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4 **Contrasting patterns of coupling between the CH stretches and the large-**
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7 **amplitude motions in the molecules, CH_3NH_2 , CH_3OH_2^+ and $\text{CH}_3\text{CH}_2\cdot$**
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Abstract

In each of the title molecules, torsional and inversion tunneling occurs between six equivalent minima. The coupling between these large-amplitude motions and the CH stretch vibrations stems from the variation of the CH stretching force constants as a function of the torsional and inversion coordinates. First principles 2-dimensional maps of the variation of the CH-stretch force constants are reported. Although the torsional barriers differ by more than a factor of 20, the torsion-inversion-vibration coupling is similar for two of the species, CH_3NH_2 and $\text{CH}_3\text{CH}_2\cdot$, but is much weaker and qualitatively different in form for the third species, CH_3OH_2^+ .

Keywords: Torsion, inversion, methylamine, ethyl radical, protonated methanol, maps of torsion-inversion-vibration couplings

1. Introduction

Methylamine, ethyl radical and protonated methanol (CH_3XH_2 with $\text{X}=\text{N}, \text{C}, \text{O}$) belong to the G_{12} molecular symmetry group [1]. Each of them has two large-amplitude degrees of freedom, the methyl torsion and inversion at X, which together connects six equivalent potential wells [2-8]. CH_3NH_2 has a high barrier to inversion ($\sim 1950 \text{ cm}^{-1}$) [3,9-11], whereas in protonated methanol, CH_3OH_2^+ , the barrier is lower ($\sim 875 \text{ cm}^{-1}$) [3]. In the ethyl radical, $\text{CH}_3\text{CH}_2\cdot$, there is no barrier to inversion, only a low-barrier internal rotation path [3,5-8,12]. Methylamine, protonated methanol and ethyl radical have torsional barriers of 703.8 cm^{-1} , 399.6 cm^{-1} and 8.0 cm^{-1} , respectively [3].

Although the torsional and inversion barrier heights are different, the torsion-inversion coupling is similar in these three molecules [3]. For each molecule, the dominant torsion-inversion coupling has the form $V_{1,3}t\cos 3a$, where α is the torsional angle and τ is the inversion angle in radians. In each case, the coupling strength $V_{1,3}$ is similar, falling in the range, 280 to 450 cm^{-1} , despite the very wide range of the barriers to torsion and inversion [3]. In this paper, we address the coupling of the large-amplitude motions (LAM) to the CH-stretch vibrations. Does the similarity of coupling between the LAM on very different potential energy surfaces apply also to the coupling of the LAM with the high-frequency, small-amplitude vibrations?

To date, the coupling of CH stretch vibrations to large-amplitude torsional motion has been investigated most extensively in methanol. In methanol, which has a torsional barrier of 373 cm^{-1} and belongs to the G_6 molecular symmetry group, the

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4 asymmetric CH stretches, ν_2 and ν_9 , were found to have inverted torsional tunneling
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7 splittings relative to the vibrational ground state [13,14]. Since that discovery, many
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9 theoretical papers [15-22] have addressed the roles of CH-stretch-torsion coupling, of
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11 symmetry, and of geometric phase in bringing about this anomalous level ordering.
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14 In each of the three title molecules with G_{12} symmetry [1,2,4], large-amplitude
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16 inversion motion combines with torsional tunneling to give 6 equivalent minima [2-
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18 9]. Whereas in methanol, there is a tunneling doublet (A and E species), in the G_{12}
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20 molecules, the tunneling multiplet has four distinct levels - A, B, E_1 , and E_2 species
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22 [4]. The ordering of the 4-level tunneling pattern varies in different G_{12} molecules
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24 according to the reduced masses and barrier heights involved [23]. Nonetheless, the
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26 tunneling patterns in the asymmetric CH stretch excited states are altered relative to
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28 the ground state [2,24]. Consequently, knowledge of the potential couplings of the
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30 CH stretch to the torsion and inversion coordinates is necessary for understanding the
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32 spectra and dynamics of the CH stretch excited states in these molecules.
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38 The potential couplings of the CH-stretch to the torsional angle, α , may be
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40 categorized by their α -dependence. The symmetry-allowed coupling that is lowest-
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42 order in α involves the dependence of the force constants on $\cos\alpha$. Such coupling,
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44 which has been invoked [14] to account for the inverted tunneling splittings in
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46 methanol, has been identified as analogous to a first-order Jahn-Teller effect (JT1)
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48 [15,21,22]. The JT1 coupling results in a geometric phase of -1 accumulated for the
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50 asymmetric CH stretch vibrations on a 2π torsional rotation [17]. The $\cos 2\alpha$
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52 coupling was also derived [14] and has the form of a second-order Jahn-Teller effect
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54 (JT2) [15], analogous to the Renner-Teller effect in linear molecules [21,22]. It is
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4 now recognized that in methanol the JT2 coupling is slightly larger than the JT1
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6 coupling, which yields a geometric phase of +1 for a 2π torsional rotation [21,22].
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8 Both the JT1 and JT2, separately or in any combination, yield the inverted torsional
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10 tunneling splittings found experimentally in methanol.
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14 Where both JT1 and JT2 couplings present, these two kinds of coupling may
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16 cancel at certain locations in the large-amplitude coordinate space, which causes the
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18 two coupled vibrations to become degenerate at that point. Such localized vibrational
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20 degeneracies in methanol have been recognized as vibrational conical intersections
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22 (CIs) [25]. In the context of such vibrational CIs, the high-frequency CH stretch
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24 vibrations are regarded as functions of certain low-frequency large-amplitude
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26 coordinates, which in the case of methanol were the torsional angle and the COH
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28 bend angle.
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33 The present work is a systematic investigation of coupling in the title
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35 molecules between the CH stretches and the large-amplitude coordinates, α and τ .
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37 First principles 2-dimensional maps in the large-amplitude space are presented for the
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39 local CH stretch force constant and for the local-local CH stretch coupling, so that the
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41 relative strengths of JT1- and JT2-like couplings can be evaluated. The similarities
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43 and differences among the molecules, CH_3NH_2 , $\text{CH}_3\text{CH}_2\cdot$ and CH_3OH_2^+ , are
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2. Computational method

The present calculations are based on the previously reported torsion-inversion potential energy surfaces, $V(\alpha, \tau)$, for the title molecules (Fig. 2 of Ref. [3]). Each point on these surfaces represents partially optimized geometries in which the 13 other vibrational coordinates were optimized at the MP2/aug-cc-pVTZ level with constrained values of α and τ . The energy at each partially optimized geometry was calculated at the CCSD(T)/aug-cc-pVTZ level [26]. For the present work, 60 unique grid points on each surface were selected at which the single-bond CH force constants and the coupling between the CH stretches are computed numerically. The selected points were in the range $0^\circ \geq \alpha \geq 360^\circ$ and $0^\circ \geq \tau \geq \tau_{\max}$ with $\tau_{\max} = 66^\circ, 42^\circ$, and 55° for methylamine, ethyl radical and protonated methanol respectively.

Starting with the partially optimized geometry at each selected (α, τ) point, single point energies were calculated (CCSD(T)/aug-cc-pVTZ) with one CH bond constrained at seven different bond lengths, $r = r_e + \delta$ where $\delta = -0.036, -0.068, -0.09, 0.0, 0.052, 0.094, 0.125$ Å and r_e is the partially optimized bond length. The seven computed energies were then fit to an anharmonic function [27] of the CH bond length,

$$V(r) = V(r_e) + \frac{1}{2}k_{ii}(r - r_e)^2 + g(r - r_e)^3 + j(r - r_e)^4 \quad (1)$$

The values of the harmonic single-bond force constant k_{ii} and anharmonic force constants g and j are tabulated in the supplementary Table S1. As in the previous work [3], the force constants in the tables and figures of this paper are given in the units of $\text{cm}^{-1}(\text{Å})^{-2}$. Since the typical zero-point amplitude of a local CH stretch vibration is 0.1 Å, these units provide a qualitative measure of the potential impact of the variation of each force

constant on the relevant spectra. For the reader's convenience, the equivalence is $1 \text{ cm}^{-1} (0.1 \text{ \AA})^{-2} = 1.986 \times 10^{-3} \text{ mdyne/\AA}$.

The orientation of the stretched CH bond relative to the molecular frame at each combination of the torsion and inversion coordinates is depicted in Fig. 1(a). The map of k_{ii} in the (α, τ) space is invariant under the operations $(\alpha, \tau) \rightarrow (60^\circ - \alpha, -\tau)$, $(240^\circ - \alpha, \tau)$ and $(180^\circ + \alpha, -\tau)$, and thus has C_{2h} point group symmetry with the σ_h plane intersecting the figure at $\alpha = 120^\circ$ and 300° . In the present partially optimized calculations, the torsional angle α was specified by constraining only one dihedral angle ($H_1\text{-C-X-H}_4$), and the inversion angle τ was specified by constraining a different dihedral angle ($H_4\text{-C-X-H}_5$) where H_4 and H_5 are bonded to the X atom. As in the previous work (Eq. 1 and 2 of [3]), properly symmetrized values of α and τ were computed for the purpose of the analysis. With this procedure, the computed force constant maps $k_{ii}(\alpha, \tau)$ conform as closely as possible to the required C_{2h} symmetry and the potential surfaces $V(\alpha, \tau)$ to G_{12} symmetry. To a check on any small systematic errors resulting from the asymmetrical constraints in the partial optimization procedure, the calculations were computed over the whole range $0^\circ \geq \alpha \geq 360^\circ$, even though the smaller range $0^\circ \geq \alpha \geq 180^\circ$ is in principle sufficient for use with properly symmetrized fit functions.

The force constant data are fit to products of cosine Fourier terms in α and polynomial terms in τ , keeping only the symmetry-allowed terms,

$$\begin{aligned}
 k_{ii}(\alpha, \tau) = & B_{00} + B_{02}\tau^2 + B_{04}\tau^4 + B_{11}\tau \cos(\alpha - \phi) + B_{13}\tau^3 \cos(\alpha - \phi) \\
 & + B_{20} \cos 2(\alpha - \phi) + B_{22}\tau^2 \cos 2(\alpha - \phi) + B_{24}\tau^4 \cos 2(\alpha - \phi). \quad (2) \\
 & + B_{31}\tau \cos 3(\alpha - \phi) + B_{33}\tau^3 \cos 3(\alpha - \phi) + B_{40} \cos 4(\alpha - \phi)
 \end{aligned}$$

The choice of phase angle, $\phi = 120^\circ$, corresponds to the geometries illustrated in Fig. 1(a) and to the plots in Fig. 2. The symmetrically equivalent phase angles, $\phi = 0^\circ$ and 240° , would cause the plots in these figures to be shifted by $\pm 120^\circ$.

The off-diagonal force constant, k_{ij} , represents the potential energy contribution to the local-local coupling between two single-bond CH stretches. In the local mode picture [28], the local-local coupling, including both the potential and kinetic contributions, is responsible for the large splittings (34 to 68 cm^{-1}) between the symmetric and asymmetric methyl CH stretches in a variety of hydrocarbon molecules [28]. In this paper, we investigate the variation of the potential contribution, k_{ij} , in the large-amplitude (α, τ) coordinate space.

Values of k_{ij} are calculated numerically by varying the length two CH bond lengths relative to the partially optimized geometry at each selected (α, τ) point,

$$k_{ij} \approx \frac{1}{\delta^2} [E(r_{ie}, r_{je}) + E(r_{ie} + \delta, r_{je} + \delta) - E(r_{ie}, r_{je} + \delta) - E(r_{ie} + \delta, r_{je})]. \quad (3)$$

The bond lengths, r_{ie} and r_{je} correspond to the CH bond lengths at the partially optimized geometries of each of the titled molecules at constrained values of α and τ . For the calculations reported here, the increment δ in the equilibrium CH bond length was chosen to be 0.125 Å, which is approximately the classical outer turning point for the zero-point vibrational level of the local CH stretch. As can be seen from Fig. 1(b), the map $k_{ij}(\alpha, \tau)$ space also has C_{2h} point group symmetry but here with the σ_h plane intersecting the figure at $\alpha = 0^\circ$ and 180° .

The variation of k_{ij} with α and τ is fit to the following expression,

$$k_{ij}(\alpha, \tau) = A_{00} + A_{02}\tau^2 + A_{04}\tau^4 + A_{11}\tau \cos(\alpha - \phi) + A_{20} \cos 2(\alpha - \phi) + A_{22}\tau^2 \cos 2(\alpha - \phi) + A_{24}\tau^4 \cos 2(\alpha - \phi) + A_{31}\tau \cos 3(\alpha - \phi), \quad (4)$$

and the resulting coefficients are given in Table 1(b). The phase angle $\phi = 0^\circ$ corresponds to the geometries illustrated in Fig. 1(b) and to the plots in Fig. 4.

3. Results

The variation of CH single-bond force constants, k_{ii} , with torsion and inversion coordinates is depicted in Fig. 2 and tabulated in the Supplementary Tables S.1, 2, 3. The residuals between the *ab initio* data and the fits are less than 1% of the plotted ranges for all three molecules. For methylamine and the ethyl radical, the range of the variation of k_{ii} in the large-amplitude space is about 8%; however for protonated methanol, it is much less, only about 2%. The qualitative difference between the neutral species, methylamine and ethyl, on one hand, and the charged species CH_3OH_2^+ on the other, is also evident in the shape of the surfaces plotted in Fig. 2. One can see from Fig. 3 and Table 1(a) that for the neutral molecules the JT2-like coupling terms in $\cos 2(\alpha - \phi)$ are much larger than the JT1-like terms in $\cos(\alpha - \phi)$, but that on the other hand in CH_3OH_2^+ the reverse is true.

The variation of the local-local coupling, k_{ij} , with torsion and inversion coordinates is depicted in Fig. 4 and tabulated in the Supplementary Tables S.1, 2, 3. The first thing to be noted is that the variation of k_{ij} in the large-amplitude space is typically an order of magnitude smaller than the variation of diagonal force constant k_{ii} . On that reduced scale, the qualitative comparisons among the three molecules is similar. Both the magnitude and the variation of k_{ij} is much larger in the neutral species than in

CH₃OH₂⁺, and the $\cos 2\alpha$ terms dominate in the neutral species but are near zero in CH₃OH₂⁺ (Fig. 3 and Table 1(b)).

These same calculations were also carried out at the MP2/6-311++(3df,2p) level to test the dependence on calculation level. While, as expected, the MP2 level yielded higher force constants, the appearance of the coupling data is essentially identical to that shown in Figs. 2 and 4.

4. Discussion and Conclusion

The present results show that the dominant potential coupling between the CH stretch vibrations and the large-amplitude torsional and inversion coordinates (α , τ) arises from the variation of the single-bond force constants in the large-amplitude space (Fig. 2). The variation of the local-local coupling (Fig. 4) is about an order of magnitude smaller.

To determine the variation of the harmonic CH stretch frequencies in the large-amplitude space, one needs the variation of the diagonal and off-diagonal CH force constants as discussed above and also the variation of the g -matrix elements for the CH vibrations [29]. The CH harmonic frequencies might be used, for example, to consider the vibrationally adiabatic CH-stretch dynamics [17,19,30] or to look for vibrational conical intersections in the torsion-inversion space [25]. First consider the dependence of the local CH stretch harmonic frequency on α and τ . The diagonal g -matrix element for the CH stretch internal coordinate is $g_{ii} = m_H^{-1} + m_C^{-1}$ [29], which is independent of α and τ . Hence, the torsional dependence of the local CH stretch frequency is entirely attributable to the torsional dependence of the diagonal force constant, k_{ii} . Within the 3-dimensional CH stretch space, normal mode CH frequencies can also be computed with

the aid of the off-diagonal force constants k_{ij} and the off-diagonal g-matrix elements, g_{ij} .

There is a modest variation of $g_{ij} = \frac{m_C m_H}{m_C + m_H} \cos q_{ij}$ [29] with α and τ because of the slight

flexing of the methyl group manifested as a small variation of the H_iCH_j angle, θ_{ij} .

However in the present molecules, the fractional variation of g_{ij} is only about 20 to 25% of the variation of k_{ij} . Overall then for all three molecules, the variation of the CH harmonic frequencies in the (α, τ) space is mainly determined by the variation of the force constants (Figs. 2 and 4), with variation of the CH inertial properties contributing only about 1 to 2%. Note that the above discussion of the role of g-matrix elements is based on consideration of only the three CH stretch coordinates. A full-dimensional treatment will show a more complicated (α, τ) -dependence of the inertial constants for motion along each of the “CH-stretch” normal coordinates.

How should we explain the qualitative difference in behavior between methylamine and ethyl on one hand and protonated methanol on the other, with the CH-LAM coupling in the latter being much weaker and different in form? In protonated methanol, the $\cos 2\alpha$, “JT2-like” coupling is negligible leaving only a small JT1-like coupling (Fig. 3). This contrasting behavior is surprising given that the coupling between the two LAMs is similar in both magnitude and form across the three molecules [3]. Since the torsional and inversion barriers in CH_3OH_2^+ are intermediate between the higher barriers in CH_3NH_2 and the much lower barriers in CH_3CH_2^+ , the differences in barrier height cannot be responsible for the anomalous coupling behavior. However, CH_3OH_2^+ is the only charged species of the three studied molecules. The net positive charge gives rise to higher partial positive charges on the methyl protons and

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4 consequently to a more splayed methyl geometry with larger HCH angles (about 113°
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6 versus about 108°). While we do not have a clear causal relationship, these changes,
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8 associated with a net positive charge, are correlated with the contrasting coupling
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10 behaviors documented in Figs. 2 and 4.
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Table 1. Fit parameters for the CH stretch force constant surfaces.^a

Parameter	Operator	CH ₃ NH ₂		CH ₃ CH ₂ •		CH ₃ OH ₂ ⁺	
		CCSD(T) ^b	MP2 ^c	CCSD(T) ^b	MP2 ^c	CCSD(T) ^b	MP2 ^c
(a) Diagonal single bond force constants, $k_{ii}(\alpha, \tau)$							
B ₀₀	constant	2577.61(27)	2680.68(30)	2582.12(24)	2688.35(22)	2809.43(05)	2902.48(16)
B ₀₂	τ^2	40.47(92)	39.7(12)	37.5(29)	37.3(28)	-5.33(30)	-4.02(31)
B ₀₄	τ^4	-3.67(82)	-4.52(87)	-9.5(51)	-11.2(48)	2.97(31)	1.93(32)
B ₁₁	$\tau\cos(\alpha-\phi)$	69.56(76)	69.07(83)	41.73(98)	37.83(98)	22.44(17)	22.04(18)
B ₁₃	$\tau^3\cos((\alpha-\phi)$	-27.08(71)	-25.56(77)	-27.9(24)	-26.1(22)	-2.62(23)	-1.86(25)
B ₂₀	$\cos2(\alpha-\phi)$	-87.48(38)	-88.08(43)	-91.92(35)	-84.74(33)	-0.36(08)	-0.25(08)
B ₂₂	$\tau^2\cos2(\alpha-\phi)$	46.8(15)	48.4(17)	43.7(42)	41.7(39)	2.17(44)	-0.54(45)
B ₂₄	$\tau^4\cos2(\alpha-\phi)$	-4.5(10)	-6.2(13)	-10.5(74)	-10.7(69)	-1.98(45)	-0.09(47)
B ₃₁	$\tau\cos3(\alpha-\phi)$	6.07(60)	5.94(79)	8.77(99)	8.21(93)	5.49(16)	5.91(17)
B ₃₃	$\tau^3\cos3(\alpha-\phi)$	-1.30(53)	-0.95(73)	-2.8(23)	-2.5(21)	-1.80(22)	-1.93(23)
B ₄₀	$\cos4(\alpha-\phi)$	-1.44(20)	-1.23(23)	-3.11(19)	-2.73(18)	0.09(03)	0.17(04)
V _{rms} ^d		1.52	1.68	1.36	1.27	0.28	0.29
(b) Off-diagonal local-local force constants, $k_{ij}(\alpha, \tau)$							
A ₀₀	constant	29.47(08)	32.51(12)	23.63(07)	25.09(08)	8.90(08)	9.03(08)
A ₀₂	τ^2	-4.25(35)	-4.59(49)	-3.93(82)	-3.79(98)	-0.64(42)	-0.12(42)
A ₀₄	τ^4	0.32(25)	0.68(34)	-0.8(14)	0.1(17)	-0.24(43)	-0.67(44)
A ₁₁	$\tau\cos(\alpha-\phi)$	-1.60(08)	-1.64(12)	-2.34(12)	-2.24(14)	-0.90(08)	-1.09(08)
A ₂₀	$\cos2(\alpha-\phi)$	-13.19(12)	-13.32(17)	-8.83(09)	-8.42(11)	-0.15(11)	0.19(11)
A ₂₂	$\tau^2\cos2(\alpha-\phi)$	6.87(50)	7.11(69)	7.7(12)	7.4(14)	0.2(6)	-0.06(60)
A ₂₄	$\tau^4\cos2(\alpha-\phi)$	-0.58(36)	-0.65(50)	-0.5(20)	-2.2(24)	-0.09(06)	-0.01(62)
A ₃₁	$\tau\cos3(\alpha-\phi)$	0.36(08)	0.48(12)	0.13(12)	0.12(14)	0.07(08)	0.06(08)
V _{rms} ^d		0.67	0.92	0.54	0.63	0.54	0.55

^a Numbers in parentheses are one standard deviation in units of the last digit.^b Single point calculations at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ.^c Single point calculations at MP2/6-311++G(3df,2p)//MP2/6-311++G(3df,2p).^d Root-means-square deviation of the fitted surface from the *ab initio* points.

Figures

Fig. 1. Contour plots of (a) the CH_3NH_2 local CH stretching force constant, k_{ii} , and (b) of the local-local coupling constant, k_{ij} , with the large-amplitude torsion-inversion (α , τ) space. The orientations of the local CH stretches (red arrows) relative to the molecular frame are shown for certain combinations of α and τ . The contours of k_{ii} and k_{ij} are given

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4 in $\text{cm}^{-1} (0.1 \text{ \AA})^{-2}$ relative to the zero contour at $2473.69 \text{ cm}^{-1} (0.1 \text{ \AA})^{-2}$. The solid black
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7 circles indicate the positions of the 6 equivalent potential energy minima and the open
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9 circles indicate the torsional saddle points [3].
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Fig. 2. Variation of the local CH stretching force constants, k_{ii} with torsion (α) and inversion (τ) coordinates for (a) methylamine, (b) ethyl radical, and (c) protonated methanol. The plotted data points are relative to the baseline values of 2473.69, 2480.47, and 2783.56 cm^{-1} ($0.1 \text{ \AA})^{-2}$ respectively for the three panels. The solid and open black circles on the lower planes indicate the global minima and torsional saddle points respectively.

Fig. 3. Fourier components of the local CH stretching force constants given in Fig. 2. The curves displayed, as obtained from the fits to Eq. (2), are polynomial functions of the inversion angle, τ .

Fig. 4. Variation of the local-local coupling constant, k_{ij} with torsion (α) and inversion (τ) coordinates for (a) methylamine, (b) ethyl radical, and (c) protonated methanol. The solid and open black circles on the lower planes indicate the global minima and torsional saddle points respectively.