The proton-transfer surface of CH₃OHF[−]

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Diverse aspects of the potential surface for the proton-transfer reaction CH₃OH $+F^- \rightarrow CH_3O^- + HF$ have been investigated by means of high-level *ab initio* electronic structure methods based on single-reference wave functions, namely, Møller-Plesset perturbation theory from second through fourth order (MP2-MP4), the configuration interaction and coupledcluster singles and doubles methods (CISD and CCSD), and CCSD theory augmented by a perturbative correction for connected triple excitations [CCSD(T)]. The one-particle Gaussian basis sets for (C,O,F;H) ranged in quality from [4s2p1d;2s1p] to [14s9p6d4f;9s6p4d], including as many as 482 atomic orbitals for the CH₃OHF⁻ system. The ion-molecule complex on the proton-transfer surface is a tight, hydrogen-bonded structure of $CH_3OH \cdot F^-$ character, exhibiting a nearly linear -OHF⁻ framework, an elongated O–H distance of 1.07(1) Å, and a small interfragment separation, r(H-F) = 1.32(1) Å. Improved structural data for $F^- \cdot H_2O$ are obtained for calibration purposes. A large fluoride affinity is found for the CH₂OHF⁻ adduct, $D_0 = 30.4 \pm 1$ kcal mol⁻¹, and a bonding analysis via the Morokuma decomposition scheme reveals considerable covalent character. The harmonic stretching frequencies within the -OHF⁻ moiety are predicted to be 421 and 2006 cm^{-1} , the latter protonic vibration being downshifted 1857 cm⁻¹ relative to ω_1 (O–H) of free methanol. A systematic thermochemical analysis of the reactants and products on the CH₃OHF⁻ surface yields a proton-transfer energy of 10.6 kcal mol⁻¹, a gas-phase acidity for methanol of $381.7 \pm 1 \text{ kcal mol}^{-1}$, and $D_0(CH_3O-H) = 104.1 \pm 1$ kcal mol^{-1} , facilitating the resolution of previous inconsistencies in associated thermochemical cycles. A minimum-energy path in geometric configuration space is mapped out and parametrized on the basis of constrained structural optimizations for fixed values of an aptly chosen reaction variable. The evaluation of numerous energy points along this path establishes the nonexistence of either a proton-transfer barrier, an inflection region, or a secondary minimum of CH_3O^- · HF type. The mathematical considerations for a classical multipole analysis of reaction path asymptotes are outlined for ion-dipole systems and applied to the CH₃OHF⁻ surface with due concern for bifurcations in the exit channel for the proton-transfer process. A global analytic surface for vibrational stretching motion in the -OHF⁻ moiety of the CH₃OHF⁻ system is constructed, and a suitable dynamical model is tested which involves an effective, triatomic hydrogen pseudobihalide anion, [-OHF]⁻. Converged variational eigenstates of [-OHF]⁻ to one-half its dissociation limit are determined using vibrational configuration interaction expansions in terms of self-consistent-field modals. The fundamental stretching frequencies of the CH_3OHF^- complex predicted by the [-OHF]⁻ model are 504 (+84) and 1456 (-549) cm⁻¹, the corresponding anharmonicities appearing in parentheses.

I. OVERVIEW

An *ab initio* quantum chemical investigation of gasphase proton transfer between methanol and the fluoride ion is the focus of the current paper, which reports not only geometric structures, vibrational frequencies, quantitative energetics, and bonding analyses of relevant stationary points but also a parametrization of internal coordinates along the reaction path and an associated two-dimensional model surface for the proton-transfer process. These theoretical predictions serve various purposes. First, detailed dynamical studies are facilitated for a polyatomic protontransfer reaction possessing more degrees of freedom than

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in most cases investigated heretofore. Second, inconsistencies in ion-molecule thermochemical cycles involving the gas-phase acidity of methanol and the electron affinity of the methoxy radical are elucidated with concomitant implications for the determination of bond energies and intrinsic acidities of model organic compounds.¹⁻³ Third, the mathematical description of the anionic CH₃OHF⁻ surface required to quantify the Franck-Condon overlap with the transition-state region of the corresponding neutral hydrogen-transfer surface is provided, thus assisting the interpretation of recent photodetachment experiments on the methanol-fluoride complex.^{4,5} The utilization of such photodetachment processes to effectuate spectroscopy of transition states is a topic of considerable current interest. Finally, the structure of the vibrational eigenstates for motion of the central proton in the CH₃OHF⁻⁻ complex is established as a paradigm for nearly centrosymmetric species in the diverse class of [AHB]⁻ ions.

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II. BACKGROUND

A. Transition-state spectroscopy via photodetachment of anions

Historically, features of transition states have been deduced from observations of the asymptotic properties of reactions, ranging from traditional kinetic determinations of rate coefficients and activation barriers to microscopic probes of state-specific product angular and energy distributions. In recent years, however, the direct spectroscopic characterization of transition states for simple chemical reactions has evolved into a powerful technique.^{5,6} The most successful applications of transition-state spectroscopy have involved half-collision experiments, in which the transition state is accessed via photoexcitation of a stable precursor rather than a direct scattering event. As such, the extensive averaging over reactant initial conditions is averted by geometric restrictions, thus revealing sharp structure characteristic of resonances involving quasibound vibrational states in the transition-state region. The photodetachment of negative ions is a principal means by which such geometric constraints are imposed.

A rich history is associated with the photodetachment of anionic intermediates in the gas phase. While only a few apposite studies can be mentioned here, reviews of the extensive body of theoretical and experimental investigations on this subject can be found elsewhere.⁶ Lineberger and co-workers⁷ have revealed details of the rapid isomerization of the vinylidene radical to acetylene by applying photoelectron spectroscopy to $[C_2H_2]^-$. In experiments by Bowen et al.,⁸ the NH_4^- ion has been confirmed to be an ammonia-solvated hydride ion rather than an $NH_2^- \cdot H_2$ complex by analysis of the intensity profile of the photoelectron spectrum. Brauman and co-workers^{2,3,9,10} have also used photodetachment techniques as a qualitative probe of geometric structures. In one such study,³ the structures of ROHF⁻ complexes were examined in relation to the gas-phase acidities of the component alcohols by measurement of photodetachment cross sections in the visible and near-ultraviolet regions. Only for complexes containing alcohols more acidic than hydrogen fluoride was photodetachment observed for wavelengths greater than 365 nm. From this observation, qualitative onedimensional representations of both the anionic and neutral potential surfaces involved in the photodetachment process were proposed, as depicted in Fig. 1. More recently the Neumark group has used photoelectron spectroscopy¹¹⁻¹⁴ and threshold photodetachment¹⁵ techniques to investigate both symmetric^{11,13-15} and asymmetric¹² hydrogen bihalide systems, $[XHY]^-$, where $\{X,Y\} = \{Cl, Br, I\}$. The spectra exhibit well-resolved vibrational progressions associated with antisymmetric hydrogen stretching in quasibound states of the transitory [XHY][•] radicals and thus provide a direct probe of the corresponding transition states for hydrogen abstraction.

In photodetachment experiments in which both the hydrogen-bonded anionic complex and the neutral hydrogen-transfer transition state are centrosymmetric, the only structural concern with regard to Franck–Condon



FIG. 1. Schematic potential energy surfaces for $ROHF^-$ and ROHF systems. The solid and dashed anionic curves correspond to alcohols less and more acidic than HF, respectively. In the former case, photodetachment accesses the reactant valley of the neutral hydrogen-transfer surface. In ICR experiments, the onset of fluoride photodetachment at 365 nm effectively obscures the measurement of photodetachment cross sections for $ROHF^-$ systems in which the alcohol is less acidic than HF, as indicated by the cutoff affixed to the solid vertical line.

overlap is the separation of the donor and acceptor atoms. However, for asymmetric systems the position of the transferring hydrogen along the reaction coordinate becomes a central concern, as highlighted by Brauman and coworkers³ in their study of ROHF⁻ complexes. In mixed hydrogen bihalide systems, both the proton-transfer and the hydrogen-abstraction reactions

 $XH + Y^{-} \rightarrow [XHY]^{-} \rightarrow X^{-} + HY$ (1)

and

$$XH + Y \rightarrow [XHY]^{\dagger} \rightarrow X + HY$$
(2)

are exothermic, assuming Y precedes X in the halogen series. Because the gas-phase acidities of HX then exceed those of HY, the intermediate ion-molecule complexes are of $X^- \cdot HY$ character, and photodetachment of these anionic precursors accesses the *product* valley of reaction (2), as shown in Fig. 2. In contrast, the proton-transfer reactions between many simple aliphatic alcohols and the fluoride ion,

$$ROH + F^{-} \rightarrow [ROHF]^{-} \rightarrow RO^{-} + HF, \qquad (3)$$

are endothermic in the gas phase,¹⁶ even though the corresponding hydrogen-abstraction reactions

$$ROH + F \rightarrow [ROHF]^{\dagger} \rightarrow RO + HF$$
(4)

are exothermic. In accord with the acidity ordering of the neutral fragments, the intermediate complexes for reaction (3) resemble $ROH \cdot F^-$ rather than $RO^- \cdot HF$, and photodetachment accesses the *reactant* valley of reaction (4). Such structural dissimilarities in the potential energy surfaces of alcohol-fluoride systems relative to hydrogen bihalide species in part stimulated recent photodetachment ex-

2060



FIG. 2. Schematic potential energy surfaces for XHY^- and XHY systems, where Y precedes X in the halogen series. Photodetachment accesses the product valley of the neutral hydrogen-transfer surface.

periments by Neumark and co-workers⁴ on the CH₃OHF⁻ and C₂H₅OHF⁻ anions. While the photoelectron spectra of these ROHF⁻ species exhibit sharp vibrational structure similar in nature to that observed for the hydrogen bihalides, the maximum spectral intensity occurs near the asymptote on the neutral surface for dissociation into reactants rather than the energetically lower products.

B. Thermochemistry and proton-transfer barriers for [AHB]⁻ systems

For numerous Brønsted acids, gas-phase halide affinities have been determined experimentally by Larson and McMahon¹⁷⁻²⁰ and Caldwell and Kebarle.²¹ These investigations have employed a technique²² in which relative ion signals of complexes involved in halide-exchange equilibria are used to extract equilibrium constants and hence relative halide binding energies within a given set of compounds. Absolute halide affinities are then obtained by anchoring the scale to binding energies established for selected reference compounds. In this way the binding enthalpy of the fluoride ion to methanol was ascertained¹⁷ to be $\Delta H_{298}^{\circ}=29.6$ kcal mol⁻¹ based on an absolute fluoride affinity for H₂O of $\Delta H_{298}^{\circ}=23.3$ kcal mol^{-1.23} The CH₃OHF⁻ complex thus exhibits a particularly strong hydrogen bond among ion-molecule species, as gauged by the criterion of Emsley.²⁴

In gas-phase kinetic experiments it has been observed that exothermic proton-transfer reactions involving localized anions generally proceed at or near the collision rate, suggesting that the potential surfaces for such reactions are featureless.^{25–27} For the fast thermal proton-transfer reactions $Y^- + HX \rightarrow HY(v) + X^-$ (X=Cl,Br,I; Y=F,Cl), nascent vibrational product distributions measured via infrared chemiluminescence detection in a flowing afterglow apparatus are consistent with a single, deep well on the reaction surface.^{28,29} For delocalized anions or sterically hindered species, proton transfer occurs more slowly, indicating the possible presence of energetic barriers.^{30–32} In the CH₃OHF⁻ system, the reaction of CH₃O⁻ with HF belongs to the class of fast proton-transfer processes.³³ Product branching ratios from infrared multiphoton dissociation experiments have confirmed that the preferred fragmentation path of the CH₃OHF⁻ complex yields CH₃OH $+F^{-34}$ There is no kinetic evidence for the existence of a barrier to proton transfer or a secondary minimum of $CH_3O^- \cdot HF$ character. Kinetic measurements for such reactions are not always amenable to simple interpretation, however, as illustrated by the observation of protontransfer rates between alcohols and alkoxides which are much slower than anticipated from the features of theoretical potential energy surfaces for these reactions.^{35,36} A definitive ab initio characterization of the reaction path for proton transfer in the CH₃OHF⁻ system is thus warranted.

The existence or nonexistence of proton-transfer barriers in [AHB]⁻ complexes of various types has been the subject of numerous theoretical investigations.^{17,37-66} In the symmetric hydrogen bihalides, [XHX]⁻, a single, centrosymmetric minimum is definitively predicted if correlated wave functions and large atomic-orbital basis sets are used,³⁷⁻⁴⁴ even though Hartree–Fock theory predicts $C_{\alpha\nu}$ structures in the bichloride and bibromide cases.^{41,42} For the oxyanions [HOHOH]⁻ and [CH₃OHOCH₃]⁻, the shape of the proton-transfer surface is less certain due to basis set restrictions and limited correlation treatments in the best available ab initio predictions.45-51 For [HOHOH]⁻ a proton-transfer barrier of 4.3 kcal mol⁻¹ is found at the 6-311G** MP3 level,49 whereas for $[CH_3OHOCH_3]^-$ a 2.2 kcal mol⁻¹ barrier given by 6-31G* restricted Hartree-Fock (RHF) theory⁴⁸ essentially disappears when single-point 6-31+G* and 6-31G** MP2 energies are computed at the 6-31G* RHF optimum structures.⁵¹ Among the anionic systems which seem unambiguously to have a double-minimum potential are $[H_2NHNH_2]^{-,49,50}$ [NCHCN]⁻,^{50,58} [HCCHCCH]^{-, 50,58} and [H₃CHCH₃]^{-,50} but single wells are clearly exhibited by [CNHNC]^{-,58} [FHCN]^{-,62} [FHNC]^{-,62} [FHCl]^{-,66} [HOHCN]^{-,50,62} and [HOHNC]^{-.50,62} Some success has been achieved in the construction of Marcus theory models to account for the presence or absence of proton-transfer barriers in asymmetric [AHB]⁻ complexes on the basis of observed energy profiles for proton migration in the corresponding symmetric anions.⁵⁰

C. Vibrational spectroscopy of [AHB]⁻ complexes

As demonstrated by the investigations cited above, the vibrational motion of the central proton in various $[AHB]^-$ systems occurs on surfaces of widely disparate character. While vibrational spectroscopy of these complexes can be a sensitive probe of the underlying proton-transfer surfaces, high-resolution studies of polyatomic anions in the gas phase have only recently become feasible. A pioneering study in 1986 by Kawaguchi and Hirota⁶⁷ identified absorptions attributable to $[FHF]^-$ in a discharge by means of velocity-modulated infrared diode laser spectroscopy. Further work^{68,69} by these researchers using this

technique on both the $[FHF]^-$ and $[CIHCl]^-$ systems has provided the only gas-phase geometric structures and fundamental frequencies currently available for hydrogen bihalide anions. The application of high-resolution vibrational spectroscopy to CH_3OHF^- and similar systems has yet to be realized.

Reliable theoretical predictions of the vibrational spectra of [AHB]⁻ anions require not only flexible atomicorbital basis sets and rigorous electron correlation techniques but also careful treatments of vibrational anharmonicity. In many cases the potential surface along the minimum energy pathway for proton transfer is very flat, and the antisymmetric hydrogen stretching mode is highly anharmonic. The central issues pertaining to the vibrational dynamics of hydrogen bihalide prototypes have been reviewed and addressed in a recent, extensive paper on the [FHCl]⁻ anion by Allen and co-workers,⁶⁶ which reports a global analytic potential surface for the [FHCl]⁻ system constructed at the TZ(+)(3d,3p) CCSD level of theory, as well as the complete vibrational eigenspectrum determined by rigorous variational techniques to near the $HF+Cl^{-}$ interchange dissociation threshold. The form of the analytic surface used for [FHC1]⁻ is readily adapted to the description of proton transfer in other complexes, including the CH₃OHF⁻ system under investigation here. Also of particular relevance is the ab initio work of Yates et al.⁶¹ on the vibrational spectrum of $F^- \cdot H_2O$, in which geometric structures and harmonic vibrational frequencies were determined at the CISD level with large basis sets, and a complete RHF quartic force field was used to account for vibrational anharmonicity. Direct theoretical studies^{4,5,52} on the CH_3OHF^- complex have been limited, the most recent results being obtained by Neumark and co-workers⁴ as an aid to the interpretation of their photodetachment experiments. The computations entailed the determination of 6-31++G** RHF and MP2 geometric structures, harmonic vibrational frequencies, and dissociation energies followed by MP4 energetic refinements. More comprehensive *ab initio* predictions for the CH₃OHF⁻ system are derived here by the utilization of flexible basis sets ranging from DZ(d,p) to [13s8p6d4f, 8s6p4d](+) and detailed treatments of electron correlation at various levels of Møller-Plesset, configuration interaction, and coupledcluster theory.

III. THEORETICAL METHODS

The atomic-orbital basis sets employed in this study are denoted as DZ(d,p), TZ(+)(d,p), QZ(+)(2d,2p), QZ(+)(2d1f,2p1d), and [13s8p6d4f,8s6p4d](+) and are comprised of 68, 97, 136, 181, and 482 contracted Gaussian functions, respectively, for the CH_3OHF^- system. In the first four designations of the form A(x,y), A is broadly descriptive of the sp basis [DZ,TZ,QZ=double,triple, and quadruple zeta], and x and y specify the number and types of polarization manifolds appended to the (C,O,F) and H atoms, respectively. In the notation for the last basis set, the number of shells of each orbital type is explicitly listed for the (C,O,F) and H atoms, in order. The suffix (+) in all cases signifies the addition of single sets of diffuse s and p functions to the heavy-atom centers and a diffuse s orbital to the hydrogen involved in proton transfer.⁷⁰ Diffuse orbitals were not appended to the methyl hydrogens.

For carbon, oxygen, and fluorine, the DZ sp basis consists of the (9s5p) Gaussian primitives of Huzinaga⁷¹ and the (4s2p) contractions of Dunning;⁷² the corresponding hydrogen basis is a (4s/2s) set in which the exponents are scaled by the customary factor of $1.2^{2.72}$ In the TZ and QZ cases, the heavy-atom sp sets are Huzinaga-Dunning (10s6p/5s3p) and (10s6p/5s4p) contractions,^{71,73} respectively, whereas for hydrogen an analogous (5s/3s) basis is utilized in both instances with a scale factor of $1.49^{2,73}$ which is optimum for H_2O . The sp space of the [13s8p6d4f,8s6p4d] basis is comprised of the uncontracted primitives of van Duijneveldt.⁷⁴ For the diffuse orbitals constituting the (+) augmentations, the following exponents were employed, as derived by even-tempered extension of the respective valence sp sets: TZ and QZ, $\alpha_s(C)$ =0.045 61, $\alpha_p(C)$ =0.033 44, $\alpha_s(O)$ =0.084 58, $\alpha_p(O)$ =0.056 54, $\alpha_s(F)$ =0.1087, $\alpha_p(F)$ =0.069 04, and $\alpha_s(H)$ =0.070 94; [13s8p6d4f,8s6p4d], $\alpha_s(C)$ =0.039 90, $\alpha_p(C)$ =0.027 665, $\alpha_s(O) = 0.074$ 19, $\alpha_p(O) = 0.049$ 21, $\alpha_s(F)$ =0.093 077, $\alpha_p(F)$ =0.059 326, and $\alpha_s(H)$ =0.029 254.

The DZ(d,p) basis set is built up from the DZ atomic orbitals by the addition of polarization functions to all atoms, the exponents being $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.0$, and $\alpha_p(H) = 0.75$, which are representative of optimum values for Hartree-Fock wave functions.⁷⁵ To provide more accurate energetic predictions, the correlation-optimized exponents given by Dunning⁷⁶ are utilized in the polarization manifolds of the TZ and QZ basis sets. In the [13s8p6d4f, 8s6p4d] set, the polarization exponents are selected as members of geometric series with ratios of 0.4 which fully span the regions critical to the recovery of valence-shell correlation energy. The first exponents in these series are $\alpha_d(C) = 7.12$, $\alpha_f(C) = 3.42$, $\alpha_d(O) = 12.65, \quad \alpha_f(O) = 6.07, \quad \alpha_d(F) = 16.01, \quad \alpha_f(F)$ =7.68, $\alpha_p(H)$ =9.88, and $\alpha_d(H)$ =4.0. In actuality, the [13s8p6d4f, 8s6p4d] basis consists of the uncontracted primitives within the atomic-natural-orbital (ANO) basis sets of Almlöf and Taylor⁷⁷ less the g and f manifolds for the (C,O,F) and H atoms, respectively. In the DZ(d,p), TZ(+)(d,p), and QZ(+)(2d,2p) cases, the d sets are comprised of six Cartesian components, while in the QZ (+)(2d1f,2p1d) and [13s8p6d4f,8s6p4d](+) basis sets the supernumerary d orbitals are excluded, except in one instance.⁷⁸ In all basis sets the f manifolds involve only real combinations of the l=3 spherical harmonics.

Reference electronic wave functions were determined in this investigation by the single-configuration, selfconsistent-field, restricted Hartree–Fock (RHF) method.⁷⁹⁻⁸¹ Various formalisms were invoked to account for dynamical electron correlation, including the configuration interaction singles and doubles method (CISD),^{82–84} Møller–Plesset perturbation theory through fourth order [MP2, MP3, and MP4(SDTQ)],^{85–88} and coupled-cluster and Brueckner theory incorporating various degrees of excitation [CCSD,^{89–94} CCSD(T),^{95,96} BD, BD(T), and $BD(TQ)^{97,98}$]. To maintain continuity of the CH₃OHF⁻ proton-transfer surface, the separated reactants and products were treated as CH₃OH+F⁻ and CH₃O⁻+HF supermolecules in the CISD computations, thereby including 191 380 configuration state functions of C_s symmetry. The 1s core orbitals of the C, O, and F atoms were excluded from the active space in the correlation treatments as well as the high-lying; core-localized virtual orbitals appearing above selected energy thresholds. The total number of such frozen virtual orbitals in the DZ(d,p), TZ(+)(d,p), $QZ(+)(2d,2p), QZ(+)(2d1f,2p1d),^{78} and [13s8p6d4f,$ 8s6p4d (+) correlation treatments were 3, 5, 5, 3, and 105, respectively. The electronic structure computations were performed by sundry implementations of the program packages PSI,⁹⁹ CADPAC,¹⁰⁰ and GAUSSIAN (86, 88, 90, and 92).¹⁰¹ Absolute total energies for most computations are documented as supplementary material.¹⁰²

Analytic gradient techniques¹⁰³⁻¹⁰⁵ for the RHF, MP2, and CISD methods were used to perform complete and constrained geometry optimizations to 10^{-6} Å or rad in the internal coordinate space. Quadratic force fields and dipole-moment derivatives were evaluated via analytic second-derivative techniques for RHF^{103,106} and MP2^{107,108} wave functions. In the harmonic vibrational analyses reported here, normal modes were quantitatively assigned in internal coordinates by the total energy distribution (TED) method advocated by Pulay and Török,¹⁰⁹ and integrated infrared band intensities were computed within the double-harmonic approximation^{110,111} via the formula $A_i = 42.254\ 72\ |\partial \mu / \partial Q_i|^2$, where A_i is in km mol⁻¹, and μ is in D Å⁻¹ amu^{-1/2}. Improved force fields at salient points on the CH₃OHF⁻ surface were obtained according to the scaled quantum mechanical (SQM) force field method,¹¹²⁻¹¹⁶ as calibrated on empirical data for the fundamental frequencies of methanol. A recent paper by Allen et al.¹¹⁷ succinctly presents the formalism of the SOM procedure and reviews the plethora of previous applications of this technique.

IV. CHARACTERIZATION OF THE CH₃OHF⁻ COMPLEX

A. Geometric structures

A graphical representation of the CH₂OHF⁻ system illustrating the atomic connectivity and numbering is given in Fig. 3. An analysis of geometric structures on the CH₃OHF⁻ surface is best initiated by a brief calibration of theoretical methods on the widely studied^{4,47,48,51,118-122} methanol fragment. In Table I equilibrium structural parameters for CH₃OH are listed for several levels of theory. As anticipated for small, saturated organic compounds,⁸⁰ the structural predictions are rather insensitive to variations in the theoretical treatment. The TZ(+)(d,p)RHF→CISD correlation shifts for the C-O and O-H bond lengths are both near +0.011 Å, and the analogous changes in the C-H distances are $\sim +0.004$ Å. The TZ (+)(d,p) RHF \rightarrow MP2 shifts are essentially twice as large as their CISD counterparts, demonstrating the propensity of MP2 theory to overestimate correlation effects on optimum bond lengths. The $TZ(+)(d,p) \rightarrow QZ(+)(2d,2p)$



FIG. 3. Atomic numbering and connectivity of the CH_3OHF^- system in C_s symmetry. Selected internal coordinates are also depicted whose equilibrium values are listed in Table III.

RHF comparison confirms that contractions of less than 0.01 Å of the bond lengths predicted with the TZ(+)(d,p) basis set are expected as the one-particle RHF, MP2, and CISD limits are approached. The ranges predicted for equilibrium bond angles in Table I are less than 0.8° except in the $\alpha(C_1-O_5-H_6)$ case, for which correlation effects favor a more strongly bent moiety by roughly 2°-3°. Both the TZ(+)(d,p) MP2 and CISD equilibrium coordinates compare very favorably with their experimental r_s counterparts,¹²³ especially considering the residual zero-point vibrational effects and the constraint of a symmetric methyl group present in the empirical structure. The experimental r_e geometry of methanol is not known.

Predicted geometric structures for the proton-transfer products $CH_3O^- + HF$ are provided in Table II, wherein the variations among optimum parameters are seen to closely mimic those observed for methanol. Nevertheless, the structure of methoxide is shown to be rather peculiar, as noted by others for both the parent ion^{122,124} and halogen-substituted derivatives.^{122,125-128} In particular, the C-O bond in methoxide is 0.07 Å shorter and the C-H bonds are roughly 0.035 Å longer than in the methanol prototype, strikingly large shifts which are accompanied by a substantial increase in the H–C–O angles to near 115°. These phenomena can be explained by invoking the concept of negative hyperconjugation,^{129,130} a process which in this case involves the redistribution of excess negative charge¹³¹ from the high-lying oxygen lone pairs into an empty manifold of degenerate C–H antibonding orbitals.

In Table III optimum geometric parameters for the C_s symmetry CH₃OHF⁻ minimum are tabulated. The methanol framework essentially remains intact upon adduct formation, although the O-H distance is clongated by 0.06– 0.11 Å in the final theoretical structures. Accordingly, the predicted coordinates, less $r(O_5-H_6)$, for the CH₃OH fragment are not particularly sensitive to the level of theory, generally displaying the aforementioned trends for the free methanol molecule. In contrast, the interfragment separation $r(H_6-F_7)$ in CH₃OHF⁻ varies significantly with improvements in the theoretical treatment, as observed for numerous other ion-molecule complexes such as

TABLE I. Geometric structure of CH ₁ O)Н."
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Level of theory	DZ(<i>d</i> , <i>p</i>) RHF	TZ(+)(d,p) RHF ^b	QZ(+)(2d,2p) RHF	TZ(+)(d,p) MP2	TZ(+)(d,p) CISD	Expt.° (<i>r</i> _s)
Coordinates		<u></u>				
$r(C_1 - H_{2.3})$	1.0900	1.0874	1.0846	1.0954	1.0913	1.094 ^d
$r(C_1 - H_4)$	1.0840	1.0817	1.0793	1.0898	1.0858	1.094 ^d
$r(C_1 - O_5)$	- 1.4019	1.4052	1.4017	1.4301	1.4161	1.421
$r(O_5-H_6)$	0.9445	0.9412	0.9388	0.9630	0.9526	0.963
$\alpha(H_2-C_1-H_3)$	108.71	108.99	108.96	109.22	109.06	108.5 ^d
$\alpha(H_{2,3}-C_1-O_5)$	112.00	111.73	111.76	111.79	111.79	112.0
$\alpha(H_4-C_1-O_5)$	107.29	107.21	107.26	106.54	106.97	107.2
$\alpha(C_1 - O_5 - H_6)$	109.74	109.74	109.97	106.84	107.95	108.0
$\tau(H_4-C_1-O_5-H_6)$	180.00	180.00	180.00	180.00	180.00	180.0

^aBond distances in Å, angles in deg. See Fig. 3 for structural depictions and numbering of atoms.

^bAnalogous optimum parameters for eclipsed methanol, as ordered vertically in the table: (1.0845, 1.0860, 1.4091, 0.9392, 108.84, 109.57, 111.94, 110.30, 0.0).

1.4091, 0.9392, 108.84, 109.57, 111.94

^cReference 123.

^dThe methyl group is assumed to be symmetric.

 $F^- \cdot H_2O$, [FHCl]⁻, $Cl^{-} \cdot CH_{3}Cl$, and ClCH₂CN \cdot Cl⁻.^{61,66,132} For CH₃OHF⁻ this sensitivity is a consequence of the remarkably flat energy profile along the proton-transfer path in the vicinity of the minimum; n.b., along the reaction path mapped out in Sec. V, a displacement from equilibrium of 0.18 Å increases the potential energy only 0.86 kcal mol⁻¹. The DZ(d_{p}) RHF $r(H_{6}-F_{7})$ value of 1.359 Å increases to 1.461 Å when the TZ(+)(d,p) basis set is employed to adequately describe the diffuseness of the electron density. However, this shift is closely balanced by interfragment contraction arising from electron correlation effects, gauged, e.g., by the TZ(+)(d,p) MP2 distance $r(H_6-F_7) = 1.328$ Å.¹³³ By comparison, the H-F distance in the principally electrostatic $F^- \cdot CH_3F$ complex¹³⁴ is 2.602 Å and that in the covalent [FHF]⁻ ion is 1.1389 Å.^{67,68} The conspicuous inverse correlation of $r(O_5-H_6)$ and $r(H_6-F_7)$ in the theoretical structures can be illated by simple chemical intuition, but the similar relationship observed between $\alpha(O_5)$ H_6-F_7) and $r(H_6-F_7)$ is more obscure. As elucidated in Sec. V, the $\alpha(O_5-H_6-F_7)$ variations are consonant with the migration of the optimum position of F^- on a reaction path which originates asymptotically along the dipole moment of methanol and proceeds toward a linear, centrosymmetric conformation of the [-OHF]⁻ moiety as charge transfer ensues.

The changes in the theoretical equilibrium internal coordinates of methanol engendered by fluoride complexation nicely exhibit chemical aspects of the bonding in CH₃OHF⁻. These shifts are plotted in Figs. 4 and 5 and are listed in Table III for the TZ(+)(d,p) RHF, MP2, and CISD structural data. In the plots an unmistakable connection of complexation shifts to the $r(H_6-F_7)$ distance is established, revealing that variations among the predicted shifts are primarily caused by changes in the optimum interfragment separation alone, merely being indirect consequences of the different levels of electron correlation treatment. Moreover, the apparent trends in the complexation shifts can be understood as parts of a monotonic evolution of the methoxy moiety from a methanol to a methoxide optimum structure (cf. Tables I and II). For example, the TZ(+)(d,p) RHF, CISD, and MP2 predictions for the change in $r(C_1-O_5)$ upon adduct formation are -0.025, -0.029, and -0.031 Å, respectively, which comprise 36.8%, 41.0%, and 43.7% of the corresponding methanol-methoxide shifts, as a consequence of the decreasing order of optimum $r(H_6-F_7)$ distances, 1.461, 1.359, and 1.328 Å. Likewise, the RHF, CISD, and MP2 results for the shift in $\alpha(H_2-C_1-H_3)$ vary in the sequence -1.4° , -2.4° , and -2.6° as the equilibrium interfragment separation is reduced, constituting 25.8%, 41.2%, and 44.4% of the overall changes attending the proton-transfer

1130000 11. Ocometric structure of CH ₃ O \pm 11	IADLE II. Geo	metric	structure	σ	CH ₂ O	+	HP	
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Level of theory	DZ(<i>d</i> , <i>p</i>) RHF	TZ(+)(d,p) RHF	QZ(+)(2d,2p) RHF	$\frac{\mathrm{TZ}(+)(d,p)}{\mathrm{MP2}}$	TZ(+)(d,p) CISD
Coordinates		- · ·			
$r(C_{1}-H_{2,3,4})$	1.1288	1.1191	1.1163	1.1276	1.1228
$r(C_1 - O_5)$	1.3274	1.3362	1.3314 -	1.3587	1.3456
$r(O_5 - H_6)$	8	8	00	8	80
$r(H_6 - F_7)$	0.9034	0.9001	0.8983	0.9203	0.9109
$\alpha(H_2 - C_1 - H_{3.4})$	102.37	103.52	103.59	103.29	103.28
$\alpha(H_{2,3,4}-C_{1}-O_{5})$	115.88	114.92	114.86	115.11	115.12

^aBond distances in Å, angles in deg. See Fig. 3 for structural depictions and numbering of atoms.

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TABLE III. Geometric structure of the CH₃OHF⁻ complex.^{a,b}

Level of theory	DZ(<i>d</i> , <i>p</i>) RHF	TZ(+)(d,p) RHF ^c	QZ(+)(2 <i>d</i> ,2 <i>p</i>) RHF	TZ(+)(<i>d</i> , <i>p</i>) MP2	TZ(+)(d,p) CISD
Coordinates					
$r(C_1 - H_{23})$	1.0986	1.0935 (61)	1.0911	1.1043 (89)	1.0990 (77)
$r(C_1 - H_4)$	1.0974	1.0919 (102)	1.0895	1.1009 (111)	1.0965 (107)
$r(C_1 - O_5)$	1.3725	1.3798 (-254)	1.3755	1.3989 (-312)	1.3872 (-289)
$r(O_{s}-H_{s})$	1.0371	1.0037 (625)	1.0016	1,0741 (1111)	1.0432 (906)
$r(H_{6}-F_{7})$	1.3588	1.4614	1.4605	1.3280	1.3593
$\alpha(H_2-C_1-H_3)$	106.31	107.58 (-1.41)	106.99	106.59 (-2.63)	106.68 (-2.38)
$\alpha(H_2 - C_1 - O_5)$	113.12	112.48 (0.75)	112.50	112.76 (0.97)	112.70 (0.91)
$\alpha(H_4-C_1-O_4)$	110.12	109.51 (2.30)	109.51	109.80 (3.26)	109.82 (2.85)
$\alpha(C_1 - O_5 - H_6)$	107.40	107.89 (-1.85)	107.98	105.21 (-1.63)	106.23 (-1.72)
$\alpha(O_{5}-H_{6}-F_{7})$	174.68	174.01	174.53	176.08	175.48
$\tau(H_4-C_1-O_5-H_6)$	180.00	180.00	180.00	180.00	180.00
$\tau(C_1 - O_5 - H_6 - F_7)$	0.00	0.00	0.00	0.00	0.00

^aBond distances in Å, angles in deg. See Fig. 3 for structural depictions and numbering of atoms.

^bFor the TZ(+)(d,p) entries, complexation shifts relative to the corresponding coordinates for free methanol (Table I) are given in parentheses for all of the last digits affected.

^oAnalogous optimum parameters for eclipsed CH₃OHF⁻, as ordered vertically in the table: (1.0952, 1.0887, 1.3819, 1.0032, 1.4587, 106.96, 111.44, 108.07, 173.25, 0.00, 0.00).

process. While the connection of the RHF, CISD, and MP2 points by dashed lines in Figs. 4 and 5 is to be interpreted as a data correlation with respect to $r(H_6-F_7)$ rather than a genuine functional dependence, useful estimates of shifts at higher levels of theory can nevertheless be derived therefrom provided the optimum value of $r(H_6-F_7)$ is approximately known. Therefore, full geometry optimizations of intractable proportions can be obviated by exploitation of the apparent trends involving the equilibrium interfragment distance.

The system which most effectively facilitates the calibration of interfragment structural predictions for CH_3OHF^- is the $F^- \cdot H_2O$ complex, for which theoretical equilibrium coordinates are given in Table IV. The TZ (+)(d,p) results for the r(O-H) and r(H-F) distances in $F^- \cdot H_2O$ are, respectively, 0.003–0.010 shorter and 0.036– 0.041 Å longer than their CH₃OHF⁻ analogs, but the variations among the RHF, MP2, and CISD values are essentially the same. For example, the RHF/CISD and MP2/ CISD differences in r(H-F) are 0.101 and -0.027 Å for $F^- \cdot H_2O$, as compared to 0.102 and -0.031 Å for CH_3OHF^- . For $F^- \cdot H_2O$ the accuracy of the TZ(+)(d,p) predictions can be ascertained by comparison with rigorous QZ (+)(2d1f,2p1d) CCSD(T) optimum geometric parameters determined here (Table IV), which considerably advance previous knowledge⁶¹ of the structure of this complex. The salient feature of the QZ(+)(2d1f,2p1d) CCSD(T) data is the small interfragment separation r(H-F) = 1.366 Å, which demonstrates that the complex continues to contract as more flexible and highly polarized basis sets are employed in conjunction with higher-order correlation treatments. The TZ(+)(d,p) MP2 level of theory reproduces





FIG. 4. Correlation of complexation shifts in the optimum bond distances of methanol with the equilibrium interfragment separation $r(H_6-F_7)$ as given by the TZ(+)($d_{,p}$) RHF, MP2, and CISD levels of theory.

FIG. 5. Correlation of complexation shifts in the optimum bond angles of methanol with the equilibrium interfragment separation $r(H_6-F_7)$ as given by the TZ(+)(d,p) RHF, MP2, and CISD levels of theory.

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

TABLE IV.	Geometric structu	re of the F ⁻	• H ₂ O complex. ^{a,t}
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Level of theory	$TZ(+)(d_p)$ RHF	$\frac{\mathrm{TZ}(+)(d,p)}{\mathrm{MP2}}$	TZ(+)(d,p) CISD	TZ2P+diff CISD°	$\begin{array}{c} \text{QZ}(+)(2d1f,2p1d)\\ \text{CCSD}(\text{T}) \end{array}$
Coordinates		· · · · · · · · · · · · · · · · · · ·			······································
r(O-H')	0.9409 (-17)	0.9617 (-11)	0.9535	0.949	0.9587 (10)
r(O-H)	1.0007 (+581)	1.0637 (+1009)	1.0383	1.022	1.0584 (+987)
r(H-F)	1.4974	1.3686	1.3960	1.453	1.3664
$\alpha(H-O-H')$	102.94 (-3.18)	100.69 (-2.56)	101.38	102.8	101.70(-2.27)
α (O-H-F)	172.96	175.96	175.17	175.5	176.76
Total energy	-175.551 000	-176.006 511	-175.970 603	- 176.018 787	-176.135 542
$\omega_1(a')$	4171 (-46)	3892 (-62)	•••	4044	•••
$\omega_2(a')$	2985 (-1129)	2134 (-1697)	•••	2670	[2164] ^d
$\omega_3(a')$	1843	1714	• •••	1789	···· • ••
$\omega_4(a')$	563	585	· · · •	562	•••
$\omega_{5}(a')$	324	394		346	جري المعام يتدبع
$\omega_6(a'')$	1143	1187	•••	1125	and the second

^aBond distances in Å, angles in deg, total energies in hartree, and harmonic frequencies in cm⁻¹.

^bComplexation shifts relative to the corresponding coordinates for free H₂O are given in parentheses for all of the last digits affected.

^cReference 61.

^dEstimated by substituting the QZ(+)(2d1f,2p1d) CCSD(T) diagonal force constant, $f_{rr}(O-H) = 2.5177 \text{ mdyn } \text{\AA}^{-1}$, into the TZ(+)(d,p) MP2 force field in the normal coordinate analysis. 1.5 3.1

QZ(+)(2d1f,2p1d) CCSD(T) predictions most closely due to a fortuitous but advantageous cancellation of errors. By utilizing the comparisons in Table IV as a guide to the assessment of the CH₃OHF⁻ data, $r(O_5-H_6) = 1.07(1)$ Å, $r(H_6-F_7) = 1.32(1)$ Å, and $\alpha(O_5-H_6-F_7) = 177(1)^\circ$ are surmised as equilibrium parameters for the methanolfluoride complex. From the $r(H_6-F_7)$ distance, final estimates of the complexation shifts in the geometry of the methanol fragment are extracted from the correlations rein Figs. 4 and 5, vealed viz., $\delta r(C_1 - H_{2,3})$ Å, $\delta r(C_1 - H_4) = +0.011$ =+0.009Å, $\delta r(O_5 - H_6) = +0.11$ Å, $\delta r(C_1 - O_5) = -0.032$ $\delta \alpha (H_{2,3}-C_1-O_5) = +1.0^\circ,$ $\delta \alpha (H_2 - C_1 - H_3) = -2.7^\circ$, $\delta \alpha (H_4 - C_1 - O_5) = +3.4^\circ$, and $\delta \alpha (C_1 - O_5 - H_6) = -1.6^\circ$. The $\delta r(O_5-H_6)$ shift of 0.11 Å lies between the 0.045 and 0.22 Å elongations^{66–68} of r(H-F) observed in the [FHCl]⁻ and $[FHF]^-$ adducts, respectively. In addition, $r(H_6-F_7)$ in CH₃OHF⁻ is 44% longer than the equilibrium distance of free hydrogen fluoride, whereas the analogous interfragment separations⁶⁶⁻⁶⁸ in [FHCl]⁻ and [FHF]⁻ are, in order, 52% and 24% longer than the corresponding r_{e} values of the free HCl and HF monomers.

B. Vibrational spectra

The CH₃OHF⁻ system was subjected here to a quantitative, a priori vibrational analysis by means of the scaled quantum mechanical (SQM) force field procedure calibrated on four isotopomers of methanol. The initial step of the analysis entailed the determination of TZ(+)(d,p)RHF and MP2 quadratic force fields for CH₃OH, from which the harmonic vibrational frequencies appearing in Table V were computed. Excluding the highly anharmonic torsional mode involving internal rotation of the methyl group, the TZ(+)(d,p) RHF and MP2 frequencies (ω_i) lie uniformly above the experimental fundamental frequencies¹³⁵ (v_i) by 8.2%–13.1% and 1.7%–7.6%, respectively, the median overestimation being 9.6% and 3.0% in the two cases. In brief, the theoretical results are in accord

with systematic studies^{80,108,116,136-138} which have established the accuracy expected at these levels of theory, and no anomalous or peculiar experimental assignments are apparent. Similar agreement is observed for all of the gasphase fundamentals of CH₃OD, CD₃OH, and CD₃OD,¹³⁵ providing a total of 47 empirical frequencies for an optimization of SQM scale factors for the TZ(+)(d,p) MP2 force field. The low-frequency torsional modes for CH₃OD, CD₃OH, and CD₃OD were included in the data set, but that for CH₃OH itself was omitted due to excessively large tunelling splitting and vibration-rotation interaction.

The set of internal symmetry coordinates utilized in the SQM vibrational analysis is defined in Table VI. As shown therein, six chemically distinct scale factors $(f_1$ f_6) were assigned to the 12 internal coordinates (L_1-L_{12}) of the methanol group. The least-squares fit to the spectral data for the four methanol isotopomers gave the following optimum scale factors: f_1 (C–O str.) =0.958(14), f_2 (C–H str.)=0.892(4), $f_3(O-H str.)=0.921(6)$, $f_4(CH_3 def.)$ =0.940(5), f_5 (C-O-H bend)=0.956(15), and f_6 (CH₃ int. rot.) = 0.724(2), which collectively reduce the rms error in the final SQM frequencies to only 0.89%. Fermi resonance and differential anharmonicity effects essentially limit further improvements.^{114,117} The values of f_1-f_5 are representative of the TZ(+)(d,p) MP2 level of theory; the diminished magnitude of f_6 reflects the phenomenological nature of quadratic force constants derived via a direct fit to highly anharmonic vibrational frequencies. A summary of the SQM analysis for CH₃OH, including the total energy distributions (TEDs) for the normal vibrations, is also given in Table V. Analogous tables for the other three isotopomers of methanol, as well as a tabulation of the final TZ(+)(d,p) MP2/SQM quadratic force field, are provided as supplementary material.¹⁰² Previous theoretical studies of the vibrational spectrum of methanol include the analysis of Blom *et al.*¹¹⁸ in which a somewhat different scaling procedure was used to refine 4-31G RHF force

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IABLE V. VIDIATIONAL ANALYSIS OF $C\Pi_3$	O	2(
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Normal-mode	CERTIFICATION CONTRACTOR OF THE PARTY OF T			· · ·		IR	Total energy distribution
description	Assignment	$\omega(RHF)^{a}$	$\omega(MP2)^*$	v(SQM) ⁶	$\nu(\text{expt.})^c$	intensity	(TED) ²
OH stretch	$v_1(a')$	4162	3863	3707	3681	31.9	L ₄ (100)
CH ₃ asym. stretch	$v_2(a')$	3265	3193	3016	3000	16.3	$L_3(94) + L_2(6)$
CH ₂ sym. stretch	$v_3(a')$	3151	3061	2891	2844	47.8	$L_2(94) - L_3(6)$
CH ₂ scissor	$v_4(a')$	1627	1536	1489	1477	5.8	$L_6(87) + L_7(9)$
CH ₃ umbrella	$v_5(a')$	1601	1498	1452	1455	4.4	L ₅ (99)
COH bend	$v_6(a')$	1474	1385	1351	1345	18.1	$L_8(65) + L_7(28) - L_6(7)$
CH ₁ tilt	$v_7(a')$	1162	1091	1063	1060	0.2	$L_7(41) - L_1(40) - L_8(18)$
CO stretch	$v_8(a')$	1146	1061	1036	1033	115.3	$L_1(62) + L_7(22) - L_8(16)$
CH ₃ asym. stretch	$v_{q}(a'')$	3202	3133	2959	2960	38.2	$L_{9}(100)$
CH ₂ rock	$v_{10}(a'')$	1618	1519	1475	1477	4.7	$L_{10}(96) + L_{11}(5)$
CH ₂ twist	$v_{11}(a'')$	1272	1185	1149	1165	0.3	$L_{11}(95) - L_{10}(5)$
CH ₃ internal rotation	$v_{12}(a'')$	325	317	269	295	126.0	$L_{12}(102)$

^aUnscaled harmonic frequencies (cm^{-1}) determined at the TZ(+)(d,p) RHF and MP2 levels of theory.

^bSQM vibrational frequencies (cm⁻¹) derived from the TZ(+)(d,p) MP2 quadratic force field.

^cGas-phase fundamental frequencies from Ref. 135.

^dTheoretical infrared intensities (km mol⁻¹) within the double-harmonic approximation based on the unscaled TZ(+)(d,p) MP2 quadratic force constants and dipole-moment derivatives.

The percentage proportions k of the total energy (kinetic and potential) of the normal vibrations ascribed to the individual internal coordinates L_i are indicated by $L_i(k)$ entries. The signs preceding these entries denote the relative phases of the internal coordinates in the normal-mode eigenvectors.

constants on matrix-isolation frequencies of methanol and 11 deuterated variants. Perhaps the highest-level *ab initio* results to date for the geometric structure and harmonic frequencies of methanol appear in a 1992 paper by Lee and Rice.¹¹⁹

In Table VII, TZ(+)(d,p) RHF and MP2 harmonic vibrational frequencies and associated complexation shifts are listed for the CH₃OHF⁻ adduct. An SQM analysis of the TZ(+)(d,p) MP2 quadratic force constants was performed by employing the complete set of internal coordinates specified in Table VI and choosing the optimum f_1-f_6 values for methanol as scale factors for coordinates L_1-L_{12} of the complex. For the interfragment modes $(L_{13}-L_{15})$, scale factors of unity were assumed. The resulting v(SQM) frequencies and corresponding TEDs in Table VII constitute our final predictions for the overall vibrational spectrum of the CH₃OHF⁻ complex. The selection of internal coordinates for the analysis is shown to be perspicacious by the clear dominance of the leading component of the TEDs for all normal vibrations. The underlying TZ(+)(*d*,*p*) MP2/SQM quadratic force field of CH₃OHF⁻ is given in the supplementary tabulations.

The interfragment vibrational modes of CH₃OHF⁻ give rise to the fundamental frequencies $v_9(a')$, $v_{10}(a')$, and $v_{13}(a'')$, which appear at 420, 177, and 1226 cm⁻¹, respectively, according to the SQM analysis. The in-plane

TABLE VI. Definition of symmetry coordinates for the methanol-fluoride system.^a

Symmetry coordinate	Irrep.	Scale factor	Description
$L_1 = r(1,5)$	a'	f_1 :	CO stretch
$L_2 = 3^{-1/2} [r(1,2) + r(1,3) + r(1,4)]$	<i>a</i> ′	f_2	CH ₃ sym. stretch
$L_3 = 6^{-1/2} [2r(1,4) - r(1,2) - r(1,3)]$	a'	f_2	CH_3 asym. stretch
$L_{4} = r(5,6)$	a'	f_3	OH stretch
$L_{5} = 3^{-1/2} [\alpha(2,1,3) + \alpha(2,1,4) + \alpha(3,1,4)]$	<i>a</i> ′	f_4	CH ₃ umbrella
$L_6 = 6^{-1/2} [2\alpha(2,1,3) - \alpha(2,1,4) - \alpha(3,1,4)]$	a'	f_4	CH ₂ scissor
$L_{\tau} = 6^{-1/2} [2\alpha(4,1,5) - \alpha(2,1,5) - \alpha(3,1,5)]$	a'	f_{4}	CH ₃ tilt
$L_{\rm e} = \alpha(1.5.6)$	a'	fs	COH bend
$L_0 = 2^{-1/2} [r(1,2) - r(1,3)]$	<i>a</i> "	f_2	CH_1 asym. stretch
$L_{10} = 2^{-1/2} [\alpha(3,1,4) - \alpha(2,1,4)]$	<i>a</i> ″	f_	CH ₂ rock
$L_{11} = 2^{-1/2} [\alpha(2,1,5) - \alpha(3,1,5)]$	<i>a</i> "	f_4	CH_2 twist
$L_{12} = \tau(4, 1, 5, 6)$	<i>a</i> "	f_6	CH_3 internal rotation
$L_{12} = r(5,7)$	a'	1	F ⁻ stretch
$L_{14} = \alpha(1.5.7)$	a'	1	F ⁻ in-plane bend
$L_{15} = \theta_x(5,6,7)$	<i>a</i> "	1	-OHF linear bend

^aSee Fig. 3 for structural depictions and numbering of atoms; r(i,j) = i - j bond distance, $\alpha(i,j,k) = i - j - k$ bond angle, and $\tau(i,j,k,l)$ =dihedral angle between ijk and jkl planes. In addition, $\theta_x(O_5-H_6-F_7)$ is the x component of the unit vector directed from H₆ to F₇ in the coordinate system in which the O₅-H₆ bond defines the z axis and the C₁ atom lies in the yz plane along the +y direction. As such, $\theta_x(O_5-H_6-F_7)$ is a dimensionless, out-of-plane bending coordinate for which the bending planes are defined instantaneously by the molecular framework.

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

TABLE VII.	Vibrational	analysis	of the	CH ₃ OHF ⁻	complex. ^{a,b}
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Normal-mode description	Assignment	ω(RHF)	ω(MP2)	v(SQM)	IR intensity	Total energy distribution (TED)
CH ₃ asym. stretch	$v_1(a')$	3125 (-140)	3045 (148)	2876 (140)	94.8	$L_3(95) + L_2(5)$
CH ₃ sym. stretch	$v_2(a')$	3094 (-57)	2971 (-90)	2806 (85)	134.4	$L_2(95) - L_3(5)$
OH stretch	$v_3(a')$	2874 (-1288)	1986 (-1877) ^c	1909 (→1798)°	2148.7	L ₄ (92)
COH bend	$v_4(a')$	1728 (+254)	1652 (+267)	1612 (+261)	64.8	$L_8(97) + L_7(5) + L_{14}(-4)$
CH ₂ scissor	$v_5(a')$	1624 (-3)	1528 (-8)	1482 (-7)	5.2	$L_{6}(92)$
CH ₃ umbrella	$v_6(a')$	1585 (-16)	1464 (-34)	1419 (-33)	24.3	L ₅ (95)
CH ₃ tilt	$v_7(a')$	1215 (+53)	1163 (+72)	1128 (+65)	85.2	$L_{7}(89)$
CO stretch	$v_8(a')$	1187 (+41)	1124 (+63)	1100 (+64)	134.5	L ₁ (101) F-
F ⁻ stretch	$v_{9}(a')$	335	421	420	115.3	$L_{13}(95)$
F ⁻ in-plane bend	$v_{10}(a')$	171	177	177	18.6	$L_{14}(101)$
CH ₃ asym. stretch	$v_{11}(a'')$	3107 (95)	3004 (-129)	2837 (-122)	140.5	$L_{9}(100)$
CH ₂ rock	$v_{12}(a'')$	1602 (-16)	1499 (-20)	1451 (24)	0.1	$L_{10}(96)$
-OHF ⁻ linear bend	$v_{13}(a'')$	1274	1234	1226	12.2	$L_{15}(93)$
CH ₂ twist	$v_{14}(a'')$	1242 (-30)	1178 (-8)	1150 (+1)	13.7	$L_{11}(91) + L_{15}(5)$
CH ₃ internal rotation	$v_{15}(a'')$	97 (-228)	88 (-229)	75 (—194)	0.2	L ₁₂ (97)

^aSee footnotes a, b, d, and e of Table V.

^bComplexation shifts in the vibrational frequencies are given in parentheses.

Final predictions derived in the text (Secs. IV and VII): $\omega_3 = 2006$; $\delta\omega_3 = -1857$; $\nu_3 = 1456$; and $\delta\nu_3 = -2225$ cm⁻¹.

normal vibrations for fluoride excursions are described efficaciously by the O-F stretching (L_{13}) and C-O-F bending (L_{14}) coordinates alone, each producing a leading TED component within 5% of unity. Because dispersion forces significantly enhance ion-molecule binding in the CH₃OHF⁻ complex, the F⁻ stretching vibration is increased substantially by electron correlation effects; specifically, the TZ(+)(d,p) RHF \rightarrow MP2 shift in ω_0 is +86 cm⁻¹. Such occurrences are indeed prevalent in ionmolecule systems.⁶⁶ A useful comparison in assessing the value of v_0 (SOM) in CH₃OHF⁻ is provided by the analogous interfragment stretching frequency in the appreciably electrostatic $F^- \cdot CH_3F$ adduct, which is 240 cm⁻¹ smaller in magnitude.¹³⁴ The out-of-plane $v_{13}(a'')$ mode of CH₃OHF⁻, which is principally a perpendicular motion of the central proton, can be viewed aptly as a linear bending vibration of a hydrogen pseudobihalide anion [-OHF]⁻. The value of v_{13} (1226 cm⁻¹) is remarkably similar to the 1286 cm⁻¹ gas-phase bending fundamental of [FHF]^{-.68}

Of the 12 vibrational modes associated with the methanol fragment in CH₃OHF⁻, three exhibit fundamental frequencies which are dramatically different from their analogs in free methanol—the C-O-H bend (v_4) , the CH₃ internal rotation mode (v_{15}) , and the O-H stretch (v_3) . The close proximity of the fluoride ion to the hydroxyl group in the adduct increases v_6 at 1351 cm⁻¹ in CH₃OH to v_4 at 1612 cm⁻¹ in CH₃OHF⁻, with a concomitant aggrandizement of the IR intensity by a factor of 3.6. The considerable mixing of C-O-H bending and CH₃ tilting motions in v_6 (CH₃OH) is not present in v_4 (CH₃OHF⁻), and the latter mode is perhaps best considered the in-plane counterpart of the aforementioned -OHF⁻ linear bending fundamental of the complex, $v_{13}(a'') = 1226 \text{ cm}^{-1}$. The effective SQM torsional frequency for methyl rotation in CH₃OHF⁻, v_{15} =75 cm⁻¹, is a factor of 3.6 smaller than in CH₃OH, due to a significant decrease in the torsional barrier upon adduct formation.⁴ Both TZ(+)(d,p) RHF and CISD single-point energies, computed at the staggered and

eclipsed optimum TZ(+)(d,p) RHF structures reported in Tables I and III and appurtenant footnotes, confirm the reduction of the torsional barrier. For methanol the RHF and CISD vibrationless barriers are 1.18 and 1.22 kcal mol⁻¹, respectively, in excellent agreement with the effective, empirical barrier of 1.07 kcal mol^{-1,139} By comparison, the corresponding RHF and CISD torsional barriers for CH₃OHF⁻ are only 0.51 and 0.47 kcal mol⁻¹, respectively. Finally, the O-H stretching vibration (ν_3) in CH₃OHF⁻ is downshifted by ~2000 cm⁻¹ relative to





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Normal-mode description	Assignment	ω(RHF)	ω(MP2)	v(SQM)	IR intensity	Total energy distribution (TED)
CH ₂ sym. stretch	$v_1(a_1)$	2835	2732	2580	601.5	L ₂ (100)
CH ₂ umbrella	$v_2(a_1)$	1579	1478	1433	100.5	$L_{5}(102)$
CO stretch	$v_{3}(a_{1})$	1217	1128	1105	373.2	$L_1(103)$
CH ₂ asym. stretch	$v_{4}(e)$	2734	2669	2521	473.3 (2)	$L_3(100), L_9(100)$
CH. deformation	$v_s(e)$	1584	1482	1437	7.0 (2)	$L_6(99), L_{10}(99)$
CH ₃ tilt	$v_6(e)$	1262	1177	1141	1.0 (2)	$L_7(99), L_{11}(99)$

TABLE VIII.	Vibrational	analysis	of	CH ₃ O	Ξ.	\$
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*See footnotes a, b, d, and e of Table V.

 $v_1(CH_3OH)$. The predicted position of $v_3(CH_3OHF^-)$ is very sensitive to level of theory, and since this intense band is central to the characterization of CH_3OHF^- , special consideration is warranted.

In Table IV theoretical vibrational frequencies and complexation shifts for the F^- ; H_2O complex are listed as an aid to the accurate determination of v_3 (CH₃OHF⁻), and in Fig. 6 predicted downshifts in the harmonic frequency $\omega(O-H)$ and the quadratic force constant f_{rr} (O-H) are plotted for both F⁻ · H₂O and CH₃OHF⁻ relative to the associated changes in r(O-H). The expected correlation of increasing downshifts, $\delta\omega(O-H)$ and δf_{r} (O-H), with increasing displacements, δr (O-H), is evident for both species across levels of theory. The key observation is that for $F^- \cdot H_2O$ the $(\delta f_{rr}, \delta r)$ points in the TZ(+)(d,p) MP2 and QZ(+)(2d1f,2p1d) CCSD(T) cases are almost identical, (-6.034, 0.1009) vs (-5.985, 0.1009)0.0987) (mdyn $Å^{-1}$, Å), respectively. In brief, the balance of sizeable basis set and electron correlation errors at the modest $TZ(+)(d_p)$ MP2 level is such that rigorous predictions for $\delta f_{rr}(O-H)$ are well reproduced. While this fortunate occurrence is in part happenstance, it should nevertheless persist in the chemically similar CH₃OHF⁻ case. Accordingly, the TZ(+)(d,p) MP2 complexation shift for CH₃OHF⁻, $\delta f_{rr} = -6.250$, is modified slightly to $\delta f_{rr} = -6.20 \text{ mdyn Å}^{-1}$ on the basis of the F⁻ · H₂O calibration and adopted here as a final prediction. The frequency downshift resulting from this modification in the unscaled quadratic force field of the adduct is $\delta\omega_3(CH_3OHF^-)$ = -1857 cm⁻¹, a reduction 172 cm⁻¹ larger in magnitude than the previous $(6-31 + +G^{**} MP2)$ value of Bradforth et al.4 To derive an absolute result for the O-H harmonic stretching frequency in CH₃OHF⁻, it is noted that the TZ(+)(d,p) MP2 method yields $(\omega_1,\omega_3) = (3831,3954)$ cm^{-1} for H₂O, as compared to the firmly established experimental values $(\omega_1, \omega_3) = (3832, 3942)$ cm⁻¹.¹⁴⁰ Thus, there is reason to accept without modification the absolute TZ(+)(d,p) MP2 results for $f_{rr}(O-H)$ and $\omega(O-H)$ of CH₃OH, giving the final proposals f_{rr} (CH₃OHF⁻)=2.14 mdyn Å⁻¹ and ω_3 (CH₃OHF⁻)=2006 cm⁻¹. As in the $F^- \cdot H_2O$ case, the O-H stretching vibration in CH₃OHF⁻ exhibits a large, negative anharmonicity. Derivation of an effective fundamental frequency by the SQM procedure is not really appropriate in this instance; thus, modification of the v_3 (CH₃OHF⁻) = 1909 cm⁻¹ result in Table VII is necessary. Evaluation of the anharmonic component of the

O-H stretching mode in CH_3OHF^- is reserved for the variational vibrational analysis of Sec. VII.

The locations of the remaining nine fundamental frequencies pertaining to the methanol moiety in CH₃OHF⁻ become perspicuous upon consideration of the frequency shifts for the methanol to methoxide transformation. For this purpose, TZ(+)(d,p) RHF, MP2, and MP2/SQM spectral data for CH₃O⁻ were obtained, as presented in Table VIII. Because experimental information on the vibrational spectrum of gaseous CH₃O⁻ is severely limited, optimum scale factors for methanol were assumed in the SOM procedure for methoxide. Relative to CH₃OH, the C-H stretching frequencies of CH_3O^- , v_{4a} , v_1 , and v_{4b} , are reduced by 495, 311, and 438 cm^{-1} , in order, and the C–O stretching fundamental (v_3) is increased by 69 cm⁻¹, in accord with the underlying shifts in the equilibrium distances brought on by negative hyperconjugation. In CH_3OHF^- , the complexation shifts (in cm⁻¹) for the C-H stretches, $\delta v_1(-140)$, $\delta v_2(-85)$, and $\delta v_{11}(-122)$, thus exhibit about 28% of the total effect of proton transfer, while the analogous change in the C–O stretch, δv_8 (+64), ostensibly includes almost all of the methanol to methoxide shift. It is noteworthy that the extensive mixing of C–O stretching and CH₃ tilting motions in v_8 (CH₃OH) is completely absent in CH₃OHF⁻ (cf. TEDs in Tables V and VII) and that all of the C-H fundamental bands in methanol become more intense by at least of factor of 3 upon fluoride complexation. The deformation frequencies of the methyl group in the 1400–1500 cm^{-1} region vary only a limited amount during the proton-transfer process. In particular, the triad $(v_4, v_5, v_{10}) = (1489, 1452, 1475)$ cm^{-1} correlates in CH₃OH to (v_5, v_6, v_{12}) = (1482,1419,1451) cm⁻¹ in CH₃OHF⁻, and ultimately to $(v_{5a}v_2, v_{5b}) = (1437, 1433, 1437)$ cm⁻¹ in CH₃O⁻. Each of these fundamental absorptions is relatively weak in CH₃OH, but the lower-frequency umbrella mode selectively becomes more intense as proton transfer occurs. The last two fundamental vibrations of the methyl group in CH₃OH, $(v_7, v_{11}) = (1063, 1149)$ cm⁻¹, form a closely spaced doublet in CH₃OHF⁻, $(v_7, v_{14}) = (1128, 1150)$ cm^{-1} , and finally coalesce into the degenerate CH₃ tilting manifold in CH₃O⁻, $(v_{6a}, v_{6b}) = (1141, 1141)$ cm⁻¹. The predominant mechanism of this progression is the unmixing of the large C-O stretching component from the v_7 mode in CH₃OH to yield a pure CH₃ tilting vibration at

TABLE IX. Proton-transfer energy for $CH_3OH + F^- \rightarrow CH_3O^- + HF$.^a

and the second second	DZ(<i>d</i> , <i>p</i>) (68)	TZ(+)(d,p) (97)	QZ(+)(2d,2p) (136)	QZ(+)(2d1f,2p1d) (181)	[13s8p6d4f,8s6p4d](+) (482)
ΔE _e [RHF]	11.73	19.82	18.67	17.76	16.28
δ[MP2]	-5.03	-2.34	-1.77	2.24	1 59
δ[MP3]	+1.63	-0.73	0.69	-0.57	[-0.57]
$(\delta[MP4],\delta[CCSD])$	(-2.49,na)	(+1.39, +0.77)	(+0.95, +0.69)	(+0.81, +0.70)	[+0.81, +0.70]
δ [CCSD(T)]	(na,na)	(-0.87, -0.25)	(-0.26, -0.50)	(-0.69, -0.58)	[-0.69, -0.58]
$\Delta E_e(\text{corr})$	na	17.27	16.40	15.07	[14.24]
$\Delta E_0 = \Delta E [\text{fp}] + \Delta [\text{ZPVE}]$	= 14.24 - 3.68(20) =	$=10.56 \text{ kcal mol}^{-1}$			

 $\Delta H_{acid}^{\circ}(CH_{3}OH) = \Delta E_{0} + \Delta H_{f,0}^{\circ}(H^{+}) + \Delta H_{f,0}^{\circ}(F^{-}) - \Delta H_{f,0}^{\circ}(HF) = 10.56 + 365.22 - 59.91 + 65.13 = 381.00 \ [381.7 \pm 1]^{b} \ \text{kcal mol}^{-1}$ $D_{0}(CH_{3}O-H) = \Delta H_{acid}^{\circ}(CH_{3}OH) - I.P.(H) + E.A.(CH_{3}O) = 381.00 - 313.75 + 36.20 = 103.45 \ [104.1 \pm 1]^{b} \ \text{kcal mol}^{-1}$

^aAll entries in kcal mol⁻¹; na=not available. The TZ(+)(d,p) CISD supermolecule geometries of Tables I and II are assumed as reference structures. Beneath each basis set the corresponding number of contracted Gaussian functions for CH₃OHF⁻ is listed. The symbol δ denotes the *increment* in the reaction energy (ΔE_e) relative to the preceding level of theory. In evaluating these contributions, the MP3 \rightarrow (MP4,CCSD), \rightarrow CCSD(T) higher-order correlation sequences are constructed as complementary indicators. For the [13s8p6d4f,8s6p4d](+) basis set, the increments in brackets are assumed values based on the QZ(+)(2d1f,2p1d) CCSD(T) predictions. The estimated [13s8p6d4f,8s6p4d](+) net reaction energy, $\Delta E_e(\text{corr})$, is equivalent to the energy change, $\Delta E_e[fp]$, predicted at the focal-point (fp) level of theory described in the text. ^bFinal fp predictions derived from the reaction CH₃OH+OH⁻ \rightarrow CH₃O⁻ +H₂O.

higher frequency as local C_{3v} symmetry develops in the methoxy moiety.

C. Thermochemistry

The proton-transfer energy for the $CH_3OH + F^-$ reaction is merely the difference between the gas-phase acidities of methanol and hydrogen fluoride. While $\Delta H^{\circ}_{acid}(HF)$ is firmly established,¹⁴¹ inconsistencies of a few kcal mol⁻¹ in thermochemical cycles involving $\Delta H^{\circ}_{acid}(CH_3OH)$ have appeared in the literature over the last 15 years. Relative acidities of alcohols and alkanethiols derived from protontransfer equilibria in an ion-cyclotron resonance (ICR) cell were reported by Bartmess and McIver¹⁴² in 1977, giving $\Delta H_{acid}^{\circ}(CH_3OH) = 378.4 \text{ kcal mol}^{-1}$ assuming $\Delta H^{\circ}_{acid}(HF)$ as a reference. From this gas-phase acidity, coupled with I.P.(H) and a contemporaneous value¹⁴³ for DH^o(CH₃O-H), an electron affinity of 39 ± 3 kcal mol⁻¹ was surmised for the methoxy radical. In 1978, Engelking, Ellison, and Lineberger¹⁴⁴ produced methoxide ions in an electrical discharge of CH₃OH/N₂O or CH₃OH alone and used photoelectron spectroscopy to determine an improved electron affinity, E.A. $(CH_3O) = 36.20 \pm 0.25 \text{ kcal mol}^{-1}$. Subsequently, the thermochemical cycles of Bartmess and McIver were inverted to yield $DH^{\circ}(CH_{3}O-H) = 100.9 \pm 1$ kcal mol^{-1} from the directly measured E.A.(CH₃O) and $\Delta H^{\circ}_{acid}(CH_3OH)$ quantities. This revision was at variance not only with the aforementioned value of Benson and Shaw $(103.6\pm2 \text{ kcal mol}^{-1})^{143}$ but also with the dissociation energy deduced by Batt and McCulloch¹⁴⁵ (104.0 ± 0.2 kcal mol⁻¹), who studied the pyrolysis kinetics of dimethyl peroxide and determined $\Delta H_f^{\circ}(CH_3O) = 3.8$ kcal mol⁻¹ from the Arrhenius parameters for O–O bond fragmentation.

A compilation of gas-phase acidities of 81 oxygen, nitrogen, carbon, sulfur, and phosphorus acids measured via ICR spectronomy was published by Bartmess *et al.*¹⁴⁶ in 1979. In assessing this comprehensive set of data, including their revised acidity for methanol (379.2 kcal mol⁻¹), the authors argued that "the excellent correlation between sev-

eral anchor points and the relative acidity scale precludes any major systematic accumulation of errors and leads to an estimated uncertainty of ± 2 kcal mol⁻¹" in the ΔH°_{acid} values. Nonetheless, it was noted that the acidities for aliphatic alcohols and acetone determined by ICR methods were consistently about 2 kcal mol⁻¹ smaller than corresponding values calculated from associated electron affinities and A-H bond energies, a discrepancy which was attributed to small activation barriers for radical-radical recombination in the kinetic experiments from which the bond energies were ascertained. The ICR value for $\Delta H_{acid}^{\circ}(CH_{3}OH)$ was subsequently disputed, however. In 1984 Moylan and Brauman¹⁴⁷ pointed out that the indirect result for ΔH_{acid}° (381.4 kcal mol⁻¹) given by the best electron affinity and bond energy data is supported by the relative proton-transfer rates observed for the reactions of benzyl and neopentyl alcohol with the fluoride ion. Then in 1986 Meot-Ner and Sieck¹⁴⁸ directly measured the gasphase acidity of CH₃OH relative to H₂O via variabletemperature pulsed high-pressure mass spectrometry, arriving at $\Delta H_{acid}^{\circ}(CH_{3}OH) = 381.6 \pm 0.7 \text{ kcal mol}^{-1}$. Quite recently, Bauschlicher and co-workers¹⁴⁹ performed an *ab* initio study of the bond dissociation energies of methanol. in which results at the modified coupled-pair functional (MCPF) level of theory obtained with a $[4s_3p_2d_1f/$ 4s2p1d] atomic natural orbital basis set were adjusted with bond additivity corrections derived from H₂O calibrations. Based on their final prediction, $D_0(CH_3O-H) = 105.0 \pm 2$ kcal mol⁻¹, the bond energy initially derived¹⁴⁴ from the acidity/E.A. cycle is clearly ruled out, but the empirical values of Benson and Shaw¹⁴³ and Batt and McCulloch¹⁴⁵ appear to be only slightly low, giving credence to the $\Delta H^{\circ}_{acid}(CH_3OH)$ result¹⁴⁷ based thereon.

In Table IX theoretical data obtained here in a concerted effort to establish the proton-transfer energy for $CH_3OH+F^- \rightarrow CH_3O^- + HF$ are presented, followed by reevaluations of $\Delta H^{\circ}_{acid}(CH_3OH)$ and $D_0(CH_3O-H)$. Hartree–Fock theory provides a good first description of the isogyric proton-transfer process, apparently predicting

	DZ(<i>d</i> , <i>p</i>) (68)	$\begin{array}{c} \mathrm{TZ}(+)(d_{2}p)\\ (97) \end{array}$	QZ(+)(2d,2p) (136)	QZ(+)(2d1f,2p1d) (181)	[13s8p6d4f,8s6p4d](+) (482)
$\Delta E_{e}[RHF]$	-34.06	-24.59	-24.66	-24.80	-25.08
δ[MP2]	-8.14	4.47	-4.07	- 5.05	-4.47
δ[MP3]	+1.98	-0.57	-0.51	[0.51]	[-0.51]
$(\delta[MP4],\delta[CCSD])$	(-2.10,na)	(+1.27, +0.94)	(+0.91, +0.91)	[+0.91, +0.91]	[+0.91, +0.91]
δ [CCSD(T)]	(na,na)	(-0.87, -0.54)	(-0.80, -0.79)	[-0.80, -0.79]	[-0.80, -0.79]
$\Delta E_e(\text{corr})$	na	-29.23	29.13	[-30.24]	[-29.95]
$\Delta E_0 = \Delta E_e[\text{fp}] + \Delta [\text{ZPVE}]$	=-29.95-0.49=	$-30.44 \text{ kcal mol}^{-1}$,

TABLE X. Complexation energy for $CH_3OH + F^- \rightarrow CH_3OHF^{-,a}$

^aAll entries in kcal mol⁻¹; na=not available. See footnote a of Table IX.

 ΔE_e within 3 kcal mol⁻¹ of the full configuration interaction limit for each basis set. After a sizeable increase in the endoergicity of the reaction upon basis set augmentation with diffuse orbitals,¹⁵⁰ the RHF results for ΔE_{\bullet} steadily decrease to 16.28 kcal mol⁻¹ for the [13s8p6d4f, 8s6p4d](+) basis, a value which should be close to the Hartree-Fock limit since a composite of 482 functions is included in the computation. The δ [MP2] correlation term displays some oscillation in the basis set series while diminishing to -1.59 kcal mol⁻¹ in the final prediction, the differential correlation effect favoring $CH_3O^- + HF$ over CH_3OH $+F^-$. None of the individual higher-order correlation terms for the larger basis sets exceeds 1 kcal mol^{-1} , and the net higher-order effect is only about -0.5 kcal mol⁻¹. The crux of the convergence analysis in Table IX is that the higher-order correlation contributions vary insignificantly past the TZ(+)(d,p) level. For example, the δ [MP3] value in the DZ(d,p) case is +1.63, but the three succeeding entries in the basis set series are -0.73, -0.69, and -0.57 kcal mol⁻¹. Such occurrences have been observed repeatedly in our laboratory, 151-153 suggesting the addition ofa that QZ(+)(2d1f,2p1d) \rightarrow [13s8p6d4f,8s6p4d](+) MP2 basis set shift to QZ (+)(2d1f,2p1d) CCSD(T) predictions provides an excellent approximation to full [13s8p6d4f, 8s6p4d](+)CCSD(T) results. Following a previously used designation,¹⁵² this procedure is termed the focal-point (fp) level of theory here. In Table IX, values assumed in the fp approximation are shown in brackets, leading to a final prediction of $\Delta E_{a}[fp] = 14.2 \text{ kcal mol}^{-1}$.

The zero-point vibrational energy (ZPVE) contribution to the proton-transfer energy is ascertained as follows. For methanol and methoxide, the formula

$$ZPVE = \sum_{i} \{v_i(SQM) + 3(0.98) \\ \times \omega_i[TZ(+)(d,p)MP2]\}/8$$
(5)

is employed, which amounts to treating the vibrational modes of these species as independent anharmonic oscillators¹⁵⁴ and estimating the TZ(+)(*d*,*p*) MP2 harmonic frequencies to be 2% too large on average. For hydrogen fluoride, a ZPVE of 2047 cm⁻¹ arises from the accepted spectroscopic constants ω_e =4138.3 and $\omega_e x_e$ =89.88 cm⁻¹.¹⁵⁵ Hence, Δ [ZPVE]=-3.68±0.20, and ΔE_0 [fp]=10.6 kcal mol⁻¹. Adopting the heats of formation of

H, H⁺, F⁻, and HF from the JANAF Thermochemical Tables,¹⁴¹ as well as E.A.(CH₃O) from Engelking *et al.*,¹⁴⁴ ΔH°_{acid} (CH₃OH, 0 K)=381.0 and D_0 (CH₃O-H)=103.5 kcal mol⁻¹ are computed from ΔE_0 [fp].

Assessment of the accuracy and probable direction of error in the thermochemical predictions in Table IX is paramount. By applying theoretical methods to an appropriate overall proton-transfer process rather than the halfreaction $CH_3OH \rightarrow CH_3O^- + H^+$, errors arising from numerous sources are balanced in the determination of $\Delta H_{acid}^{\circ}(CH_{3}OH)$, including those due to basis set incompleteness, core electron correlation, and limitations of the valence-shell correlation treatment. For the half-reactions $HF \rightarrow H^+ + F^-$ and $H_2O \rightarrow H^+ + OH^-$, the fp method overestimates the experimental ΔH_0° values [370.44 (HF) and 389.48 (H₂O) kcal mol⁻¹]¹⁴¹ as a consequence of basis set superposition errors, inter alia; however, the corresponding discrepancies are merely 1.42 and 0.76 kcal mol^{-1} . Thus, if the gas-phase acidity of H₂O is determined theoretically from the reaction $H_2O + F^- \rightarrow OH^- + HF$ using the experimental $\Delta H^{\circ}_{acid}(HF)$ as a reference, an underestimation of only 1.42-0.76=0.66 kcal mol⁻¹ occurs. In essence, this differential error is responsible for engendering shifts of +0.66 kcal mol⁻¹ in the thermochemical predictions for methanol if the reaction CH₂OH $+F^- \rightarrow CH_3O^- + HF$ is replaced by CH₃OH $+OH^- \rightarrow CH_3O^- + H_2O$ as the basis for the analysis, as summarized in Table IX. Insofar as the chemical foundations for this latter approach are preferred, $\Delta H_{acid}^{\circ}(CH_{3}OH, 0, K) = 381.7 \pm 1$ and $D_{0}(CH_{3}O-H)$ = 104.1 ± 1 kcal mol⁻¹ constitute the final proposals and error estimates derived from our theoretical considerations.

If standard statistical thermodynamic formulas¹⁵⁶ are invoked with the SQM vibrational frequencies of methanol and methoxide (Tables V and VIII), the $T=0\rightarrow 298$ K correction for ΔH°_{acid} (CH₃OH) is found to be 1.18 kcal mol⁻¹. Thus, the empirical acidity of Meot-Ner and Sieck¹⁴⁸ corresponds to ΔH°_{acid} (CH₃OH, 0 K)=380.4±0.7 kcal mol⁻¹, whose upper limit lies well within the error bars of our final theoretical recommendation. In summary, an internal consistency exists between independent empirical^{143,145} and theoretical¹⁴⁹ values for D_0 (CH₃O–H), the experimental electron affinity of CH₃O,¹⁴⁴ direct relative acidity measurements for water and methanol,¹⁴⁸ and our

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high-level $\Delta H^{\circ}_{acid}(CH_3OH)$ prediction. Thus, all of the more recent information supports the contention that the earlier ICR acidity values^{142,146} for methanol and the O-H bond energy derived from them¹⁴⁴ are ~3 kcal mol⁻¹ in error.

A systematic analysis of the fluoride complexation energy of CH₃OHF⁻ is detailed in Table X. The DZ(d,p)binding energies are 9–14 kcal mol $^{-1}$ too large, primarily because the lack of diffuse orbitals in the basis has far more severe consequences for the atomic fluoride ion than for the spatially extended ion-molecule complex. The use of the TZ(+)(d,p) basis ameliorates this situation considerably. The TZ(+)(d,p) RHF complexation energy (24.59) kcal mol⁻¹) increases by only 0.5 kcal mol⁻¹ as the Hartree-Fock limit is approached. The associated secondorder correlation term accounts for the bulk of the dispersion component of the binding energy; in particular, the TZ(+)(d,p) δ [MP2] value is -4.47 kcal mol⁻¹, a result which is reproduced in the final [13s8p6d4f, 8s6p4d](+) δ [MP2] prediction after variations in the basis augmentation series of the order of 0.5 kcal mol^{-1} . As observed for the proton-transfer energy (Table IX), the higher-order correlation terms for the fluoride affinity are quite insensitive to basis set variations and largely cancel one another, giving a net higher-order contribution of only about -0.4kcal mol⁻¹ and thus a total dispersion component approaching 5 kcal mol⁻¹. In comparison, correlation contributions to ion-molecule binding energies of 2.5-4.5 kcal mol^{-1} have been observed in previous *ab initio* studies of $[FHCN]^{-,62}$ $[FHNC]^{-,62}$ $[FHC1]^{-,66}$ and $ClCH_2CN \cdot Cl^{-,132}$ After the fp extrapolation of the [13s8p6d4f, 8s6p4d](+) MP2 and QZ(+)(2d, 2p)CCSD(T) results, a final prediction of $\Delta E_e[fp] = -29.95$ kcal mol⁻¹ is ascertained.

The effect of zero-point vibrational energy on the fluoride affinity of methanol proves to be quite peculiar. By employing Eq. (5) for all of the vibrational modes in both CH₃OH and CH₃OHF⁻, a ZPVE binding-energy enhancement of 0.39 kcal mol⁻¹ is computed. This prediction can be refined by substitution of a more rigorous result for the ZPVE component arising from the highly anharmonic O-H and F⁻ stretching modes in CH₃OHF⁻. According to the variational analysis of Sec. VII, the ground-state vibrational energy attributable to the two-dimensional stretching space of the -OHF⁻ hydrogen pseudobihalide anion is 1141 cm⁻¹, as compared to 1176 cm⁻¹ from Eq. (5). With this modification the ZPVE enhancement of the binding energy is not only maintained but actually increased to 0.49 kcal mol⁻¹. The source of this effect is clearly the prodigious reduction of the O-H stretching frequency upon adduct formation. However, the most unusual characteristic of the CH₃OHF⁻ system is that the resulting decrease in the intramolecular ZPVE of methanol is not overcome by the newly quantized interfragment vibrations.

The ZPVE effect engenders a final energetic prediction of $\Delta E_0 = 30.4 \pm 1$ kcal mol⁻¹ for the complexation reaction. Ostensibly this result is in good agreement with the fluoride affinity of methanol (29.6 kcal mol⁻¹) determined by Larson and McMahon¹⁷ via ICR experiments. However, the empirical value is properly an enthalpy of dissociation at 298 K. Based on the vibrational data reported here, the corresponding ΔH_0° should be 0.7–1.0 kcal mol⁻¹ smaller, depending on whether methyl internal rotation is treated as a hindered rotor or a harmonic vibration.¹⁵⁶ Therefore, the thermal correction serves to shift the experimental fluoride affinity somewhat outside the error bars of the theoretical prediction.

D. Bonding analysis

Some insight into the nature of fluoride binding to Brønsted acids is gained from relationships among empirical gas-phase acidities (ΔH°_{acid}) and fluoride affinities, as revealed in the ICR studies of Larson and McMa-hon.^{17,18,157} Among groups of organic species of comparable acidity, saturated aliphatic alcohols exhibit the largest F^- binding energies. Moreover, plots of fluoride affinity vs $\Delta H_{\rm acid}^{\circ}$ within homologous series of alcohols, including those both more and less acidic than HF, display a near linear dependence with a slope of 0.5 over a remarkably large range. These observations have been adduced¹⁷ in characterizing ROHF⁻ ions as significantly covalent complexes with near equal sharing of the central proton in single-minimum potentials or double-well potentials with small proton-transfer barriers. The Cl⁻ adducts of Brønsted acids also exhibit a correlation of halide affinity with $\Delta H_{\rm acid}^{\circ}$,²⁰ whose physical basis has been linked to an inverse dependence of the electrostatic potentials surrounding the chloride ion and the acidic proton in these appre-ciably electrostatic complexes.^{66,132} For homologous ROHCl⁻ complexes, the chloride affinity varies linearly with ΔH_{acid}° as in the fluoride case, but the slope of the plot is only 0.2, implicating substantially reduced covalency in the hydrogen bonds. A simple empirical equation which reproduces A⁻ · HB binding energies to the level of 2-3 kcal mol^{-1} for sundry ion-molecule complexes has been formulated¹⁵⁸ in terms of the electronegativities of the groups A and B and the gas-phase acidities of HA and HB.

To definitively characterize the bonding in CH₃OHF⁻, the energy decomposition scheme of Morokuma¹⁵⁹⁻¹⁶² was implemented here using the TZ(+)(d,p) basis set and the corresponding CISD optimum geometric structures reported above. The bonding analysis was comprised of the following sequential steps: (a) The RHF energy and molecular orbitals were determined for each of the F⁻ and CH₃OH fragments to obtain the individual Hartree-Fock wave functions $\Psi^{\circ}(F^{-})$ and $\Psi^{\circ}(CH_{3}OH)$ and the composite energy E_1 . (b) The nascent hydrogen bond was formed by placing the fluoride ion adjacent to the methanol framework at an r(O-F) distance of 2.4007 Å and an α (C-O-F) angle of 103.67°, i.e., the optimum position relative to the carbon and oxygen atoms in the final ionmolecule complex. (c) The energy (E_2) of the unrelaxed, composite Hartree product wave : function $\Psi^{\circ}(F^{-})\Psi^{\circ}(CH_{3}OH)$ was evaluated to quantify the electrostatic binding component $\epsilon_{\rm ES} = E_2 - E_1$. (d) Orbital relaxation within each fragment was allowed in the presence of mutual electrostatic interactions, giving the optimum Har-

product energy (E_3) and wave function tree $\Psi(F^{-})\Psi(CH_{3}OH)$, and hence the polarization contribution $\epsilon_{\rm PL} = E_3 - E_2$. (e) A fully antisymmetrized composite Hartree-Fock wave function was constructed from the unrelaxed, overlapping molecular orbitals of the fragments, yielding a resultant energy (E_4) and the interfragment exchange repulsion term, $\epsilon_{\rm EX} = E_4 - E_2$. (f) The geometry of the hydrogen-bonded complex was relaxed to its optimum structure, primarily by elongating the O-H distance by 0.0906 Å. (g) The proper RHF energy (E_5) of the complex was determined at the relaxed geometry. Because the portion of the RHF binding energy $(E_5 - E_1)$ not accounted for by the electrostatic, polarization, and exchange terms is attributable to charge-transfer (ϵ_{CT}) and higherorder mixing (ϵ_{MIX}) components, the sum $\epsilon_{CT} + \epsilon_{MIX} = E_5$ $-E_4-E_3+E_2$ was thus ascertained. No attempt was made to evaluate the CT term separately by means of the refined procedure of Kitaura and Morokuma.¹⁶⁰ (h) The correlation-energy shift in the fluoride binding energy, as given by the CISD method, was equated to the dispersion contribution (ϵ_{DISP}) to the hydrogen bond. Note that the effect of geometry relaxation within the methanol moiety during adduct formation, which amounts to -1.56 kcal mol^{-1} at the RHF level, is attributed to the CT+MIX term alone. This ascription is physically appealing, albeit not unique because the components of the Morokuma decomposition are not invariant to the path assumed in formation of the complex.¹⁶²

According to the TZ(+)(d,p) Morokuma analysis, the fluoride affinity of methanol is comprised of the components $\epsilon_{\rm ES} = -41.03$, $\epsilon_{\rm EX} = 39.83$, $\epsilon_{\rm PL} = -10.55$, $\epsilon_{\rm CT}$ $+\epsilon_{MIX} = -12.84$, and $\epsilon_{DISP} = -3.94$ kcal mol⁻¹. The electrostatic contribution to the binding energy is clearly the largest stabilizing influence, but the considerable exchange repulsion within the tight CH₃OHF⁻ complex almost completely balances the $\epsilon_{\rm ES}$ term. While polarization and dispersion effects jointly stabilize the adduct by 14.5 kcal mol^{-1} , the large fluoride affinity of methanol is ultimately realized only after charge transfer and higher-order mixing occur. These results are elucidated by comparison with the binding-energy components (in kcal mol⁻¹) of the pre-dominantly electrostatic [FHCl]⁻ complex.⁶⁶ The $\epsilon_{\rm ES}$ term (-27.3) for [FHCl]⁻ is substantially greater than $\epsilon_{\rm EX}$ (+18.3), while $\epsilon_{\rm PI}$ (-5.2) and $\epsilon_{\rm CT} + \epsilon_{\rm MIX}$ (-5.0) are less than half of their corresponding magnitudes for CH₃OHF⁻; the dispersion components in the two cases are commensurate. Moreover, the ES stabilization in [FHCl] is described well by a point-charge model in that the electrostatic potential surrounding free hydrogen fluoride at the position $\mathbf{x}(\mathbf{Cl}^{-})$ of the chloride ion in the adduct corresponds to a binding energy of $-e\phi[\mathbf{x}(Cl^{-})] = -26.20$ kcal mol⁻¹, only 1.1 kcal mol⁻¹ smaller in magnitude than $\epsilon_{\rm ES}$ itself.⁶⁶ Application of this point-charge model to CH₃OHF⁻ yields $-e\phi[\mathbf{x}(\mathbf{F}^{-})] = -31.27$ kcal mol⁻¹ which differs from the associated $\epsilon_{\rm FS}$ value by almost 10 kcal mol^{-1} . In brief, the strong hydrogen bond in CH₃OHF⁻, and presumably other alcohol-fluoride complexes, exhibits substantial covalent character to the degree that the electrostatic bonding models which have been applied with some success to the chloride adducts of Brønsted acids²⁰ are likely to be rather deficient for their fluoride analogs.

Final qualitative information regarding the redistribution of charge attending the formation of the methanolfluoride complex is contained in the net atomic charges of the TZ(+)(d,p) RHF Mulliken population analysis of CH_3OHF^- at the corresponding optimum geometry, viz., q(F) = -0.89, q(O) = -0.48, q(C) = -0.15, $q(H_{2.3})$ =0.06, $q(H_4)=0.04$, and $q(H_6)=0.37$ e. The charge transferred from the fluoride ion, 0.11 e, is considerably larger than that exhibited by the electrostatic chloride adducts [FHC1]⁻ and ClCH₂CN · Cl⁻.^{66,132} The Mulliken net charges for free methanol reveal that during formation of CH₃OHF⁻, the oxygen and hydrogen atoms in the hydroxyl group become more negatively and positively charged, respectively, by roughly equal amounts (0.11 e). Therefore, the TZ(+)(d,p) RHF Mulliken analysis suggests that the net redistribution of charge involves electron transfer from the fluoride ion to the methyl moiety, in essence a nascent negative hyperconjugation which is manifested in the geometric structural shifts discussed above.¹³¹

V. MINIMUM ENERGY PATH FOR PROTON TRANSFER

Among the numerous theoretical studies which have investigated the existence or nonexistence of protontransfer barriers in [AHB]⁻ complexes,^{17,37-66} rigorous characterizations of the structure of proton-transfer surfaces at reliable levels of theory are rare. For example, it has been shown⁶¹ that in the $F^- \cdot H_2O$ complex, the energy profile for proton migration from equilibrium with the O-F distance fixed exhibits a shallow secondary minimum for Hartree-Fock wave functions and an inflection region in correlated treatments. For CH₃OHF⁻, analogous $6-31 + +G^{**}$ RHF and MP2 one-dimensional energy curves display inflection regions only, although a secondary plateau is quite pronounced in the RHF case.⁴ However, observations such as these are susceptible to misinterpretation and certainly do not rule out the existence of proton-transfer paths exclusively of positive curvature. The lack of a proton-transfer barrier on a multidimensional surface is demonstrated if a continuous, minimum energy path (MEP) can be mapped out whose energy dependence is at least monotonic, if not devoid of the inflection regions of negative curvature typified in Figs. 1 and 2. In constructing such a path, a continually increasing geometric variable is selected which drives the excursion between initial and final configurations, and constrained optimizations of all remaining coordinates are performed for each value of this reaction variable. However, pitfalls must be avoided in this approach, most notably, an improper choice of the reaction variable which can lead to an unphysical MEP in certain circumstances.¹⁶³ Whenever a barrier to proton transfer exists, a jump discontinuity in the MEP and an associated change in sign of the energy gradient are generally observed in the region of the transition state.¹⁶³ In this

TABLE XI. Optimum TZ(+)(d,p) CISD geometric structures along the minimum energy path (MEP) for proton transfer.^{a,b}

* 5			y (Å)	· · · ·	
	······································	-0.223 52	0.0	0.282 84	+ ∞
Coordinates					· · · ·
$r(C_1 - H_{2,3})$	1.0913	1.0990	1.1040	1.1104	1.1228
$r(C_1-H_4)$	1.0858	1.0965	1.1008	1.1076	1.1228
$r(C_1 - O_5)$	1.4161	1.3872	1.3776	1.3665	1.3456
$r(O_5-H_6)$	0.9526	1.0432	1.1639	1.4054	00
$r(H_{6}-F_{7})$	00	1.3593	1.1639	1.0054	0.9109
$\alpha(H_2-C_1-H_3)$	109.06	106.68	106.13	104.95	103.28
$\alpha(H_{2,3}-C_{1}-O_{5})$	111.79	112.70	113.31	114.04	115.12
$\alpha(H_4-C_1-O_5)$	106.97	109.82	111.11	112.62	115.12
$\alpha(C_1 - O_5 - H_6)$	107.95	106.23	107.65	110.27	0.0
$\alpha(O_5-H_6-F_7)$	122.42	175.48	178.14	179.51	180.00
$\tau(H_4-C_1-O_5-H_6)$	180.00	180.00	180.00	180.00	180.00
$\tau(C_1 - O_5 - H_6 - F_7)$		0.00	, × 0.00	0.00	0.00
F_{11} -	4.495	4.621	4.652	4.778	5.166
Relative energy	+28.53	0.00	+1.52	+ 5.63	+46.65

^aBond distances in Å, angles in deg, and relative energies in kcal mol⁻¹. The F_{11} values are quadratic force constants for the symmetric stretching coordinate (S_1) of the -OHF⁻ molety in units of mdyn Å⁻¹. See Fig. 3 for structural depictions.

^bAdditional data: $[S_1^{\circ}(y), y] = \{(2.3038, 1.0), (2.2595, -1.0)\}; [\alpha(C_1 - O_5 - H_6), y] = \{(0.0, 5.0), (15.250, 3.0), (114.490, 2.0), (115.280, 1.0), (106.940, -1.0)\}; [\alpha(O_5 - H_6 - F_7), y] = \{(147.96, -1.0), (124.67, -1.5), (105.890, -2.0), (67.041, -3.0), (92.506, -5.0)\}.$

case an unconstrained search for the transition state by one of the myriad available algorithms is necessitated, after which a canonical reaction path (RP) between protontransfer intermediates can be determined by perturbing the system along the transition vector and following trajectories of steepest descent off both sides of the saddle point.^{164–169} In the CH₃OHF⁻ system the possibility of a reaction path of this variety is dismissed by the identification and parametrization of a continuous MEP with no inflection points connecting the CH₃OH·F⁻ and CH₃O⁻ · HF regions of configuration space.

A trenchant choice of the reaction variable for proton transfer in CH_3OHF^- is the antisymmetric stretching coordinate

÷.,

(C1-05) (Å)

1.42

1.40

1.38

1.36

1.34

-2

$$y \equiv S_2 = 2^{-1/2} [r(O_5 - H_6) - r(H_6 - F_7)], \qquad (6)$$

1.416

which monotonically changes from $-\infty$ to $+\infty$ as the transformation CH₃OH+F⁻ \rightarrow CH₃O⁻+HF proceeds. The first step in the construction of the corresponding MEP in this study involved the determination of fully optimized structures at the TZ(+)(*d*,*p*) CISD level of theory for the fixed *y* (Å) values ($-\infty$, -0.22352, 0.0, 0.28284, $+\infty$), the resulting geometric parameters being collected in Table XI. The structures for $y=(-\infty, -0.22352, +\infty)$ correspond to the CH₃OH, CH₃OHF⁻, and CH₃O⁻ + HF optimum TZ(+)(*d*,*p*) CISD supermolecule geometries reported above in Tables I, II, and III. The *y*=(0.0, 0.28284) augmentations are intended to judiciously sample regions of [CH₃O·H·F]⁻ and [CH₃O·HF]⁻ type, respectively.

The variations of the optimal $r(C_1-O_5)$, $r(C_1-H_4)$,



A conserved



-1

0

y (Å)

2

FIG. 8. Variation of the C-H distances in CH_3OHF^- along the MEP for proton transfer.

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994



FIG. 9. Variation of the unique H–C–H angle in CH_3OHF^- along the MEP for proton transfer.

 $r(C_1-H_{2,3})$, $\alpha(H_2-C_1-H_3)$, $\alpha(H_{2,3}-C_1-O_5)$, and $\alpha(H_4-C_1-O_5)$ coordinates in the methanol framework are plotted in Figs. 7-10. In each instance a smooth, monotonic dependence on y is exhibited which is fit well by the generic functional form

$$S_{\text{MeOH}}^{\circ}(y) = a_1 + a_2 \tanh[b_1(y - b_2)], \tag{7}$$

in which a_1 and a_2 are determined directly from the asymptotic limits, and b_1 and b_2 are adjusted to describe intermediate regions. A complete specification of the analytic forms which parametrize the optimal coordinates along the MEP is provided in Table XII. The interfragment degrees of freedom in the proton-transfer process are represented by the symmetric stretching coordinate S_1 $=2^{-1/2}[r(O_5-H_6)+r(H_6-F_7)]$ and the angular variables $\alpha(C_1-O_5-H_6)$ and $\alpha(O_5-H_6-F_7)$, whose overall y variations are revealed only after additional, constrained TZ



FIG. 10. Variation of the H–C–O angles in CH_3OHF^- along the MEP for proton transfer.

(+)(d,p) CISD optimizations. By assuming the analytic representations previously derived for the intrafragment methanol coordinates and optimizing the remaining variables for $y=\pm 1.0$ Å, the expected hyperbolic form of the optimum S_1 values is made apparent, as shown in Fig. 11. A satisfactory fit of the data is provided by the function

$$S_{1}^{\circ}(y) = 2^{-1/2} [r_{e}(H-F) + r_{e}(O-H)] + 2^{-1/2} [r_{e}(H-F) - r_{e}(O-H)] \tanh(y) + \sqrt{y^{2} + h(y)}, \qquad (8)$$

where $r_e(H-F)$ and $r_e(O-H)$ are the equilibrium bond distances in HF and CH₃OH, respectively, and h(y) is the rational fitting function specified in Table XII. The additional $y = \pm 1.0$ Å points are not sufficient to fully outline the variations of the angular coordinates, however. By adding Eq. (8) to the set of assumed analytic forms, the data for $\alpha(C_1-O_5-H_6)$ and $\alpha(O_5-H_6-F_7)$ were thus extended to y=(2.0, 3.0, 5.0) and (-5.0, -3.0, -2.0, -1.5) Å, respectively. The intriguing y dependence of these angles is depicted in Figs. 12 and 13 and quantified in footnote b of Table XI.

While the path of F^- approach in the formation of CH₃OHF⁻ and the path of HF departure subsequent to proton abstraction can be inferred from the profiles of $\alpha(C_1-O_5-H_6)$ and $\alpha(O_5-H_6-F_7)$ in Figs. 12 and 13, the nature of the MEP is best elucidated by the trajectories appearing in Figs. 14 and 15, which are traced on the basis of the interfragment angle parametrizations reported in Table XII. In the $CH_3OH + F^- \rightarrow CH_3OHF^-$ step, the fluoride ion approaches along the dipole moment vector of methanol, which is directed 122.42° away from the C-O bond axis according to the TZ(+)(d,p) CISD predictions. For relatively large interfragment separations, the O-H bond is essentially rigid, and thus optimization of the fluoride position for a given y value amounts to minimization of the long-range interaction energy on a ring centered at the acidic proton. Accordingly, the partial positive charge on the methyl hydrogens engenders a leftward deflection of the incoming fluoride ion from the dipole-moment asymptote. Eventually the MEP brings F⁻ close to the C-O axis on the backside of the methyl group before changing directions and skirting the periphery of the methanol moiety to enter the deep potential well of the optimum ionmolecule complex. In viewing the MEP in reverse, the fluoride ion dissociates from methanol by hugging the methyl substituent rather than detaching along a least-motion path. The asymptotic value of $\alpha(O_5-H_6-F_7)$ and the physical origin of its reduction to less than 70° near y = -3.0 Å are thus readily explained by the parametric plot of the MEP. Moreover, it becomes apparent from the MEP why levels of theory which yield tighter equilibrium structures for the CH_3OHF^- complex, with optimal values of y approaching zero, also predict optimum $\alpha(O_5-H_6-F_7)$ angles closer to 180°, as noted in Sec. IV.

The synthesis of a coherent explanation of the MEP trajectory for the dissociation step $CH_3OHF^- \rightarrow CH_3O^- + HF$ is somewhat more involved than in the fluoride association case. The multipole analysis described in Sec. VI of the charge density in the meth-

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

TABLE XII. Analytic representation of internal coordinates and energy profile along the MEP for proton transfer in CH₃OHF⁻.^a

 $r(C_1-O_5) = 1.380 81 - 0.035 243 \tanh[1.209 53(y+0.074 00)]$ $r(C_1-H_{2,3}) = 1.10703 + 0.01576 \tanh[1.52894(y-0.13747)]$ $r(C_1-H_4) = 1.10431 + 0.01848 \tanh[1.25367(y-0.14469)]$ $\alpha(H_2-C_1-H_3) = (180/\pi)\{1.853\ 02 - 0.050\ 45\ \tanh[1.2399(y+0.056\ 967)]\}$ $\alpha(H_{2,3}-C_1-O_5) = (180/\pi) \{1.980\ 08 + 0.029\ 04\ tanh[1.6808(y-0.059\ 327)]\}$ $\alpha(H_4 - C_1 - O_5) = (180/\pi) \{1.938\ 00 + 0.071\ 11\ \tanh[1.4225(y + 0.008\ 379)]\}$ $\alpha(O_5-H_6-F_7) = (180/\pi) \{0.502\ 48 + 2.639\ 11\ \tanh[z_1(y)] - 0.967\ 03\ \exp[-z_2(y)^2]\}$ $z_1(y) = (1.70044 + 2.24231y + 2.31281y^2 + 1.99769y^3)(1 + y^2)^{-1}$ $z_2(y) = 0.301\ 60(y+3)\{1+\exp[0.599\ 43(y+3)]\}$ $[0.942\ 04 + z_{3,4,5}(y) + 0.35\{\exp[-1.1(y-1.6)] + \exp[1.5(y-1.6)]\}^{-1}$ $\alpha(C_1 - O_5 - H_6) = (180/\pi)$ $-0.13\{\exp[-1.8(y+0.18)]+\exp[3.0(y+0.18)]\}^{-1}$ $\pi \tanh(y-2.96)$ $z_3(y) = -0.59972$ $\frac{1}{2}$ + 20(y-2.96) P[lm] $z_4(y) = -0.599\ 72\ \tan^{-1}[20(y-2.96)]$ P[0] $z_5(y) = z_3(y) + 0.628755\{1 + \tanh[1.8(y-1.8)]\}$ $P[\pi]$ $S_1^{\circ}(y) = 2^{-1/2} [r(O_5 - H_6) + r(H_6 - F_7)] = 1.317\ 672 - 0.029\ 536\ \tanh(y) + [y^2 + h(y)]^{1/2}$ $h(y) = (0.101725 - 0.015904y - 0.086169y^2)(1+y^2)^{-1}$ $E^{\bullet}(y) + 215.277\ 6756$ $= 0.015 \ 631 \ \tan^{-1}\{w_1[u(y)]\}[w_2[u(y)](1+0.636 \ 62 \ \tan^{-1}\{w_3[u(y)]\}) + 2^{-1}\{1+\tanh[u(y)]\}]$ $w_1(u) = 2(\Delta E_e)\pi^{-1}(\mu_{\text{CH},\text{OH}}/2)^{-1}[1 + \exp(-u)][u^2/\tanh(u) + 5.2u]$ $w_2(u) = 1.14272 \operatorname{sech}\{(u+a)[-0.0045195 - 1.0417 \tanh(u+a)]\}$ $1 - 0.633223(u+a) + 0.010723(u+a)^2 + 0.0122526(u+a)^2$ $-0.0026974(u+a)^4+0.00381276(u+a)^5$ $+0.962 \ 1986\{1-\tanh[0.46(u-0.1)]\}\ (a=2.311 \ 13)$ $w_3(u) = 2(\Delta E_e) \pi^{-1} (\mu_{\rm HF}/2)^{-1} [1 + \exp(u)] [u^2 / \tanh(u) + 2.6u]$ u(y) = 1.8897260(y-1.28) $\Delta E_e = 0.0245533 \text{ a.u.} \quad \mu_{\rm HF} = 0.7160 \text{ a.u.}^{b} \quad \mu_{\rm CH_3OH} = 0.6688 \text{ a.u.}^{c}$ ^aBond distances and y in Å, angles in deg, and E^o(y) in hartree.



oxide ion reveals two possible asymptotic channels for the MEP, viz., exit of the HF dipole along either end of the C-O axis. The choice of the antisymmetric stretching coordinate as the MEP reaction variable happens to select the FH-CH₃O⁻ dissociation asymptote, for reasons similar to those which cause the deflection of F^- to the backside of the methyl group in the association step. Therefore, the path labeled P[0] in Figs. 12 and 15, which corresponds to $\alpha(C_1 - O_5 - H_6) = 0.0^\circ$ at infinity, is the actual trajectory followed by the MEP here. The parametrization of P[0] is effectuated by using the function $z_4(y)$ in the analytic form for $\alpha(C_1 - O_5 - H_6)$ in Table XII. A model MEP trajectory, $P[\pi]$, leading to the CH₃O⁻-HF asymptote, and an intermediate least-motion path, P[lm], are parametrized by employing the alternate functions $z_5(y)$ and $z_3(y)$, respectively, in the $\alpha(C_1 - O_5 - H_6)$ expression. While P[0] might seem questionable on physical grounds in comparison with the $P[\pi]$ and P[lm] paths in Fig. 15, it must be realized that the region of positive electrostatic potential which normally surrounds methyl hydrogens in neutral organic species is not present in CH₃O⁻ due to the overall charge of the anion and the partial negative charge appearing on the hydrogens as a consequence of negative hyperconjugation (Sec. IV).

The complete parametrization of geometric coordinates along the MEP facilitates the mapping of the energy function for proton transfer on a fine mesh with a definitive theoretical method, providing the coup de grâce concerning the essential features of the reaction surface. The extensive analyses presented above of the geometric structures, vibrational frequencies, proton-transfer energy, and fluoride affinity of the CH₃OHF⁻ system substantiate the application of MP2 theory with suitably large basis sets in the generation of the minimum energy profile. Therefore, QZ(+)(2d1f,2p1d) MP2 energy points were determined



FIG. 11. Variation of the symmetric bond stretch coordinate $S_1 = 2^{-1/2} [r(O_5-H_6) + r(H_6-F_7)]$ in CH₃OHF⁻ along the MEP for proton transfer.

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FIG. 12. Variation of the interfragment $C_1-O_5-H_6$ angle in CH₃OHF⁻ along the MEP for proton transfer. The choice of the reaction variable according to Eq. (6) causes the MEP to recede along path P[0], which connects to the FH-CH₃O⁻ asymptote, i.e., an angle of 0° for large y. The two dashed curves depict $P[\pi]$, the alternate MEP trajectory, and P[Im], a hypothetical least-motion path with the same entrance and exit angles.

at 19 selected locations along the MEP parametric curve. In Table XIII and Fig. 16, these data are tabulated and plotted. The global features of the energy function are displayed in the first frame of Fig. 16, including the immense binding energy and the slow decay of the interaction potential characteristic of an ion-dipole system. The second frame of the figure is an expanded view of the MEP energy curve near equilibrium. The ten points clustered between y=-0.3 and +0.3 Å clearly reveal the lack of an energy barrier and secondary minimum. Nevertheless, the energy variations in the range $y \in [-0.3, 0.0]$ Å are less than 1



FIG. 14. Parametric plots of the path of fluoride approach in the YZ molecular plane of methanol. The MEP curve is the minimum energy path mapped out by selection of the reaction variable according to Eq. (6), while the RP trajectory is a canonical reaction path of steepest descent. The dipole moment vector (μ) of CH₃OH determines the asymptotic direction of approach, which emanates from an origin (Y,Z') ascertained by a multipole analysis of the charge distribution of methanol.

kcal mol⁻¹, and geometric configurations of $CH_3O^- \cdot HF$ type are fully spanned before the relative energy exceeds 5 kcal mol⁻¹. The flattening of the energy curve in the $CH_3O^- \cdot HF$ region is evident from the selective skewing away from the harmonic approximation (dashed curve a) for positive y values. The breadth of the well brought on by complexation is demonstrated by comparison with the appropriately scaled O–H harmonic stretching potential for free methanol (dashed curve b).



FIG. 13. Variation of the interfragment $O_5-H_6-F_7$ angle in CH₃OHF⁻ along the MEP for proton transfer. For negative y values, the asymptote of 122.42° arises from the direction of the dipole moment vector of methanol.



FIG. 15. Parametric plots of the path of departure of hydrogen fluoride in the YZ molecular plane of methoxide. The MEP given by selecting the reaction variable according to Eq. (6) is path P[0]; an equivalent MEP connecting to the CH₃O⁻-HF asymptote is shown as path $P[\pi]$. P[lm] is a hypothetical least-motion curve. The dashed axes intersect at the center of charge of methoxide.

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

TABLE XIII. QZ(+)(2d1f,2p1d) MP2 energy points along the MEP for proton transfer.^a

y (Å)	Total energy (hartree)	Relative energy (kcal mol ⁻¹)	
- ∞	-215.277 676	+29.65	
-1.5	-215.294 141	+19.32	
-1.0	-215.302 935	+13.80	
-0.75	-215.310 403	+9.11	
0.50	-215.318 925	+3.77	
-0.3	-215.323 984	+0.59	
-0.223 52	-215.324 804	+0.08	
-0.18	-215.324 926	0.0	
-0.15	-215.324 871-	+0.03	
-0.10	-215.324 560	+0.23	
-0.05	-215.324 035	+0.56	
0.0	-215.323 561	+0.86	
+0.1	-215.321 788	+1.97	
+0.2	-215.319 768	+3.24	
+0.282 84	-215.317 404	+4.72	
+0.75	-215.296 828	+ 17.63	
+1.0	-215.286 311	+24.23	
+1.5	-215.272 657	+32.80	
+2.5	-215.261 678	+ 39.69	
+ ∞	-215.253 122	+45.06	

^aEvaluated along the parametric curve P[0] specified analytically in Table XII; *n.b.*, details of the computations mentioned previously (Ref. 78).

An effective analytic form for the representation of the minimum energy function for proton transfer in ionmolecule systems has been developed previously by Allen. and co-workers.⁶⁶ Among the merits of this intricate form are the analytic reproduction of both the proton-transfer energy and the long-range, ion-dipole interaction energy (μR^{-2}) in each asymptotic region. The nesting of multiparameter fitting functions as arguments of smooth, monotonic functions allows local flexibility within the global constraints of the system. The final function, $E^{\circ}(y)$, derived from the QZ(+)(2d1f,2p1d) MP2 energy data is reported in Table XII. As shown in Fig. 16, the fit to the MEP energy points is excellent, the mean absolute deviation being 11.6 cm⁻¹ out of a total energy range of 15 760 cm^{-1} . The equilibrium position and binding energy given by the analytic form for $E^{\circ}(y)$ are -0.181 Å and 29.63 kcal mol^{-1} , respectively. By comparison, quadratic interpolation based on the three data points enveloping the minimum yields (-0.1795 Å, 29.65 kcal mol⁻¹), and the final values proposed in the analyses of Sec. IV are $(-0.177 \text{ \AA},$ 29.95 kcal mol^{-1}). The initial and final deflections of the MEP trajectory toward the methyl substituent surely cause perturbations in the minimum energy function for |y|>1.5 Å. No attempt was made here to determine the detailed structure of these exterior regions or to modify $E^{\circ}(y)$ to fit the subtle variations occurring therein, because all geometric configurations in this space lie at least 20 kcal mol^{-1} above the equilibrium structure of the CH₃OHF⁻ complex.

VI. MULTIPOLE ANALYSIS OF ASYMPTOTIC REACTION PATHS

Its interpretive utility notwithstanding, the MEP charted in this investigation must not be mistaken for a



FIG. 16. The energy function $E^{\circ}(y)$ along the MEP for proton transfer in CH₃OHF⁻. The first frame is a global perspective, while the second frame is an expanded view near equilibrium. In the latter plot, dashed curve a is the harmonic approximation of $E^{\circ}(y)$, and curve b is the superimposed O-H harmonic stretching potential for free methanol, as derived from Eq. (41) for $y = -\infty$.

canonical reaction path (RP) of steepest descent or the locus of classical trajectories which dominates the protontransfer kinetics. An RP for proton transfer in CH₃OHF⁻ cannot be defined in the usual manner (vide supra) because no intervening transition state between reactants and products exists for the origination of paths of steepest descent. Therefore, a sufficient set of conditions for the form of the RP in the limits of infinite separation of the reactants and products must be defined in a physically meaningful way in order for the concept of a canonical reaction path for proton transfer to remain useful. Because asymptotic regions of potential energy surfaces are governed by classical electrostatics, the specification of appropriate conditions for the RP is afforded by a multipole analysis of the long-range ion-molecule interaction energy, thus clarifying the distinction between MEP and RP in systems with no barriers for proton transfer. The relevant considerations are discussed here in the context of the CH_3OHF^- example, but the arguments are easily generalized to all ion-dipole systems.

The electrostatic energy of interaction between two separated molecular fragments A and B with disjoint charge distributions $\rho^{A}(\mathbf{x})$ and $\rho^{B}(\mathbf{x})$ is given by

$$W = \int_{B} \rho^{B}(\mathbf{x}) \Phi^{A}(\mathbf{x}) d^{3}\mathbf{x} = \int_{A} \rho^{A}(\mathbf{x}) \Phi^{B}(\mathbf{x}) d^{3}\mathbf{x}, \quad (9)$$

in which (Φ^A, Φ^B) is the electrostatic potential due to (A,B) as experienced by (B,A), and each integration is restricted to the spatial region immediately surrounding the relevant fragment. If the first relation for W is utilized, $\Phi^A(\mathbf{x})$ is assumed to vary slowly in region B whenever the interfragment separation (R) is large, allowing a corresponding expansion in rectangular coordinates to be generated about a suitable reference point **b** within fragment B. After substituting this expansion into Eq. (9), integrating over region B, and invoking $\nabla^2 \Phi^A(\mathbf{x}) = 0$, the form of the interaction energy becomes¹⁷²

$$W = q^{B} \Phi^{A}(\mathbf{b}) + \sum_{i} \mu_{i}^{B} \left(\frac{\partial \Phi^{A}}{\partial x_{i}} \right)_{\mathbf{b}} + \frac{1}{6} \sum_{ij} Q_{ij}^{B} \left(\frac{\partial^{2} \Phi^{A}}{\partial x_{i} \partial x_{j}} \right)_{\mathbf{b}} + \frac{1}{90} \sum_{ijk} M_{ijk}^{B} \left(\frac{\partial^{3} \Phi^{A}}{\partial x_{i} \partial x_{j} \partial x_{k}} \right)_{\mathbf{b}} + \cdots, \qquad (10)$$

where standard notation is assumed for the net charge (q^{B}) and dipole moment (μ^{B}) of B, while

$$Q_{ij}^{\mathbf{B}} = \int_{\mathbf{B}} (3X_i'X_j' - r'^2\delta_{ij})\rho^{\mathbf{B}}(\mathbf{x}')d^3\mathbf{x}'$$
(11)

is the traceless quadrupole moment tensor, and

$$M_{ijk}^{B} = \int_{B} \left[15x'_{i}x'_{j}x'_{k} - 3r'^{2}(x'_{i}\delta_{jk} + x'_{j}\delta_{ik} + x'_{k}\delta_{ij}) \right] \\ \times \rho^{B}(\mathbf{x}')d^{3}\mathbf{x}'$$
(12)

is its octupole counterpart. A more explicit expression for W is then obtained by means of the multipole expansion of $\Phi^{A}(\mathbf{x})$ for large R,¹⁷²

$$\Phi^{A}(\mathbf{x}) = \frac{q^{A}}{R} + \sum_{i} \frac{\mu_{i}^{A} x_{i}}{R^{3}} + \frac{1}{2} \sum_{ij} \frac{Q_{ij}^{A} x_{i} x_{j}}{R^{5}} + \frac{1}{6} \sum_{ijk} \frac{M_{ijk}^{A} x_{i} x_{j} x_{k}}{R^{7}} + \cdots, \qquad (13)$$

which after various differentiations and manipulations within Eq. (10) yields¹⁷³

$$W = q^{A}q^{B}(1/R) + [q^{B}(\mu^{A} \cdot \mathbf{n}) - q^{A}(\mu^{B} \cdot \mathbf{n})](1/R^{2})$$

$$+ \{\mu^{A} \cdot \mu^{B} - 3(\mu^{A} \cdot \mathbf{n})(\mu^{B} \cdot \mathbf{n}) + \frac{1}{2}q^{A}Q^{B}[\mathbf{n},\mathbf{n}]$$

$$+ \frac{1}{2}q^{B}Q^{A}[\mathbf{n},\mathbf{n}]\}(1/R^{3}) + \{Q^{A}[\mu^{B},\mathbf{n}] - Q^{B}[\mu^{A},\mathbf{n}]$$

$$+ \frac{5}{2}(\mu^{A} \cdot \mathbf{n})Q^{B}[\mathbf{n},\mathbf{n}] - \frac{5}{2}(\mu^{B} \cdot \mathbf{n})Q^{A}[\mathbf{n},\mathbf{n}] + \frac{1}{6}q^{B}$$

$$\times \mathbf{M}^{A}[\mathbf{n},\mathbf{n},\mathbf{n}] - \frac{1}{6}q^{A}\mathbf{M}^{B}[\mathbf{n},\mathbf{n},\mathbf{n}]\}(1/R^{4}) + \cdots, \qquad (14)$$

the scalar product between a rank m tensor **T** and a set of m vectors $\{u_i\}$ being denoted as

$$\mathbf{T}[\mathbf{u}_{1},\mathbf{u}_{2},...,\mathbf{u}_{m}] \equiv \sum_{k_{1}k_{2}...k_{m}} T_{k_{1}k_{2}...k_{m}} u_{1,k_{1}}u_{2,k_{2}...}u_{m,k_{m}}.$$
(15)

In Eq. (14) the multipole moments for A and B are computed with a common orientation of Cartesian axes but about distinct intrafragment origins \mathbf{a} and \mathbf{b} separated by a distance R; the unit vector directed from \mathbf{a} to \mathbf{b} is designated as \mathbf{n} .

The choice of **a** and **b** is arbitrary from a mathematical perspective but is a key consideration in the prescription of meaningful asymptotic conditions for reaction paths. According to a simple theorem of classical electrostatics, ¹⁷² the components of the lowest nonvanishing multipole moment of any charge distribution are invariant to translations of the origin of the coordinates, but all higher-order moments are generally dependent on the location of the origin. Therefore, the components of the second lowest nonvanishing multipole moment can be modified by varying a and b to achieve algebraic and conceptual simplifications. In the CH₃OHF⁻ system, the proton-transfer reaction is an $ion+dipole \rightarrow ion'+dipole'$ process. To provide the best point-charge representation of each ion, the intrafragment origin is selected as the center of charge, about which the dipole moment of the ion vanishes. In the case of the neutral fragments, the origin is chosen to eliminate the components of the quadrupole moment tensor which involve the dipole axis, in order to similarly optimize the dipole description of the electrostatic potential. Specifically, if γ is the dipole axis and α and β are orthogonal directions, then the origin is chosen such that $Q_{\alpha\gamma} = Q_{\beta\gamma}$ $=Q_{\nu\nu}=0$. Because the rectangular quadrupole moment tensor is traceless, these conditions imply that $Q_{\alpha\alpha} =$ $-Q_{BB}$; moreover, some choice of axis orientation for α and β will also provide $Q_{\alpha\beta}=0$. In analogy to the center of charge for ions, this choice of origin for dipolar species is referred to here as the dipole center.

The determination of intrafragment origins by the recommended prescriptions can be illustrated for the CH_3OH+F^- reactants and CH_3O^-+HF products with TZ(+)(d,p) RHF charge-moment data computed at the TZ(+)(d,p) CISD optimum supermolecule structures of Tables I and II. For methanol the reference coordinate system for the analysis is depicted in Fig. 14, wherein the carbon atom is located at the origin, the C-O bond vector is directed along the +Z axis, and the C-O-H framework lies in the YZ plane. For this orientation, the dipole and quadrupole moments of methanol are

$$\boldsymbol{\mu}_{CH_{3}OH}^{\circ}(D) = \begin{pmatrix} 0 \\ -1.5688 \\ -1.2161 \end{pmatrix};$$
$$\boldsymbol{Q}_{CH_{3}OH}^{\circ}(D \text{ Å}) = \begin{pmatrix} -0.8307 & 0 & 0 \\ 0 & 5.7930 & -9.7314 \\ 0 & -9.7314 & -4.9623 \end{pmatrix}.$$
(16)

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

2078

Thus, the dipole vector is directed away from the +Z axis by $\theta = 127.78^{\circ}$. If the coordinate system is rotated to a primed orientation in which the Z' axis is aligned with the dipole vector, then the quadrupole moment tensor becomes

$$\mathbf{Q}' = \begin{pmatrix} Q_{XX}^{\circ} & 0 & 0\\ 0 & Q_{YY}^{\circ} \cos^{2} \theta + Q_{ZZ}^{\circ} \sin^{2} \theta + Q_{YZ}^{\circ} \sin 2\theta & \frac{1}{2} (Q_{ZZ}^{\circ} - Q_{YY}^{\circ}) \sin 2\theta + Q_{YZ}^{\circ} \cos 2\theta\\ 0 & \frac{1}{2} (Q_{ZZ}^{\circ} - Q_{YY}^{\circ}) \sin 2\theta + Q_{YZ}^{\circ} \cos 2\theta & Q_{YY}^{\circ} \sin^{2} \theta + Q_{ZZ}^{\circ} \cos^{2} \theta - Q_{YZ}^{\circ} \sin 2\theta \end{pmatrix}.$$
 (17)

In order to eliminate the Y'Z' component of Q', the origin of the coordinates is moved orthogonal to the dipole vector along the Y' axis by a distance Y*. In this translated system, $(X'', Y'', Z'') = (X', Y' - Y^*, Z')$, whence

$$Q''_{YZ} = Q'_{YZ} - 3Y^* \mu'_z, \tag{18}$$

even though all other components of Q' are invariant because $\mu'_X = \mu'_Y = 0$ and q=0. Accordingly, Q''_{YZ} is zero if

$$Y^{*} = \frac{Q'_{YZ}}{3\mu'_{Z}} = \frac{1}{3\mu} \left[\frac{1}{2} \left(Q^{\circ}_{ZZ} - Q^{\circ}_{YY} \right) \sin 2\theta + Q^{\circ}_{YZ} \cos 2\theta \right],$$
(19)

which evaluates to $Y^* = 1.2820$ Å for methanol. The final values for the dipole and quadrupole moment tensors in the double-primed system are

$$\mu_{CH_{3}OH}^{"}(D) = \begin{pmatrix} 0\\0\\1.9850 \end{pmatrix};$$

$$Q_{CH_{3}OH}^{"}(D \text{ Å}) = \begin{pmatrix} -0.8307 & 0 & 0\\0 & 8.4983 & 0\\0 & 0 & -7.6676 \end{pmatrix}.$$
 (20)

Another shift of the coordinate origin parallel to the dipole vector (Z'' axis) is required to reach the dipole center. If $Z''' = Z'' - Z^*$, then

$$Q_{XX}^{'''} = Q_{XX}^{''} + 2Z^* \mu_Z^{''}, \qquad (21a)$$

$$Q_{YY}^{''} = Q_{YY}^{''} + 2Z^* \mu_Z^{''}, \tag{21b}$$

$$Q_{ZZ}^{'''} = Q_{ZZ}^{''} - 4Z^* \mu_Z^{''}, \qquad (21c)$$

the other components of \mathbf{Q}'' remaining unchanged. Therefore, by selecting

$$Z^{*} = \frac{Q_{ZZ}^{"}}{4\mu_{Z}^{"}} = \frac{1}{4\mu} \left[Q_{YY}^{\circ} \sin^{2}\theta + Q_{ZZ}^{\circ} \cos^{2}\theta - Q_{YZ}^{\circ} \sin 2\theta \right],$$
(22)

or $Z^* = -0.9657$ Å, the final multipole moments of methanol become

$$\mu_{CH_{3}OH}^{\prime\prime\prime}(D) = \begin{pmatrix} 0 \\ 0 \\ 1.9850 \end{pmatrix};$$

$$\mathbf{Q}_{CH_{3}OH}^{\prime\prime\prime}(D \text{ Å}) = \begin{pmatrix} -4.6645 & 0 & 0\\ 0 & 4.6645 & 0\\ 0 & 0 & 0 \end{pmatrix}.$$
(23)

Relative to the original coordinate system, the dipole center (a) of methanol found after the two successive translations is located at $(Y^{\circ}, Z^{\circ}) = (-0.022 \ 13, \ 1.6049)$ Å, as shown in Fig. 14. The other intrafragment origin (b) for the CH₃OH+F⁻ reactants is obviously centered on the fluorine nucleus.

For the $CH_3O^- + HF$ products, the determination of the coordinate origins involves only a single axis translation in each case. With the reference system affixed to CH_3O^- as for methanol, the dipole and quadrupole moments are computed as

$$\boldsymbol{\mu}_{CH_{3}O^{-}}^{\circ}(\mathbf{D}) = \begin{pmatrix} 0 \\ 0 \\ -5.7922 \end{pmatrix};$$

$$\mathbf{Q}_{CH_{3}O^{-}}^{\circ}(\mathbf{D} \overset{A}{\mathbf{A}}) = \begin{pmatrix} 9.6078 & 0 & 0 \\ 0 & 9.6078 & 0 \\ 0 & 0 & -19.2156 \end{pmatrix}.$$
(24)

Upon shifting the origin in the +Z direction by $Z^* = -\mu_Z^*/e = 1.2059$ Å, the dipole moment of methoxide vanishes. The center of charge $\mathbf{a} = (0,0,Z^*)$ is shown as the intersection of the dashed axes in Fig. 15. The modifications of the quadrupole components engendered by the coordinate shift are

$$Q'_{XX} = Q^{\circ}_{XX} + 2Z^*\mu^{\circ}_Z - q(Z^*)^2 = Q^{\circ}_{XX} + Z^*\mu^{\circ}_Z,$$
 (25a)

$$Q'_{YY} = Q^{\circ}_{YY} + 2Z^* \mu^{\circ}_Z - q(Z^*)^2 = Q^{\circ}_{YY} + Z^* \mu^{\circ}_Z,$$
 (25b)

$$Q'_{ZZ} = Q^{\circ}_{ZZ} - 4Z^* \mu^{\circ}_{Z} + 2q(Z^*)^2 = Q^{\circ}_{ZZ} - 2Z^* \mu^{\circ}_{Z},$$
 (25c)

and the final values of the CH_3O^- multipole moments at the center of charge are thus

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. n.

With fluorine at the origin and hydrogen along the +Z axis, the μ_i and Q_{ij} components of hydrogen fluoride are

$$\dot{\boldsymbol{\mu}}_{\rm HF}(\mathbf{D}) = \begin{pmatrix} 0 \\ 0 \\ 2.0423 \end{pmatrix};$$

$$\mathbf{Q}_{\rm HF}^{\circ}(\mathbf{D}\,\text{\AA}) = \begin{pmatrix} -2.4517 & 0 & 0 \\ 0 & -2.4517 & 0 \\ 0 & 0 & 4.9034 \end{pmatrix}.$$
(27)

Application of the first relation in Eq. (25c) for this neutral system (q=0) gives

$$Z^* = \frac{Q_{ZZ}^{\circ}}{4\mu_Z^{\circ}} = 0.6002 \text{ Å}$$
 (28)

as the axis shift which causes Q'_{ZZ} to vanish. The resulting dipole center (b) is marked in Fig. 15 by large dots appearing on the H-F bond vectors. The multipole moments of hydrogen fluoride are particularly simple when evaluated relative to this reference point:

$$\boldsymbol{\mu}_{\rm HF}^{\prime}(\mathbf{D}) = \begin{pmatrix} 0 \\ 0 \\ 2.0423 \end{pmatrix}; \quad \mathbf{Q}_{\rm HF}^{\prime}(\mathbf{D}\,\mathring{\mathbf{A}}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$
(29)

After location of the intrafragment origins **a** and **b**, the preferred starting configurations for the descent of canonical reaction paths (RP) from both the reactants and products into the intermediate ion-molecule complex can be ascertained by minimizing the long-range electrostatic energy under the constraint of a fixed interfragment separation $R = |\mathbf{a} - \mathbf{b}|$. For CH₃OH+F⁻, the application of Eq. (14) with A=CH₃OH, B=F⁻, $q^{A}=0$, $q^{B}=-e$, $\mu^{B}=0$, and $Q^{B}=0$ yields

$$W = -e(\mu^{A} \cdot \mathbf{n}) (1/R^{2}) - (e/2) \mathbf{Q}^{A}[\mathbf{n},\mathbf{n}] (1/R^{3}) - (e/6) \mathbf{M}^{A}[\mathbf{n},\mathbf{n},\mathbf{n}] (1/R^{4}) + \cdots$$
(30)

The dominant R^{-2} term reveals the expected result that W is minimized by aligning F^- with the dipole moment of CH₃OH, i.e., choosing the relative orientation vector $\mathbf{n} = (\mu^A/\mu^A)$. Consequently, $\mathbf{Q}^A[\mathbf{n},\mathbf{n}]$ vanishes because all components of \mathbf{Q}^A along the dipole axis are zero by construction at reference point **a**, and thus

$$W_{\min}(CH_3OH+F^-) = -e\mu^A R^{-2} + O(R^{-4}).$$
 (31)

For CH₃O⁻+HF, the use of Eq. (14) with A=CH₃O⁻, B=HF, q^{A} =-e, q^{B} =0, μ^{A} =0, and Q^B=0 gives

$$W = e(\mu^{B} \cdot \mathbf{n})(1/R^{2}) + \{Q^{A}[\mu^{B},\mathbf{n}] - (5/2) \\ \times (\mu^{B} \cdot \mathbf{n})Q^{A}[\mathbf{n},\mathbf{n}] + (e/6)M^{B}[\mathbf{n},\mathbf{n},\mathbf{n}]\} \\ \times (1/R^{4}) + \cdots .$$
(32)

The R^{-2} term dictates that $\mathbf{n} = -(\mu^{\rm B}/\mu^{\rm B})$ in order to minimize W, the minus sign implying that the hydrogen atom in the HF dipole is always directed toward methoxide. Nevertheless, unlike the case for the reactants, the complete specification of the relative orientation of the fragments requires an additional parameter, the angle τ between **n** and the C-O bond axis, which must be ascertained from the R^{-4} term in Eq. (32). With **n** antiparallel to the dipole vector of HF, the coefficient of this R^{-4} term becomes $\frac{3}{2} \mu^{\rm B} \mathbf{Q}^{\rm A}[\mathbf{n},\mathbf{n}] + (e/6) \mathbf{M}^{\rm B}[\mathbf{n},\mathbf{n},\mathbf{n}]$. Using the axis system of Fig. 15 for convenience, this expression can be reduced further, providing

$$W'(\tau) = -e\mu^{B}R^{-2} + (e/6)\mathbf{M}^{B}[\mathbf{n},\mathbf{n},\mathbf{n}]R^{-4} + (3/2)\mu^{B}Q_{YY}^{A}(1-3\cos^{2}\tau)R^{-4} + \cdots$$
(33)

for the electrostatic interaction energy as a function of τ when the HF dipole is aligned toward methoxide. The first two terms in Eq. (33) are invariant to τ , whereas the last term is minimized when $\tau=0$ or π radians, because Q'_{YY} is positive in Eq. (26).¹⁷³ In brief, for both the FH–CH₃O⁻ and CH₃O⁻–HF alignments the optimal long-range interaction energy

$$W_{\min}(CH_{3}O^{-} + HF)$$

= $-e\mu^{B}R^{-2} - (e/6)M^{B}[\mu^{B},\mu^{B},\mu^{B}]$
 $\times (\mu^{B})^{-3}R^{-4} - 3\mu^{B}Q_{YY}^{A}R^{-4}$ (34)

is obtained.

From the asymptotic orientations of the reactant and product species, the nature of the reaction paths for steepest descent into the ion-molecule energy minimum can be deduced. For $CH_3OH + F^- \rightarrow CH_3OHF^-$, the RP is similar to the MEP in that both are directed along the dipole vector of methanol at large distances, but the corresponding asymptotes are parallel rather than coincident. In particular, the use of S_2 as the reaction coordinate causes the MEP asymptote to pass through the equilibrium position of the acidic proton in methanol rather than the aforementioned dipole center lying near the oxygen nucleus, as in the RP case. This subtlety notwithstanding, the primary distinction between the MEP and RP curves is that the latter exhibits a much later departure from the dipole asymptote, precisely because the intrafragment origin a is chosen by conditions which maximize the radial component of the gradient vector for fluoride approach. To ascertain the point at which deflections of the RP from its limiting direction become substantial, TZ(+)(d,p) RHF Cartesian energy gradients for the fluoride ion were computed at ten positions on the dipole asymptote displaced 4, 3.5) Å. The angles of deflection of the negative energy gradient from the dipole axis were found to be, in order, $(0.00^\circ, 0.00^\circ, -0.06^\circ, -0.35^\circ, -1.31^\circ, -2.01^\circ, -2.44^\circ,$

J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

 -0.79° , $+10.94^{\circ}$, $+81.04^{\circ}$), the negative sign signifying leftward deflections toward the methyl substituent. Thus, the fluoride ion actually shifts *away* from the hydroxyl group in its initial approach. The onset of the final descent into the CH₃OHF⁻ energy minimum is marked by a sharp deflection to the right near R=4.0 Å, where the binding energy is 9.3 kcal mol⁻¹ but the μR^{-2} term in Eq. (31) is still accurate to 0.7 kcal mol⁻¹. It is inside 4 Å that the bulk (20 kcal mol⁻¹) of the complexation energy in the CH₃OHF⁻ adduct is gained, and in this interior region the RP and the MEP are in reasonable proximity to one another.

For adduct formation from the proton-transfer products, $CH_3O^- + HF \rightarrow CH_3OHF^-$, both the $\tau = 0$ and $\tau = \pi$ reactions paths, RP[0] and RP[π], remain on the Z axis in Fig. 15 until the separation between the intrafragment origins reaches ~ 5 Å, where the curvature for displacements of the HF dipole from the symmetry axis of methoxide changes from positive to negative as Pauli repulsion and chemical bonding effects overcome long-range electrostatic forces. In particular, at well-defined critical points each of the RP[0] and RP[π] paths trifurcates¹⁷⁴ abruptly into equivalent C_s -symmetry configuration spaces in which the HF unit bisects an H-C-H angle in the methyl group. In each of these configuration spaces, a CH₃OHF⁻ energy minimum is reached by separate trajectories originating from RP[0] and RP[π], as illustrated in Fig. 15 for the case of adduct formation in the YZ plane. In brief, the canonical reaction paths closely resemble the MEP curves P[0]and $P[\pi]$ presented above. In fact, the abrupt trifurcation of the reaction paths near R = 5 Å is also a characteristic of the MEPs, even though the analytic forms employed to represent P[0] and $P[\pi]$ in Table XII were chosen for convenience to decay only gradually to their respective asymptotes. As noted above, the use of S_2 as the MEP reaction variable leads to the generation of P[0] rather than $P[\pi]$, an occurrence which is now elucidated. In essence, performing constrained geometry optimizations for large positive values of S_2 is equivalent to the selection of the oxygen center in methoxide as the intrafragment origin (a) in the minimization of the long-range electrostatic energy W. However, the center of charge in methoxide is actually displaced from this location toward the methyl group by 0.14 Å, a feature which precipitates a nonequivalence of the P[0] and $P[\pi]$ exit channels with respect to the oxygen center. Consequently, P[0] becomes the preferred MEP solution because it involves a closer approach of the dipole center of HF to the center of charge of CH₃O⁻ for fixed values of S_2 . Чę.,

VII. ENERGY SURFACE AND VIBRATIONAL EIGENSTATES FOR PROTONIC MOTION IN CH₃OHF⁻⁻

The CH₃OHF⁻ complex may be characterized as a *nearly* centrosymmetric hydrogen pseudobihalide ion, displaying interfragment interactions between the extremes of covalent bonding in [FHF]⁻ and appreciably electrostatic cohesion in species such as [FHCl]⁻. The structure of the vibrational eigenstates for protonic motion in CH₃OHF⁻ is thus of interest, particularly in establishing a paradigm

for intermediate vibrational behavior within the diverse class of [AHB]⁻ ions. Toward this end, rigorous variational techniques are employed here to determine the vibrational eigenstates of the -OHF⁻ moiety, treated as an isolated triatomic system whose potential energy function is taken from the proton-transfer surface of CH₃OHF⁻. Because the coupling of protonic stretching vibrations with other modes in the CH₃OHF⁻ adduct is quite small, this approach is an effective method for dealing with the extreme anharmonicity of the proton-transfer surface. It is clearly preferable to the use of conventional second-order perturbation techniques^{137,175-178} applied to a quartic force field of CH₃OHF⁻, a procedure which is likely to give poor predictions for the stretching fundamentals of the -OHF⁻ unit due to considerable inaccuracies in the harmonic approximation as a zeroth-order solution. In summary, the variational anharmonic treatment of this section complemented by the TZ(+)(d,p) MP2/SQM normalmode analysis of Sec. IV provides an essentially complete and reliable characterization of the vibrational spectrum of CH₃OHF⁻.

The [-OHF]⁻ model triatomic system is assumed to be linear, since the best prediction for the O₅-H₆-F₇ angle in CH₃OHF⁻ is 177±1° (Sec. IV). The function for the potential energy in the stretching space of [-OHF]⁻ is adapted from the analytic form developed for the [FHCI]⁻ surface⁶⁶ and is expressed in terms of x (Å) $\equiv S_1$ $=2^{-1/2}[r(O-H)+r(H-F)]$ and y (Å) $\equiv S_2=2^{-1/2}$ [r(O-H)-r(H-F)]. Specifically,

$$V(x,y) = E^{\circ}(y) + D_{e}(y) \left(1 - \left\{\frac{\sigma^{\circ}(y)}{\sigma(x,y)}\right\} \times \exp\{-\beta^{\circ}(y) \left[\sigma(x,y)^{2} - \sigma^{\circ}(y)^{2}\right]\}\right)^{2}, \quad (35)$$

where $E^{\circ}(y)$ is the MEP energy curve (Table XII) constructed previously, involving E_0 (-215.277 6756 a.u.) as the CH₃OH+F⁻ absolute energy asymptote, and

$$D_e(y) = E_0 - E^{\circ}(y) + D_e(CH_3O-H),$$
 (36)

with $D_e(CH_3O-H)$ taken to be 0.180 71 a.u.¹⁴⁹ In addition,

$$\sigma(x,y) = x - \sqrt{\epsilon^2 + y^2} \quad (\epsilon = 0.1 \text{ Å}), \tag{37}$$

$$\sigma^{\circ}(y) = \sigma[\widetilde{S}_{1}^{\circ}(y), y], \qquad (38)$$

$$\widetilde{S}_1^{\circ}(y) = 1.317\ 672 - 0.029\ 536\ \tanh(y) - 0.046\ 2244$$

×sech(y+1) +
$$\sqrt{y^2 + \alpha^2} - \frac{\alpha^2}{2\sqrt{y^2 + \alpha^2}}$$
 (Å)
($\alpha = 0.704~505$), (39)

$$\beta^{\circ}(y) = \left(\frac{1}{2\sigma^{\circ}(y)^{2}}\right) \left[\sqrt{\frac{F^{\circ}(y)\sigma^{\circ}(y)^{2}}{2D_{e}(y)}} - 1\right] (\text{\AA}^{-2}), \quad (40)$$
and

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FIG. 17. The quadratic symmetric stretching force constant (F°) and the Varshni parameter (β°) along the MEP for proton transfer in CH₃OHF⁻.

$$F^{\circ}(y) = \eta \left[4.8305 + 0.3355 \left(\frac{2}{\pi}\right) \tan^{-1} [2.697\ 29 \times (y - 0.379\ 38)] \right] \pmod{\text{Å}^{-1}}, \tag{41}$$

the scale factor η being 0.9346. For each value of y along the proton-transfer path, Eq. (35) is an effective diatomic Varshni potential¹⁷⁹ in the shifted S_1 variable $\sigma(x,y) \approx x$ -|y|, with $D_e(y)$ as the energy of dissociation to CH₃O



FIG. 18. A contour plot of the stretching potential V(x,y) for the -OHF⁻ moiety of CH₃OHF⁻, as represented in the coordinates $x=2^{-1/2}$ [r(O-H)+r(H-F)] and $y=2^{-1/2}[r(O-H)-r(H-F)]$. The affixed labels specify relative energies in kcal mol⁻¹. The energy contour for the CH₃OH+F⁻ asymptote is shown as a dashed line, and the bound region of the surface is shaded for contrast.

 $+H+F^{-}$, $\beta^{\circ}(y)$ the curvature parameter derived from the quadratic force constant $F^{\circ}(y)$, and $\sigma^{\circ}(y)$ the position of equilibrium.⁶⁶

To evaluate $\sigma^{\circ}(y)$, the optimum value of S_1 is required along the MEP for proton transfer. The function $S_1^{\circ}(y)$ appearing in Table XII and plotted in Fig. 11 is sufficient for this purpose, but a better choice is needed if the relative values of the second partial derivatives of V(x,y) at its minimum are to closely reproduce the corresponding ratios of the quadratic force constants computed for CH₃OHF⁻ at the TZ(+)(d,p) MP2 level of theory. Therefore, a modified functional form⁶⁶ was employed in a weighted least-squares fit of the MEP data of Table XI to give $\tilde{S}_1^{\circ}(y)$. While the difference between the original and modified functions is hardly noticeable on the scale of Fig. 11, the function $S_1^{\circ}(y)$ displays a reduced curvature near y=0 and reproduces the point at y = -1.0 Å more closely. Once $S_1^{\circ}(y)$ is defined, $F^{\circ}(y)$ becomes the last unspecified component of V(x,y). The expression inside the braces in Eq. (41) arises from a fit to the TZ(+)(d,p) CISD values of $F_{11} = (\partial^2 V [CH_3 OHF^-] / \partial S_1^2)_y$ along the MEP at y (Å) $=(-\infty, -0.22352, 0.0, 0.28284, +\infty)$, as listed in Table XI. The application of the scale factor $\eta = 0.9346$ allows the empirical quadratic force constant of hydrogen fluoride^{66,155} to be exactly reproduced at $y = +\infty$ and presumably provides a favorable curvature correction for the entire MEP. The final $F^{\circ}(y)$ function is plotted in Fig. 17 along with the appropriately scaled F_{11} data and the curve for the resulting Varshni parameter β° .

A contour plot of the analytic expression for V(x,y)appears in Fig. 18. The global minimum of the analytic function lies 29.63 kcal mol⁻¹ below the $CH_3OH + F^-$ asymptote and corresponds to $r_e(O-H) = 1.0562$ Å and $r_{e}(H-F) = 1.3129$ Å; thus, the features of V(x,y) are in favorable agreement with the final proposals of Sec. IV, $D_e(CH_3OHF^-) = 30.0 \pm 1$ kcal mol⁻¹, $r_e(O-H) = 1.07$ ± 0.01 Å, and $r_{e}(H-F) = 1.32 \pm 0.01$ Å. The nearly centrosymmetric nature of the stretching potential is vividly demonstrated in Fig. 18 in that the contours in the bottom half of the well not only explore the $CH_3OH + F^-$ entrance valley but also protrude far into the $CH_3O^- + HF$ exit channel. Because V(x,y) is built up by superimposing a Varshni potential for the symmetric stretching coordinate on top of the MEP parametric curve and associated energy profile, it not only reproduces the proton-transfer path and provides a proper dissociation profile for fragmentation into $CH_3O + H + F^-$ but also possesses the desirable properties of $E^{\circ}(y)$ mentioned in Sec. V, such as the correct proton-transfer energy and long-range, ion-dipole asymptotic behavior.

The validity of any quantum-mechanical treatment of vibration in the model [-OHF]⁻ system is predicated on a satisfactory analysis of the extent of kinetic and potential energy coupling in CH₃OHF⁻ between the protonic motions in the -OHF⁻ framework and the complementary modes of vibration. The symmetric and antisymmetric harmonic stretching frequencies of the -OHF⁻ group arising from the full TZ(+)(d,p) MP2 quadratic force field of CH₃OHF⁻ are ω_9 =421 and ω_3 =1986 cm⁻¹, respectively.

If all elements of the force field which effectuate potential coupling (pc) of the stretching coordinates $(S_1 \text{ and } S_2)$ of the -OHF⁻ unit with other degrees of freedom are removed from the normal coordinate analysis, then $\omega_9[pc=0]=438$ and $\omega_3[pc=0]=1974$ cm⁻¹ are obtained. Furthermore, if the 2×2 force constant matrix for coordinates S_1 and S_2 is extracted from the TZ(+)(d,p) MP2 force field of CH₃OHF⁻ and employed in a harmonic vibrational analysis of the isolated triatomic system, [-OHF]⁻, assuming only the mass of ¹⁶O for the severed atom, then $\omega_9[pc=0, kc=0]=441$ and $\omega_3[pc=0, kc=0]$ $]=1966 \text{ cm}^{-1}$ result as the idealized frequencies in the absence of both potential and kinetic coupling (kc). In brief, the simple [-OHF]⁻ triatomic model without elaboration reproduces the harmonic stretching frequencies given by the complete quadratic force field of CH₃OHF⁻ within 20 cm^{-1} in each case, a level of approximation which is in the very least commensurate with the accuracy of the underlying potential energy surface itself. The analysis of anharmonicity in the protonic vibrations of the methanol-fluoride adduct via the triatomic [-OHF]⁻ model is thus shown to be viable.

For the [-OHF]⁻ triatomic system, the final stretching potential V(x,y) yields the harmonic frequencies $\omega_1 = 419$ and $\omega_3 = 2005 \text{ cm}^{-1}$. These results are almost identical to the best predictions for CH₃OHF⁻ deduced in Sec. IV, viz., $\omega_9 = 421$ and $\omega_3 = 2006$ cm⁻¹, a near equivalence which was intentionally established by an appropriate selection of weights in the fitting procedure used to determine $S_1^{\circ}(y)$. To facilitate the use of variational methods designed for full three-dimensional vibrational treatments of triatomic molecules, a simple bending potential in atomic units, $V_{\theta} = 0.1312 \sin^2(\theta/2)$, was appended to V(x,y). The coefficient of 0.1312 was calculated from the TZ(+)(d,p) MP2 quadratic force constant for -OHF⁻ out-of-plane bending in CH₃OHF⁻, to which the frequency $\omega_{13}(a'') = 1234 \text{ cm}^{-1}$ is attributable. A similar bending frequency, $\omega_2 = 1187 \text{ cm}^{-1}$, results from V_{θ} in [-OHF]⁻. If the kinetic coupling afforded by V_{θ} is effectively removed by increasing the coefficient of $\sin^2(\theta/2)$ to very large values, thus approximating the two-dimensional limit, v_1 decreases by ~10 cm⁻¹ and v_3 increases by less than 10 cm^{-1} in the final variational computation.

The geometric variables employed in the vibrational analysis of $[-OHF]^-$ were the Jacobi coordinates (R,r,ρ) , where R is the distance from the F^- ion to the center of mass of the -OH fragment, r is the O-H distance, and ρ is the angle subtended by the two radial direction vectors $\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}$. The total angular momentum was set to zero in the kinetic energy operator of the system.^{66,180} The variational procedure was initiated by converging the vibrational selfconsistent-field (VSCF) equations^{181,182} on the ground state of the system to obtain orthonormal sets of singlemode vibrational basis functions. The VSCF wave functions for the radial variables were determined numerically to high precision via the finite-difference boundary value method,¹⁸³ whereas the corresponding solutions for the angular coordinate were obtained in a basis of associated Legendre functions, $P_L^M(\cos \rho)$. Total vibrational wave func-

TABLE XIV. Variational vibrational levels (cm^{-1}) of the -OHF⁻ moiety in CH₃OHF^{-,a,b}

k	E_k	$(v_1v_2^lv_3)$	
1.	0.0	(0 0 ⁰ 0)	
2	503.7	$(1 \ 0^0 \ 0)$	
3	963.6	$(2 0^0 0)$	
4	1395.8	$(3 0^{\circ} 0)$	
5	1456.1	$(0 \ 0^0 \ 1)$	
6	1808.4	$(4\ 0^0\ 0)$	
7	2046.3	$(1 0^0 1)$	
. 8	2202.4	$(5 0^0 0)$	
9	2417.8	$(0\ 2^0\ 0)$	
10	2580.3	(6 0 ⁰ 0)	
11	2636.2	$(2 \ 0^0 \ 1)$	
12	2823.3	(1 2 ⁰ 0)	
13	2941.6	(7 0 ⁰ 0)	
14	3029.2	$[(0 \ 0^0 \ 2)]^c$	
15	3214.7	$(3 0^0 1)$	
16	3276.6 ~	(8 0 ⁰ 0)	
17	3324.4	(2 2 ⁰ [°] 0)	
18	3513.3	$[(1 \ 0^0 \ 2)]^{c}$	
19	3620.0	(9 0 ⁰ 0)	
20	3743.7	(4 0 ⁰ 1)	
21	3783.9	(3 2 ⁰ 0)	
22	3808.9	$(0\ 2^0\ 1)$	
23	3931.7	(10 0 ⁰ 0)	
24	4021.2	$[(2 \ 0^{\circ} \ 2)]^{c}$	
25	4182.9	(4 2 ⁰ 0)	
26	4249.6	$(11\ 0^0\ 0)$	
27	4287.4	$(5 0^0 1)$	
28	4366.1	(1 2 ⁰ 1)	

^aRelative to the ground vibrational state, which lies 2327.5 cm^{-1} above the minimum of the model triatomic surface.

^bHarmonic vibrational frequencies for the model triatomic system: $(\omega_1, \omega_2, \omega_3) = (419.4, 1186.7, 2004.9) \text{ cm}^{-1}$.

"Nominal assignments are indicated by brackets.

tions of the system were then computed as configuration interaction expansions in a set of state functions comprised of products of the VSCF modals. The individual configurations were selected by an energy criterion based on the VSCF eigenvalues of the component modals. In the final configuration interaction computation, the energy cutoff was set to E_{zp}^{VSCF} +0.10 a.u., generating a Hamiltonian matrix of dimension 1362 involving 50, 9, and 11 active singlemode functions for R, r, and ρ , in order. Systematic convergence studies were performed to ensure convergence to the level of 0.1 cm⁻¹ for the eigenstates lying less than 6700 cm⁻¹ above the minimum.

The variational vibrational procedures in this study were implemented with the program TRIVIB, whose algorithmic details have been reported in a previous communication by Schwenke.¹⁸⁴ Modifications pertinent to ionmolecule complexes are described in the recent work on [FHC1]⁻ by Allen and collaborators.⁶⁶ Briefly, the mesh size and range of the grids for the radial VSCF wave functions were determined automatically with an accuracy criterion of 10^{-8} ,¹⁸⁴ resulting in 1058 and 91 grid points for *R* and *r*, respectively. A high-order finite-difference representation of the second-derivative operator involving 27 points was used in the numerical procedures. The maximum value of *L* (62) for Legendre functions in the VSCF an-

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gular basis was also chosen automatically. In the computation of matrix elements of the potential energy function $\langle v'_1 v'_2 v'_3 | V(R,\rho,r) | v_1 v_2 v_3 \rangle$, Gauss-Legendre quadrature nodes were utilized with weights derived from the highest active single-mode wave functions in the CI procedure.¹⁸⁴ The number of quadrature points for (R,ρ,r) integrations were selected by an automatic procedure¹⁸⁴ to achieve $(10^{-8}, 10^{-8}, 10^{-6})$ relative accuracy from a total of (81,21,29) points, respectively. The effect of residual quadrature errors on the vibrational eigenvalues is deemed to be less than 0.1 cm⁻¹.

The lowest 28 vibrational levels of the [-OHF]⁻ model system are listed and assigned in Table XIV. The v_1 fundamental occurs at 503.7 cm^{-1} and displays a positive anharmonicity of 84.3 $\rm cm^{-1}$ as a consequence of the distinct asymmetry of the potential well, an unusual result for a symmetric stretching mode. By comparison, the anharmonic component of $v_1(583 \text{ cm}^{-1})^{68}$ in the [FHF]⁻ ion is approximately -30 cm^{-1} ,³⁹ and the chloride stretching fundamental (247 cm⁻¹) in [FHCl]⁻ has an anharmonicity of only $-4 \text{ cm}^{-1.66}$ The most salient feature of Table XIV is the occurrence of v_3 at 1456.1 cm⁻¹ due to a pronounced negative anharmonicity of -548.8 cm⁻¹. It is remarkable that this frequency is only 125 cm^{-1} higher than the antisymmetric stretching fundamental (1331 $(cm^{-1})^{68}$ of [FHF]⁻, even though the positive anharmonicity³⁹ present in the [FHF]⁻ vibration places the corresponding harmonic frequency over 700 cm^{-1} below its CH₃OHF⁻ counterpart. The downshift of the O-H stretching frequency of CH₃OH upon fluoride complexation is thus -2225 cm⁻¹, or 60% of the empirical v_1 fundamental of free methanol.¹³⁵ In the extreme case of [FHF]⁻, the analogous downshift is -2613 cm^{-1} , or 66%of v_0 (HF).^{68,155} According to this comparison and the criterion of Emsley,²⁴ the CH₃OHF⁻ and [FHF]⁻ adducts belong to the same class of ion-molecule complexes exhibiting "very strong" hydrogen bonding. For reference, the principal hydrogen stretching fundamental in [FHCl]⁻ lies at 2884 cm⁻¹ with an anharmonicity of -357 cm⁻¹,⁶⁶ constituting a complexation downshift of -1097 cm⁻¹, or 28% of v_0 (HF). For the F⁻ · H₂O analog of the methanolfluoride adduct, the relevant O-H harmonic frequency (ω_2) has been predicted to be 2670 cm⁻¹ at the TZ2P +diff CISD level of theory, and a total anharmonicity of -817 cm^{-1} has been estimated from a second-order perturbation analysis of off-diagonal coupling based on a TZP +diff RHF quartic force field, combined with a numerical solution of a single-mode wave equation to approximate diagonal anharmonicity.⁶¹ The data compiled here suggest that the ω_2 result is ~500 cm⁻¹ too high (Table IV) and the predicted anharmonicity is considerably overestimated. An actual value for $v_2(F^- \cdot H_2O)$ which is 200-300 cm⁻¹ lower than the previous estimate⁶¹ of 1853 cm⁻¹ seems likely.

The various data for CH_3OHF^- , $[FHF]^-$, $[FHCI]^-$, and $F^- \cdot H_2O$ suggest an intriguing interplay of harmonic and anharmonic components in the complexation downshifts of hydrogen stretching fundamentals in species of this type. For $[FHCI]^-$, an adduct of intermediate bond



FIG. 19. Contour plots in the stretching space for vibrational wave functions of the $[-OHF]^-$ triatomic model of CH₃OHF⁻ within the progression $|v_1v_2v_3\rangle = |0\ 0\ 0\rangle$, $|1\ 0\ 0\rangle$, $|2\ 0\ 0\rangle$, and $|3\ 0\ 0\rangle$. Contour lines are shown for the following values (in atomic units) of the normalized wave functions: 0.45, 0.10, -0.10, and -0.45. Positive and negative regions are illustrated using successively lighter and darker shading, respectively, superimposed on an intermediate gray background. Dashed contours of the potential energy function are also shown for reference, the outer boundary representing the CH₃OH+F⁻ dissociation limit and the inner loop one-half the ion-molecule binding energy (cf. Fig. 18).

strength, 84% of the frequency downshift of -1097 cm^{-1} is attributable to the harmonic component; however, the negative anharmonicity of the stretching fundamental is a factor of 2 greater than in the free monomer, providing a significant downshift contribution of 16%.66 For the more strongly bound CH_3OHF^- and $F^- \cdot H_2O$ complexes, with total downshifts in the 2000 cm^{-1} range, the ratio of harmonic and anharmonic contributions appears to be maintained, requiring that the negative anharmonicity of the hydrogen stretching fundamental continues to increase in magnitude. Finally, in the limit of the centrosymmetric [FHF]⁻ ion, the harmonic component of the downshift has almost reached 3000 cm^{-1} , but the anharmonicity has suddenly changed sign such that the resulting fundamental frequency is only 100–300 cm^{-1} smaller than in the nearly centrosymmetric CH_3OHF^- and $F^- \cdot H_2O$ cases.

From Table XIV the spacings $\delta_n^0 = E_n - E_{n-1}$ between successive levels in the (n,0,0) sequence of [-OHF]⁻ eigenstates are found to be $(\delta_1^0, \delta_2^0, ..., \delta_{10}^0) = (503.7, 459.9, 432.2, 412.6, 394.0, 377.9, 361.3, 335.0, 343.4, 311.7) cm⁻¹. For <math>n > 2$ the pattern of decreasing spacings is characteristic of single-mode vibrations of the F⁻ ion in a Morse-type potential, notwithstanding some erratic behavior in the highest δ_n entries due to increased state mixing. The δ_1 and δ_2 separations are somewhat anomalous be-



FIG. 20. Contour plots in the stretching space for vibrational wave functions of the [-OHF]⁻ triatomic model of CH₃OHF⁻ within the progression $|v_1v_2v_3\rangle = |600\rangle$, $|700\rangle$, $|900\rangle$, and $|1000\rangle$. See the caption to Fig. 19 for details.

cause the $\delta_2 - \delta_1$ difference is significantly larger than subsequent decrements in the sequence, for reasons evident from the wave function plots below. The spacing sequence for the (n,0,1) eigenstates is $(\delta_1^1, \delta_2^1, ..., \delta_5^1) = (590.2,$ 589.9, 578.5, 529.0, 543.7) cm⁻¹, whose individual elements are significantly larger than their δ_n^0 analogs, as observed in a less pronounced manner for [FHC1]^{-.66} Qualitatively, this shift in the two δ_n series can be accounted for by second-order perturbation theory if the anharmonic constant χ_{31} is assumed to be roughly + 100 cm⁻¹. How-ever, the comparative details of the δ_n^0 and δ_n^1 sequences elude simple explanations via this formalism. For example, constant values of $\delta_n - \delta_{n-1} = 2\chi_{11}$ are predicted by perturbation theory for both the (n,0,0) and (n,0,1) series,⁶⁶ but clearly these differences in the latter case are much smaller on average. Such occurrences confirm the necessity of a rigorous variational treatment of vibrations for the [-OHF]⁻ system.

Structural features of the wave functions for several eigenstates in the (n,0,0) and (n,0,1) sequences are revealed by the countour plots in the stretching space which comprise Figs. 19-21. The spatial extension of the nodal patterns in the lowest eigenstates propagates first along the axis of the symmetric stretching coordinate, as highlighted by the fact that in the $|2 \ 0 \ 0\rangle$ and $|3 \ 0 \ 0\rangle$ states the maximum projection into the $CH_3O^- + HF$ region actually occurs in the second lobe from the left in the plots. With further vibrational excitation in the (n,0,0) series, the formation of new wave function lobes is primarily directed into the $CH_3OH + F^-$ valley, however. This change of di-



FIG. 21. Contour plots in the stretching space for vibrational wave functions of the [-OHF] - triatomic model of CH3OHF- within the progression $|v_1v_2v_3\rangle = |0\ 0\ 1\rangle$, $|1\ 0\ 1\rangle$, $|2\ 0\ 1\rangle$, and $|3\ 0\ 1\rangle$. See the caption to Fig. 19 for details.

rection in nodal propagation is apparently the source of the anomalous δ_1 and δ_2 level spacings encountered above. Another notable feature of the (n,0,0) wave functions is the filling of the region (y>0) past the bend in the protontransfer surface as the excitation level exceeds 6. As shown in Fig. 20, this spatial extension is achieved by the formation of conspicuously long fingers emanating from the wave function lobes in the $CH_3OH + F^-$ valley. Accordingly, a catastrophic breakdown of vibrational adiabaticity between the F⁻ and O-H stretching vibrations is signaled, because the spatial extent of the wave function lobes in the direction of the antisymmetric stretching coordinate varies widely not only within each eigenstate but also throughout the entire (n,0,0) progression. In this sense the structure of the lowest ten eigenstates in the (n,0,0) progression of [-OHF]⁻ is dramatically different from that observed for [FHC1]^{-.66}

In Fig. 21 the wave function for the $|001\rangle$ eigenstate, which corresponds to the fundamental level of the antisymmetric stretch, is seen to have greatest amplitude for y > 0, i.e., in the $CH_3O^- + HF$ half of the proton-transfer surface! The positive and negative lobes of this wave function are noticeably skewed relative to each other to conform to the bent energy contours in the y=0 region. Within the first four members of the (n,0,1) series, a discernible lobe structure is maintained, in which the binodal character of the $|001\rangle$ wave function is replicated by spatial extension at a 45° angle into the $CH_3OH + F^-$ valley. Simultaneously, the concentration of wave function amplitude in the y > 0region is retained in the series by the formation of lobe

2085



FIG. 22. Contour plots in the stretching space for vibrational wave functions of the $[-OHF]^-$ triatomic model of CH₃OHF⁻. The depicted eigenstates are roots 18, 20, 24, and 27 of Table XIV. See the caption to Fig. 19 for details.

fingers comparable in length but enhanced in width relative to those identified in the (n,0,0) progression.

The eigenstates of [-OHF]⁻ encountered as the energy exceeds 3000 $\rm cm^{-1}$ relative to the ground vibrational level have increasingly irregular nodal patterns and are not amenable to unambiguous assignment. In Table XIV, root 14 is nominally assigned as the $|002\rangle$ state, but the associated wave function contours bear little resemblance to the expected pattern derived by the addition of another node to the $|001\rangle$ plot along the y coordinate without bifurcation in the orthogonal direction [cf. Fig. 21(a)]. The erratic nodal structures of higher-lying eigenstates are exemplified by the contour plots for roots 18, 20, 24, and 27, as provided in Fig. 22. The characteristics of these wave functions are suggestive of quantum ergodicity in this system at vibrational energies which are less than half of the binding energy of the CH₃OHF⁻ complex, a possibility which has concomitant implications for statistical models of the proton-transfer kinetics in the reaction of the fluoride ion with methanol.

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J. Chem. Phys., Vol. 100, No. 3, 1 February 1994

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J. Chem. Phys., Vol. 100, No. 3, 1 February 1994