_2F_2>CHF_2Cl>CHF_3. All Xcpd radicals show intense, sharp spectra with CF_4. This indication of an excited state Xcpd radical hydrogen abstraction reaction with substituted methanes is further explored by *ab initio* quantum chemistry techniques at the (7×7) CASSCF/6-31G (complete active space self-consistent field) and cc-pVDZ levels for cpd–CH_4. Calculations confirm the idea that the ground state cluster has a reaction barrier (approximately +170 kJ/mol) and a positive free energy of reaction (~80 kJ/mol). The excited cpd radical, however, can react with CH_4 along a barrierless path to generate substantial hot ground product states (C_5H_6 and CH_3). Experimental data are consistent with an Xcpd–C_2H_4 addition reaction, as well. © *1999 American Institute of Physics.* [S0021-9606(99)01410-5]

I. INTRODUCTION

Radical chemistry plays an important role in gas phase and condensed phase reactivity.[1] Radicals and other very energetic species are especially important for open systems such as flames and oxidative atmospheres. In order to describe the behavior of open systems in general, radical chemistry must be well explored and understood; however, due to the short lifetimes and high reactivities of radicals, the study of radical reactions is not always a simple task. A number of different approaches have been taken to elucidate the reactions of radicals: state selective kinetics,[2] temperature dependent reactivity,[3] van der Waals cluster chemistry,[4–11] and *ab initio* quantum chemistry reaction path calculations.[12]

van der Waals cluster chemistry consists of formation of a stable ground state van der Waals cluster between the radical or reactive intermediate and the reaction partner. This initial step is usually carried out in a supersonic expansion with an inert gas (He, Ne, Ar, etc.) and the two species of interest (e.g., a cyclopentadienyl radical and a methane molecule). The species are cooled to ~5 K in the expansion and form a van der Waals cluster. Typically an activation or reaction barrier prevents the molecules in the cluster from reacting on the ground electronic state potential energy surface of the cluster at this temperature, even if they would form products exothermically. On the other hand, reaction between the two species in a van der Waals cluster is much more likely for the radical in an excited electronic state because the reaction will almost always be exothermic with respect to ground state products, and excited state reaction barriers are usually much lower than ground state ones, due at least in part, to electron delocalization.

The major advantages of studying reactions through formation of van der Waals clusters are that the reactants are in known states, at known geometries and orientations, with known energies, and the reaction can be started at a known time upon electronic excitation at fs, ps, or ns time resolution. Thus, entrance channel control of the reactants is nearly complete. Moreover, such an experimental situation is very well designed to be modeled by potential energy surface and *ab initio* quantum chemical calculations.[13] The studies of chemical reactions in van der Waals clusters are, of course, at the mercy of the electronic transition Franck–Condon factors: that is, we can only access that part of the cluster excited state potential surface that is accessible from the ground state equilibrium van der Waals geometry, unless quite complicated experimental procedures (pump–dump and double resonance) can be usefully implemented.

The type of spectrum that can be observed from such a reacting, excited state cluster system is a sensitive function of the two potential surfaces involved, the transition Franck–Condon factors, and the lifetimes of the states accessed. In

general, if the excited state cluster is accessed on the reactant side of the reaction barrier, one might expect reactantlike spectra that are broad;[11] if the transition state is accessed, very broad spectra that are not reactantlike can be anticipated;[14] and if productlike species are accessed (unlikely due to Franck–Condon considerations), new hot spectra can be anticipated. Only in rare instances, perhaps for small product molecules (di- and tri-atomics), would one anticipate chemiluminescence—that is, excited electronic state product species.[15]

Clearly spectroscopic results for reactive clusters will not be well resolved and may indeed provide only qualitative experimental information on the systems investigated.[11] Thus, *ab initio* calculations of the surfaces and even of the Franck–Condon factors for the transitions must be a component of any program of study for chemical reactions in clusters.

In this report we present a study of the potentially reactive clusters containing cyclopentadienyl (cpd), methylcyclopentadienyl (mcpd), fluorocyclopentadienyl (Fcpd), or cyanocyclopentadienyl (CNcpd) and various substituted methanes (CH_3CH_2OH, CH_3OH, C_2H_6, CH_4, CH_3Cl, CHF_3, CH_2F_2, CHF_2Cl). Through fluorescence excitation spectroscopy of these various clusters, in conjunction with CASSCF (7×7) *ab initio* calculations, we are able to (1) elucidate the effects of different substituent groups (CH_3, H, F, CN) on cpd radical ring reactivity, (2) determine the path for the hydrogen atom abstraction reaction, and (3) analyze the role of electron withdrawing and donating groups on the substituted methane reaction partners, for both ground and excited electronic state reactions of the Xcpd radicals.

II. PROCEDURES

A. Experiment

The detailed experimental procedures for these studies are presented elsewhere.[9–11] Briefly, a pulsed supersonic nozzle expansion using He as the backing gas generates the molecular beam in a stainless steel vacuum chamber maintained at 10^{-4} Torr. Typical backing gas pressures range from 50 to 200 psig and precursor and solvent gas pressures range from 0.1% to 20% of the backing gas pressure. The precursor molecules for the Xcpd photolytic generation are methyl cyclopentadiene dimer for cpd and mcpd, o-fluoroanisole for Fcpd, and phenylazide and phenylisocyanate for CNcpd. Phenylazide is synthesized according to Ref. 16. Precursors are placed in a quartz boat in the high pressure line directly behind the nozzle entrance.

An excimer laser 193 nm output is focused at the nozzle exit to photolyze the precursors and generate radicals. The laser focus point is inside a small quartz (1 mm i.d.$\times$1 cm) tube attached to the nozzle exit to contain the precursor for photolysis and to enhance cooling through collisions. van der Waals clusters are formed as the radicals and solvent molecules co-expand at the exit of the quartz tube. The clusters are accessed about 1.0 cm from the quartz tube end by a Nd/YAG pumped dye laser. A photomultiplier tube, in a direction perpendicular to the plane containing the molecular and excitation laser beams, detects fluorescence from the clusters. The dyes employed in this study are DCM and DCM+R640 (doubled output) for Fcpd, LDS698+DCM (doubled output) for cpd and mcpd, and R590 and F548 (fundamental mixed with Nd/YAG fundamental) for CNcpd.

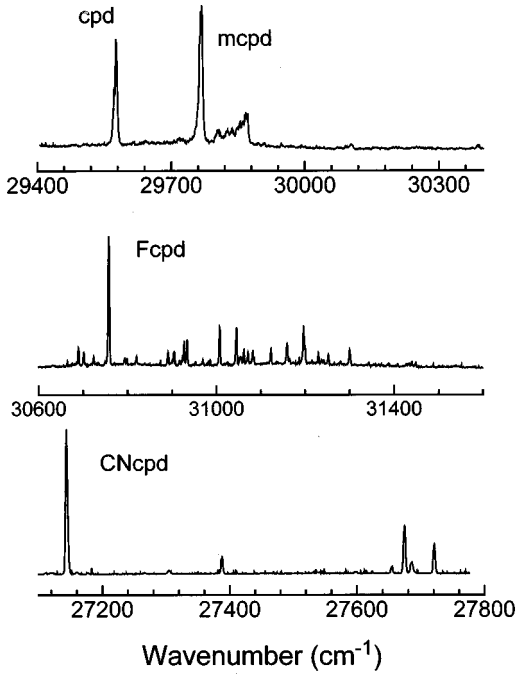

FIG. 1. Fluorescence excitation spectra of cpd, mcpd, Fcpd, and CNcpd.

B. Theory

Calculations necessary to explore and interpret the experimental results for reacting clusters are implemented on an IBM/RISC6000 workstation with 128 MB of RAM, 4 GB disk space (scratch), with a Spec fp95 of ~10. The GAUSSIAN 94[17] program suite is employed for complete active space self-consistent field (CASSCF) calculations with a number of different basis sets for reaction path generation and location of transition states.

III. EXPERIMENTAL RESULTS

A. Bare radicals

The $D_1\leftarrow D_0$ spectra[18] of the four radicals, cpd, mcpd, Fcpd, and CNcpd, are present in Fig. 1. The bare radical spectra in general show very few features, due to two reasons: (1) Franck–Condon factors that strongly favor the 0_0^0 transitions; and (2) the existence of nonradiative processes for the D_1 states that reduce the lifetimes of the vibronic states above the 0^0D_1 level. The Fcpd spectrum shown in Fig. 1 is acquired with a fast and narrow gate (10 ns with no delay) so the intensity pattern favors rapidly decaying species. The other spectra are acquired with a broader gate (100 ns) and with a 50 ns time delay between the laser pulse and the detection time, and thereby have a much smaller contribution from the short lived, higher energy vibronic states. The proximity of the cpd and mcpd origins emphasizes the small differential effect (~200 cm^{-1}) that the methyl group has on the ring system with regard to the $D_1\leftarrow D_0$ transition. Note that the F and CN groups shift the $D_1\leftarrow D_0$ transition by +1200 cm^{-1} and −2400 cm^{-1}, respectively.

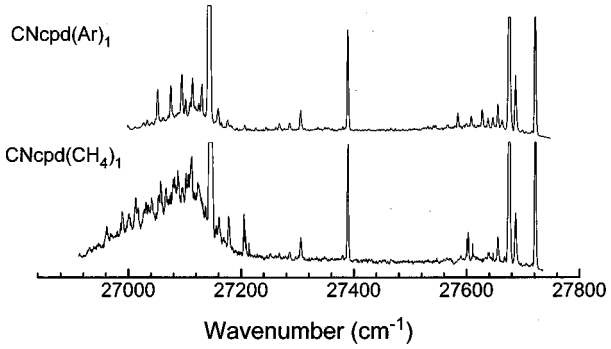

FIG. 2. Fluorescence excitation spectra of $CNcpd(Ar)_1$ and $CNcpd(CH_4)_1$ clusters. Note the $CNcpd(Ar)_1$ vibronic structure at $\sim 27\,680\ cm^{-1}$ and absence of such structure for $CNcpd(CH_4)_1$.

B. $CNcpd(CH_4)_1$

Figure 2 shows a comparison between the cluster spectra of $CNcpd(Ar)_1$ and $(CH_4)_1$ clusters. The Ar cluster spectrum consists of a series of five peaks assigned as a progression in $b^n_{yo}(n=0-4)$; the $CNcpd(Ar)_1$ cluster origin is shifted $-92\ cm^{-1}$ from the CNcpd origin at $\sim 27\,144.6\ cm^{-1}$. The CNcpd vibronic feature at $\sim 27\,675\ cm^{-1}$ can also be seen to support a nearly identical cluster spectrum. The binding energy for the $CNcpd(Ar)_1$ cluster is $\sim 500\ cm^{-1}$ in the D_1 state and one would expect to observe the $CNcpd(Ar)_1$ cluster spectrum at this vibronic feature. The small background spectrum displayed at the cluster origin is probably associated with $CNcpd(Ar)_n$, $n \geqslant 2$, clusters.

The $CNcpd(CH_4)_1$ spectrum of Fig. 2 is quite different from that just described. First, the cluster shift is exceptionally large ($-187\ cm^{-1}$) for a CH_4 aromatic molecule cluster spectrum.[19] This large shift cannot be reproduced by atom–atom potential energy calculations even though a wide variety of other clusters of methane with both molecules and radicals can be readily understood (e.g., $C_6H_5CH_2$, NCO, CH_3O, C_6H_6, etc.).[9–11,19] Second, the cluster spectrum is very crowded and is always (even at very low concentrations of CH_4) accompanied by an intense, broad background. The breadth of the $CNcpd(CH_4)_1$ spectrum and the number of features suggest that the cluster undergoes a large change in structure upon electronic excitation to the D_1 state. Third, note that no cluster spectrum is observed at the higher vibronic level of the radical. Since the binding energy of $CNcpd(CH_4)_1$ (D_1) is expected to be nearly $150\ cm^{-1}$ larger than that for the argon cluster (see paper I), one would have expected that the $CNcpd(CH_4)_1$ cluster spectrum would appear at the higher vibronic level of CNcpd at $27\,640\ cm^{-1}$, as well. Fourth, no CH_4 cluster spectra are found for cpd, mcpd, or Fcpd, while all these radicals display strong cluster spectra with other nonpolar solvents (e.g., N_2, CF_4, C_2F_6) and the Xcpd bare radical intensity decreases significantly upon addition of CH_4 to the expansion gas.

C. $CNcpd(CH_3OH)_1$

Figure 3 presents the $CNcpd(CH_3OH)_1$ cluster spectrum. The spectrum consists of a very intense origin feature (about $\frac{1}{3}$ the CNcpd bare radical intensity), shifted $+151\ cm^{-1}$ from the bare radical origin. The small feature at roughly $+46.5\ cm^{-1}$ higher energy than the cluster origin is probably due to a van der Waals mode built on this origin (see paper II). The lack of van der Waals mode intensity in this spectrum indicates that the ground and excited state structures are nearly the same in this cluster (see paper II). Despite the intensity of this spectrum, it is the only methanol cluster spectrum observed for the Xcpd radicals studies.

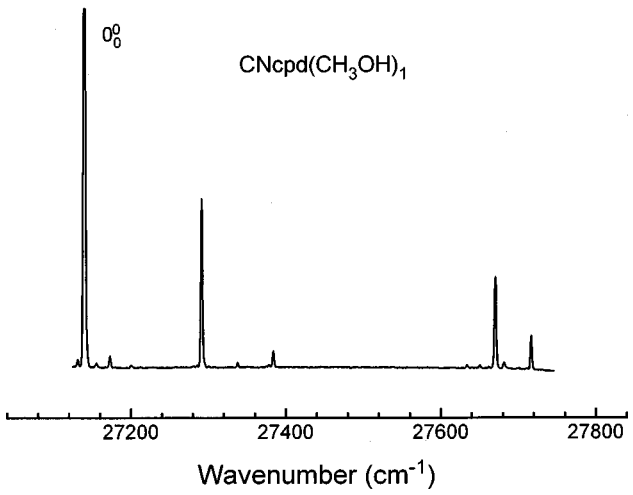

FIG. 3. Fluorescence excitation spectra of the $CNcpd(CH_3OH)_1$ cluster.

D. $CNcpd(CHF_3)_1$, $Fcpd(CHF_3)_1$, and $Fcpd(CHF_2Cl)_1$

Figure 4 presents the $CNcpd(CHF_3)_1$, $Fcpd(CHF_3)_1$, and $Fcpd(CHF_2Cl)_1$ cluster spectra. The $CNcpd(CHF_3)_1$ spec-

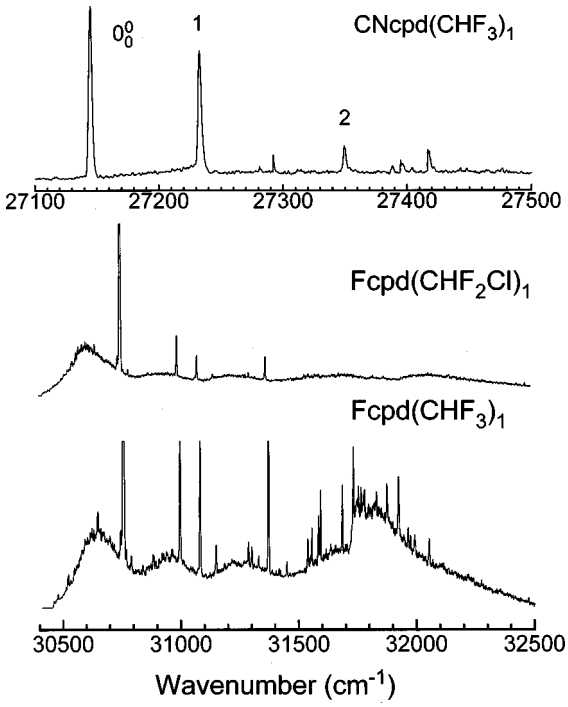

FIG. 4. Fluorescence excitation spectra of $CNcpd(CHF_3)_1$, $CNcpd(CHF_2Cl)_1$, and $Fcpd(CHF_3)_1$ clusters.

trum has an intense origin shifted $+87\ cm^{-1}$ from the bare radical origin and a van der Waals mode feature at $+79\ cm^{-1}$ from the cluster origin. This spectrum is very typical of a van der Waals cluster spectrum for a nonreactive system. In contrast, spectra for $Fcpd(CHF_3)_1$ and $Fcpd(CHF_2Cl)_1$ are broad, start at approximately $-250\ cm^{-1}$ from the bare radical origin and continue for more than $+2000\ cm^{-1}$ to the blue of the cluster origins: The spectra continue beyond this, but the presented trace in Fig. 4 ends due to the limited range of the dye laser output. The actual absorptions extend for at least another $10^3\ cm^{-1}$. The sharp features superimposed on the broad cluster spectra are due to the bare radical. As explained above, if a broad time integration window is employed to record these spectra, the vibronic peaks of the bare radical disappear, but the broad absorption, which has a long lifetime similar to that of the cluster origin, remains intense. This intensity pattern can be seen by comparing the traces for $Fcpd(CHF_3)_1$ and $Fcpd(CHF_2Cl)_1$ in Fig. 4. The $Fcpd(CHF_3)_1$ spectrum is recorded with a narrow integration centered at short times and thus the bare radical vibronic features are emphasized, whereas the spectrum for $Fcpd(CHF_2Cl)_1$ is recorded at long times with a broad integration window so only the bare radical origin and the broad spectrum are retained. Both $Fcpd(CHF_2Cl)_1$ and $Fcpd(CHF_3)_1$ cluster spectra are indicative of a reacting system[11] and are not typical for a van der Waals cluster spectrum. These broad cluster spectra are independent of solvent gas pressure in the gas mixture and cannot be attributed to larger clusters, as they retain their overall shape and breadth even at concentrations of solvent below 0.1% of the total backing gas pressure and over a wide range of total pressure.

Note too that $\sim 1\%$ CHF_3 added to the expansion gas reduces the bare radical signal by a factor of 10 for these Fcpd studies, but has little or no effect on the CNcpd bare radical intensity. Additionally, no cluster spectra are observed for cpd–CHF_3, CH_2F_2, CH_3Cl, mcpd–CHF_3, CH_2F_2, CH_3Cl, CHF_3, while CNcpd–CH_2F_2, CH_3Cl, CHF_3 show sharp van der Waals cluster spectra (see paper II).

IV. REACTION PATH CALCULATIONS

Both the observed spectra for $CNcpd(CH_4)_1$, $Fcpd(CHF_3)_1$, and $Fcpd(CHF_2Cl)_1$ and the unobserved spectra for many other Xcpd/halo-, methyl-, and other substituted methanes point to the existence of an excited state reaction between Xcpds and substituted methanes. To test this hypothesis, a series of calculations are undertaken. The first system approached is the simplest one possible for *ab initio* quantum chemistry, cpd–CH_4. Both ground and excited state radical reaction potential energy surfaces are explored at the CASSCF (7×7)/6-31G level. The active space is formed by the $3\pi+2\pi^*$ cpd orbitals and the sp^3 and sp^3* orbitals of the C–H bond of CH_4 to be broken and reformed. A number of effects and interactions are ignored at this level of quantum chemistry: basis set superposition error, dynamic electron correlation, polarized and diffuse basis sets, and other electron reorganizations in the reaction. Thus, the activation barriers are not very accurate nor are the total free energies for the reaction. A complete active space second order Møller–Plesset (CASMP2) calculation of reactant, transition states, and product would improve the quantitative results to be sure. Nonetheless, the results presented below are strongly supportive of the observations: A reaction between Xcpd and substituted methanes occurs on the excited state radical cluster potential energy surface.

The reaction coordinate chosen is the $H_3C–H\cdots C_{rn}$ distance (C_{rn} is the carbon to which the abstracted hydrogen atom is bonded). The only restriction imposed on the calculation is that the cluster structures maintain C_{2V} symmetry. No angle or bond distances are fixed. The reaction path is calculated optimizing the system structure at fixed values of the reaction coordinate r, starting at $r=3.3$ Å and ending with the product r of 1.089 Å. Structures of the reactants and products, together with the structure for the most energetic point on the reaction path as an initial guess, are used to calculate the transition state (TS). The TS final structure is tested using a normal mode calculation. The only negative frequency obtained for the final TS structure is that corresponding to the reaction coordinate motion: the $H_3C–H$ hydrogen moving between the CH_4 and C_1 carbon atoms. This confirms that the TS corresponds to a saddle point on the reaction potential energy surface.

For the excited state reaction, the products are assumed to be in their ground states because they do not have sufficient energy to be electronically excited. The excited state optimized reactant structure at $r=3.0$ Å, the ground state products, and the ground state TS structure (but with the excited state electronic configuration) are employed as the initial guess to search for the excited state TS. No excited TS is found, however, as the calculation proceeds along the reaction path without locating any potential energy gradient. We conclude that the reaction occurs on the excited state electronic potential energy surface for the cluster without an activation barrier.

The calculated transition energy for the cluster (taken as the energy difference between the ground and excited state structures at $r=3.0$ Å) is $30\,035\ cm^{-1}$; this is in excellent agreement with the experimental value of $29\,576.9\ cm^{-1}$. The calculated thermochemistry (D_0) for the reaction is 81 kJ/mol ($[E_{prod}-E_{react}(r=3.0\text{ Å})]$) in quite reasonable agreement with the experimental value of 110 kJ/mol.[20] This result seems quite useful considering the degree of approximation employed in the outlined approach.

The reaction path exhibits a very large barrier for the reaction on the ground electronic state surface (170 kJ/mol). Part of this barrier is surely due to the exclusion of dynamic electron correlation in our calculation[21] and to the limited size of the basis set. If a better basis set were employed and an MP2 calculation were performed on the (7×7) CASSCF wave function, the barrier could decrease by nearly 50%. The barrier is very close to the products (at 1.31 Å) as expected for an endothermic reaction. The TS structure is shown in Fig. 5. The angle between the two $C_{rn}–H$ bonds indicates that C_{rn} is close to sp^3 hybridized. The CH_3 hydrogens of the reactant CH_4 are almost planar, indicating that the CH_4C atom is nearly sp^2 hybridized. As soon as the reacting system surmounts the barrier and starts down the

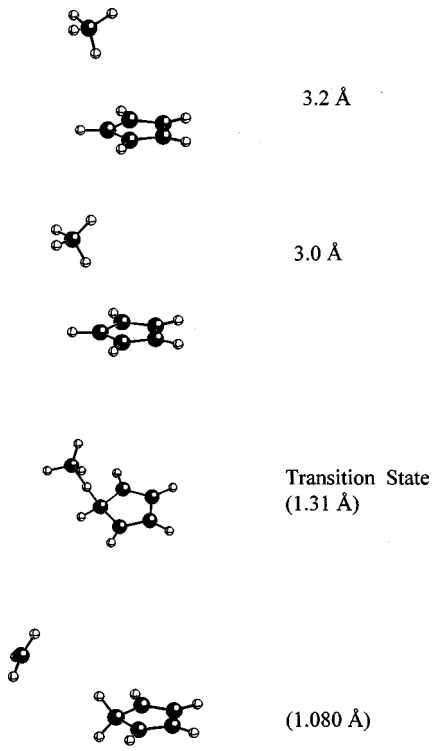

FIG. 5. Calculated structures for cpd and CH_4 at different positions along the reaction path.

product valley, the $CH_3^{*}\cdot$ and C_5H_6 products separate and the $CH_3\cdot$ carbon adopts sp^2 hybridization.

A shallow ($\sim$150 cm^{-1}) ''van der Waals potential well'' is located at roughly $r=3.2$ Å on the ground state potential energy surface. The cpd–CH_4 distance is similar to that found for the empirical potential energy Lennard-Jones form but the structure is different. The atom–atom parametized potential energy calculation places the solvent molecule CH_4 over the ring center with three hydrogen atoms towards the ring plane, interacting with the ring π-electron distribution symmetrically. The H- atom ring distance is 3.18 Å. The *ab initio* calculation (see Fig. 5) places the CH_4 molecule over C_1 and the CH_4 molecule carbon atom is off the ring. The *ab initio* binding energy for the cluster is $\sim$150 cm^{-1}, while for the potential energy calculation, it is $\sim$520 cm^{-1}. In this instance the potential energy calculation is a better estimate of the binding energy and the cluster structure because at the present level of approximation (e.g., small unpolarized basis set, no dynamic cluster correlation), the *ab initio* algorithm does not represent van der Waals–dispersion interactions well. The *ab initio* calculation focuses on the chemistry, not the dispersion interaction: the basis set superposition error at this level is certainly larger ($\sim 10^3$ cm^{-1}) than the true cluster binding energy.

The excited state reaction path does not present a barrier to the reaction at this level of theory: the reaction generates products (CH_3 and C_5H_6) that are in their ground electronic states. The excess energy following making and breaking of bonds goes into the product vibrational degrees of freedom. The reaction path for the excited state cluster suggests that the reaction is fast. The semiquantitative excited and ground state reaction paths are certainly consistent with the experimental observations.

V. DISCUSSION

The experimental data displayed in Figs. 2–4 strongly suggest the existence of a reaction between excited state Xcpd (X=H, CH_3, F, CN) radicals and various substituted methanes. This hypothesis is well supported by *ab initio* calculations for cpd–CH_4 which show no barrier on the excited state reaction path. The data show that CNcpd is the least reactive radical in this series and that mcpd and cpd are the most reactive radicals in this series. The chart below summarizes these results for the excited state radical clusters indicated.

	CNcpd	Fcpd	cpd	mcpd
C_2H_5H	+	+	+	+
CH_3H	±	+	+	+
CH_2ClH	−	+	+	+
CHF_2H	−	+	+	+
CF_2ClH	−	±	+	+
CF_3H	−	±	+	+

In this chart the entry ''+'' implies a reaction between the excited state Xcpd radical and its substituted methane coreactant, the entry ''−'' implies no reaction for the two species, and the entry ''±'' implies that a reaction between the two indicated species has been initiated.

In this section of the paper we wish to rationalize the observed excited state reactivity data for the above radical/substituted methane clusters. Perhaps we should first point out the possible correlation that does not serve to explain these results. The C–H bond energies (BE) of the methanes do not scale with the reactivity: For example,[20] $BE[H-C_2H_5]=100.5\pm0.2$ kcal/mol; $BE[H-CH_3]=104.8\pm0.2$ kcal/mol; $BE[H-CHF_2]=103.2\pm1$ kcal/mol; $BE[H-CF_2Cl]=101.6\pm1$ kcal/mol; and $BE[H-CF_3]=106.7\pm1$ kcal/mol. These bond energies are similar enough that they obviously do not dominate the behavior of the reaction and cannot be used to explain the observed trends in reactivity.

Three trends in Xcpd radical and substituted methane properties are consistent with these above cluster reactivity results: (1) Statistics for the hydrogen abstraction reaction to occur—that is, C_2H_6, CH_4, CH_3Y, CH_2Y_2, CHY_3 are in the statistical order of 6:4:3:2:1 for reactivity, irrespective of their chemical properties; (2) the thermal stabilization energies[22] of the subsequently formed product radicals following H abstraction are 2.11, −1.67, −1.89, −4.11, −4.17 kcal/mol for C_2H_5, CH_3, CHF_2, CF_2Cl, CF_3, respectively; and (3) the radical electrophilicities are in the order CNcpd>Fcpd>cpd~mcpd and the methane electrophilicities are in the order $CH_3F>CHF_2Cl>CH_2F_2>CH_3Cl>CH_4>C_2H_6$. The electrophilic trends quoted are also consistent with average electron density on the cpd ring carbons and the electron density on the carbons of the substituted methanes.

Thus, one can state that for the reactions considered, the most reactive substituted methane is C_2H_6 for three reasons: (1) The C_2H_5 radical is most stable; (2) C_2H_6 has six potential reaction sites; and (3) C_2H_6 is the most nucleophilic of

all the substituted methanes explored. Reactions in general occur for an electrophile reacting with a nucleophile. Therefore, the least electrophilic (and thus, most nucleophilic) radicals are cpd and mcpd: They are most reactive toward electrophilic substituted methanes. Fcpd has an average electrophilicity and it reacts with all but the most electrophilic of the methanes.

Cluster structure and details of the radical excited state potential energy surface surely play a role in these reactivities, but clear trends do not seem to present themselves at the present level of detail.

VI. CONCLUSIONS

The mechanism for the H atom abstraction reaction between substituted methanes and substituted excited electronic state cyclopentadienyl radicals is analyzed. Based on *ab initio* calculations, the reaction has a large barrier on the cpd–CH_4 D_0 ground electronic state potential energy surface of the cluster, but it has no barrier on the D_1 excited electronic state cluster potential energy surface. The barrier height on both surfaces is strongly influenced by electron withdrawing and electron donating groups on the Xcpd radicals: electron withdrawing groups increase the reaction barrier and electron donating groups decrease it. Thus, the H atom abstraction reactivity scale for these Xcpd radical is mcpd$\sim$cpd$>$Fcpd$>$CNcpd. Additional factors that contribute to the reactivity are degenerate pathways for the reaction if more than one hydrogen atom is available on the substituted methane, and the stabilization energy of the radical generated in the reaction.

The radical attack on the substituted methanes for H atom abstraction is electrophilic. Thus electron withdrawing groups (OH, F, Cl) on methane increase the barrier to reaction and electron donating groups (CH_3, etc.) on methane decrease the H atom abstraction reaction barrier. The broad fluorescence excitation spectra observed for Fcpd–CHF_3, CHF_2Cl, and CNcpd–CH_4 clusters are indicative of a potential excited state reaction for these clusters.

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