Hydrogen Bonding in the Mixed HF/HCl Dimer: Is It Better to Give or Receive?

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The ClH FH and FH ClH configurations of the mixed HF/HCl dimer (where the donor acceptor notation indicates the directionality of the hydrogen bond) as well as the transition state connecting the two configurations have been optimized using MP2 and CCSD(T) with correlation consistent basis sets as large as aug-cc-pV(5+d)Z. Harmonic vibrational frequencies confirmed that both configurations correspond to minima and that the transition state has exactly one imaginary frequency. In addition, anharmonic vibrational frequencies computed with second-order vibrational perturbation theory (VPT2) are within 6 cm^{-1} of the available experimental values and deviate by no more than 4 cm^{-1} for the complexation induced HF frequency shifts. The CCSD(T) electronic energies obtained with the largest basis set indicate that the barrier height is 0.40 kcal mol^{-1} and the FH ClH configuration lies 0.19 kcal mol^{-1} below the ClH FH configuration. While only modestly attenuating the barrier height, the inclusion of either the harmonic or anharmonic zero-point vibrational energy effectively makes both minima isoenergetic, with the ClH FH configuration being lower by only 0.03 kcal mol^{-1}. © 2018 Wiley Periodicals, Inc.

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Introduction

The dimers resulting from the mono-hydration of HF and HCl exhibit only a single low energy configuration, where the hydrogen halide donates the hydrogen bond to water.[1,2] Dimer configurations in which HF or HCl accepts a hydrogen bond from water have not been observed experimentally and do not correspond to minima when characterized sufficiently with robust electronic structure methods.[1–4] This information indicates that although HF and HCl are good hydrogen bond donors, they may not be the best hydrogen bond acceptors. As such, the HF/HCl mixed dimer is an interesting system because hydrogen bond formation requires one of the fragments to accept a hydrogen bond from the other. Despite exhaustive work on the related $(HF)_2$ and $(HCl)_2$ homogeneous dimers,[5–13] the mixed HF/HCl dimer has received relatively little attention. This heterogeneous dimer was first characterized in 1977,[14] but only the ClH FH configuration was detected in the microwave spectra of the molecular beam electric resonance experiments (where this donor acceptor notation has been adopted in this study to clearly indicate the directionality of the hydrogen bond). More than a decade later, Fraser and Pine observed not only the ClH FH configuration but also the FH ClH configuration in the microwave and infrared (IR) spectra of molecular beams formed by expanding a mixture of HF and HCl in helium.[15] The authors inferred that the ClH FH configuration was lower in energy than the FH ClH configuration based on the relative strengths of hyperfine transitions.[15] In 1995, Oudejans and Miller measured the dissociation energy (D_0) of the mixed dimer using vibrational predissociation spectroscopy.[16] The D_0 of the ClH FH configuration was determined to be 642 cm^{-1} (1.84 kcal mol^{-1}), however the D_0 for the FH ClH configuration was not reported because it dissociates via a different pathway that complicates such measurements.[16]

In addition to these experimental studies, a variety of theoretical investigations have examined both configurations of this simple heterodimer.[17–22] Early self-consistent field (SCF) Hartree–Fock (HF)[23–26] computations by Kollman and co-workers compared different proton donors and acceptors to characterize the orientation and strength of hydrogen bonds; this revealed that the electronic energy of the FH ClH configuration was approximately 1 kcal mol^{-1} higher in energy than that of the ClH FH configuration.[17–19] A subsequent theoretical investigation in 1988 by Latajka and Scheiner[21] included post-HF computations with second-order Møller–Plesset perturbation theory (MP2).[27] These computations indicated that the two configurations were isoenergetic (within 0.1 kcal mol^{-1}). In addition, a transition state connecting the two configurations was identified and found to be approximately 0.5 kcal mol^{-1} higher in energy. The ClH FH and FH ClH configurations remained isoenergetic after the zero-point vibrational energies (ZPVEs) were included from SCF harmonic vibrational frequency computations. In contrast, the molecular mechanics for clusters (MMC) method developed by Augspurger and Dykstra indicated that the FH ClH configuration was appreciably lower in energy whether the harmonic ZPVE was included or not (by approximately 0.3 and 0.7 kcal mol^{-1}, respectively).[22] That study also identified the corresponding transition state with a barrier height of 0.8 kcal mol^{-1}.

This study builds on the important work outlined in the previous paragraphs and provides reliable relative energetics for

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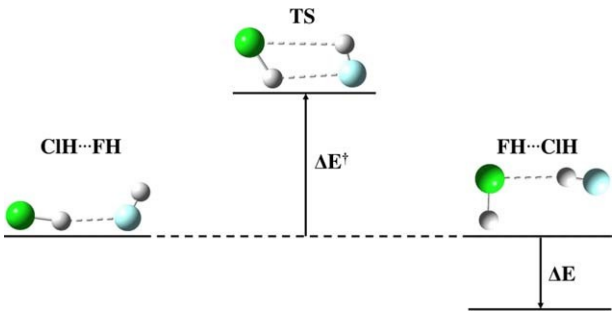

Figure 1. Depiction of the structures and energetic quantities associate with the mixed HF/HCl dimer. [Color figure can be viewed at wileyonlinelibrary.com]

the two configurations of the mixed HF/HCl dimer as well as the transition state barrier height. The CCSD(T) method and large correlation consistent basis sets are used to compute not only electronic energies near the complete basis set (CBS) limit but also optimized geometries, harmonic vibrational frequencies and anharmonic vibrational frequencies. To the best of our knowledge, the results presented here include the (i) first anharmonic vibrational analysis with ab initio electronic structure methods, (ii) the first ab initio harmonic vibrational frequencies beyond the SCF level of theory and (iii) the first ab initio relative electronic energies beyond the MP2 computations from Latajka and Scheiner[21] for this important hydrogen bonding prototype. The data presented here anchors these three key stationary points on the potential energy surface of the HF/HCl dimer system.

Methodology

Both configurations of the HF/HCl dimer and the transition state connecting the two have been optimized using MP2[27] and the CCSD(T) coupled cluster method that includes all single and double substitutions as well as a perturbative estimate of the connected triple substitutions[28,29] with a series of correlation consistent basis sets augmented with diffuse functions on non-hydrogen atoms and an extra set of tight d functions for chlorine (cc-pVXZ for H, aug-cc-pVXZ for F, aug-cc-pV(X 1 d)Z for Cl, where X 5 D, T, Q and 5; denoted ha(X 1 d)Z).[30–32] Harmonic vibrational frequencies confirmed that both configurations correspond to minima and that the transition state has exactly one imaginary frequency on both the MP2 and CCSD(T) potential energy surfaces. Anharmonic vibrational frequencies were computed using MP2 and CCSD(T) with second-order vibrational perturbation theory (VPT2).[33] No Fermi or Darling–Dennison resonances were detected at any level of theory for either configuration or the transition state.[34–36] The MP2 optimizations and harmonic vibrational frequency computations were carried out with Gaussian09[37] whereas all CCSD(T) computations and VPT2 analyses were performed with CFOUR.[38]

Results and Discussion

The two different configurations of the mixed dimer and the transition state connecting them can be seen in Figure 1. The ClH FH configuration has HCl acting as the hydrogen bond donor while HF acts as the acceptor, whereas the situation is reversed for the FH ClH configuration. The structure of the transition state closely resembles a parallelogram but is technically an irregular convex quadrilateral. Geometrical parameters for the different configurations and the transition state are reported in Table 1. The intermolecular distances (R(H A) and R(D A) in Table 1, where A stands for acceptor and D stands for donor) obtained from MP2 and CCSD(T) optimizations are remarkably similar and in good agreement with available experimental intermolecular distances (within 2%) as long as X 5 T, Q or 5. Deviations are somewhat larger for the intermolecular angles, but that is not too surprising given the floppy nature of the system and some of the approximations invoked to obtain the experimentally inferred geometrical parameters. Although no experimental intramolecular distances (R(FH) and R(ClH) in Table 1) are available, the corresponding values obtained from MP2 and CCSD(T) optimizations differ by no more than 0.5% for both configurations and the transition state when X 5 T, Q, or 5.

Energies relative to the ClH FH configuration are depicted in Figure 1 and reported in Table 2. The energy difference between the ClH FH and FH ClH configurations is given by the DE term, while DE‡ represents the energy difference between the transition state and the ClH FH configuration. The electronic energy of the FH ClH configuration is lower than the ClH FH configuration by approximately 0.2 kcal mol^{21} when X 5 T, Q or 5 with either the MP2 or CCSD(T) method as indicated by the DE$_e$ values in the DE columns of Table 2. The ZPVE effectively eliminates the energetic separation of the two minima, making both configurations essentially isoenergetic when either the harmonic or anharmonic ZPVEs are included (i.e., the DE$_0^{‡}$ and DE$_0$ entries in Table 2, respectively). CCSD(T) computations with the ha(Q 1 d)Z and ha(5 1 d)Z basis sets indicate that the FH ClH configuration is only 0.03 kcal mol^{21} higher in energy than the ClH FH configuration when anharmonic ZPVEs are included. For the transition state (DE† columns of data in Table 2), the MP2 electronic energies indicate that it lies about 0.5 kcal mol^{21} above the ClH FH configuration. This electronic barrier height (DE‡) is slightly smaller (0.4 kcal mol^{21}) at the CCSD(T) level of theory. Both harmonic and anharmonic ZPVEs attenuate the barrier to a small degree.

Table 3 reports the dissociation energies for both minima computed with the ha(5 1 d)Z basis set. With this large basis set, the Boys–Bernardi counterpoise procedure (CP) decreases the MP2 and CCSD(T) electronic dissociation energy (D$_e$) values by no more than 0.1 kcal mol^{21}. The counterpoise procedure has an even smaller effect (0.04 kcal mol^{21}) on the relative dissociation energies (DD) which suggests that the ha(5 1 d)Z energetics reported here are close to the CBS limit, where the inconsistency commonly referred to as basis set superposition error (BSSE) vanishes by definition. The harmonic or anharmonic ZPVEs decrease the dissociation energy by slightly more than 1 kcal mol^{21}. The MP2 and CCSD(T) D$_0$ values of 1.87 and 1.81 kcal mol^{21}, respectively, are in excellent agreement with the 1.84 kcal mol^{21} experimental D$_0$ obtained for the ClH FH configuration by Oudejans and Miller.[16]

Table 1. Geometrical parameters (distances R in Å, angles h in degrees and the average rotational constants B and C (B_K) in MHz) for the different configurations of the mixed HF/HCl dimer and the transition state (TS) (Fig. 1) where D and A denote the halogen atoms associated with the hydrogen bond donor and acceptor, respectively.

Config.	Level of theory	R(FH)	R(ClH)	R(H A)	R(D A)	h(D A–H)	B_K
ClH FH	MP2/ha(D 1 d)Z	0.926	1.287	2.07	3.35	119.6	3479
	MP2/ha(T 1 d)Z	0.924	1.277	2.06	3.32	116.0	3537
	MP2/ha(Q 1 d)Z	0.921	1.277	2.04	3.31	116.3	3568
	MP2/ha(5 1 d)Z	0.920	1.277	2.04	3.31	116.3	3573
	CCSD(T)/ha(D 1 d)Z	0.925	1.290	2.10	3.38	119.5	3412
	CCSD(T)/ha(T 1 d)Z	0.923	1.280	2.08	3.35	115.2	3490
	CCSD(T)/ha(Q 1 d)Z	0.920	1.280	2.06	3.33	115.3	3523
	CCSD(T)/ha(5 1 d)Z	0.919	1.280	2.06	3.33	115.2	3528
	Experiment[s]	–	–	2.08	3.37	130.0	3422
FH ClH	MP2/ha(D 1 d)Z	0.929	1.285	2.38	3.30	90.4	3673
	MP2/ha(T 1 d)Z	0.927	1.275	2.31	3.23	90.7	3825
	MP2/ha(Q 1 d)Z	0.924	1.275	2.32	3.23	89.8	3828
	MP2/ha(5 1 d)Z	0.924	1.274	2.31	3.23	89.5	3839
	CCSD(T)/ha(D 1 d)Z	0.928	1.289	2.40	3.32	91.0	3634
	CCSD(T)/ha(T 1 d)Z	0.926	1.279	2.32	3.24	91.1	3795
	CCSD(T)/ha(Q 1 d)Z	0.923	1.279	2.33	3.24	89.9	3796
	CCSD(T)/ha(5 1 d)Z	0.922	1.278	2.33	3.24	89.6	3806
	Experiment[s]	–	–	2.36	3.28	93.0	3710
TS[a]	MP2/ha(D 1 d)Z	0.927	1.286	2.53	3.25	55.2	3798
	MP2/ha(T 1 d)Z	0.924	1.276	2.44	3.23	56.2	3840
	MP2/ha(Q 1 d)Z	0.921	1.276	2.41	3.22	57.4	3861
	MP2/ha(5 1 d)Z	0.921	1.275	2.40	3.21	57.4	3875
	CCSD(T)/ha(D 1 d)Z	0.925	1.289	2.53	3.26	56.6	3771
	CCSD(T)/ha(T 1 d)Z	0.923	1.279	2.44	3.23	56.9	3832
	CCSD(T)/ha(Q 1 d)Z	0.920	1.279	2.41	3.22	58.4	3854
	CCSD(T)/ha(5 1 d)Z	0.920	1.279	2.40	3.22	58.4	3868

[a] The TS data corresponds to when D 5 Cl and A 5 F.

The harmonic vibrational frequencies for both configurations and the transition state are reported in the supplementary information. The imaginary mode of the transition state has a magnitude of 137 cm^{21} at the CCSD(T)/ha(5 1 d)Z level of theory and corresponds to the in-plane rocking motion of both hydrogens, which leads downhill to either configuration. Harmonic frequencies computed with the ha(Q 1 d)Z basis set never deviate by more than 6 cm^{21} from the corresponding ha(5 1 d)Z values. For the eighteen modes associated with the three structures, the average absolute deviation between the ha(Q 1 d)Z and ha(5 1 d)Z frequencies is 1 cm^{21} for both the MP2 and CCSD(T) methods. In light of these small deviations and the computational demands of the CCSD(T)/ha(5 1 d)Z Hessians, the CCSD(T)/ha(Q 1 d)Z VPT2 results are being used as proxies for the corresponding ha(5 1 d)Z values. The anharmonic frequencies and IR intensities for both minima are reported in the supplementary information along with the complexation induced donor and acceptor frequency shifts.

A comparison to the available experimental HF stretching frequencies (m) and shifts induced by hydrogen bond formation (Dm) are given in Table 4. For the ClH FH minimum in which HF accepts the hydrogen bond from HCl, the anharmonic CCSD(T)/ha(Q 1 d)Z frequencies from the VPT2 computations are within 2 cm^{21} of the experimental HF stretching

Table 2. Relative electronic energies (DE_e) and zero-point corrected relative energies using harmonic (DE_0^h) and anharmonic (DE_0) vibrational frequencies, where all quantities are in kcal mol^{21} and relative to the ClH FH configuration.

Basis set		MP2		CCSD(T)	
		DE	DE‡	DE	DE‡
ha(D 1 d)Z	DE_e	10.09	10.61	10.02	10.54
	DE_0^h	10.29	10.44	10.24	10.43
	DE_0	10.30	10.49	10.24	10.49
ha(T 1 d)Z	DE_e	20.19	10.53	20.22	10.45
	DE_0^h	10.07	10.34	10.05	10.33
	DE_0	10.06	10.38	10.02	10.39
ha(Q 1 d)Z	DE_e	20.16	10.50	20.19	10.41
	DE_0^h	10.06	10.34	10.03	10.31
	DE_0	10.06	10.36	10.03	10.37
ha(5 1 d)Z	DE_e	20.17	10.48	20.19	10.40
	DE_0^h	10.05	10.34	10.02	10.25
	DE_0	10.06	10.36	10.03[a]	10.36[a]

[a] Anharmonic correction from ha(Q 1 d)Z.

Table 3. Electronic dissociation energies (D_e in kcal mol^{21}), counterpoise corrected electronic dissociation energies (D_e^{CP} in kcal mol^{21}), zero-point corrected dissociation energies using harmonic (D_0^h in kcal mol^{21}) and anharmonic (D_0 in kcal mol^{21}) vibrational frequencies, and relative dissociation energies (DD in kcal mol^{21}) characterized with the ha(5 1 d)Z basis set.

	MP2			CCSD(T)		
	ClH FH	FH ClH	DD	ClH FH	FH ClH	DD
D_e	2.84	3.01	20.17	2.76	2.95	20.19
D_e^{CP}	2.78	2.91	20.13	2.71	2.88	20.17
D_0^h	1.71	1.66	10.05	1.63	1.61	10.02
D_0	1.87	1.81	10.06	1.81[a]	1.78[a]	10.03[a]

[a] Anharmonic correction from ha(Q 1 d)Z.

Table 4. Harmonic vibrational frequencies (x_e in cm^{21}) and VPT2 anharmonic corrections (d^{anh} in cm^{21}) at different levels of theory are combined to obtain anharmonic vibrational HF stretching frequencies (m in cm^{21}) and complexation induced anharmonic HF frequency shifts (Dm in cm^{21}).

Harmonic	VPT2	x_e	d^{anh}	m	Dm
ClH FH					
MP2/ha(Q 1 d)Z	MP2/ha(Q 1 d)Z	4106	2170	3936	227
MP2/ha(5 1 d)Z	MP2/ha(5 1 d)Z	4106	2171	3935	228
CCSD(T)/ha(Q 1 d)Z	MP2/ha(Q 1 d)Z	4116	2170	3946	217
CCSD(T)/ha(5 1 d)Z	MP2/ha(5 1 d)Z	4117	2171	3946	215
CCSD(T)/ha(Q 1 d)Z	CCSD(T)/ ha(Q 1 d)Z	4116	2174	3942	221
CCSD(T)/ha(5 1 d)Z	CCSD(T)/ ha(Q 1 d)Z	4117	2174	3943	220
Experiment [15]				3940	221
FH ClH					
MP2/ha(Q 1 d)Z	MP2/ha(Q 1 d)Z	4008	2158	3850	2113
MP2/ha(5 1 d)Z	MP2/ha(5 1 d)Z	4008	2159	3849	2114
CCSD(T)/ha(Q 1 d)Z	MP2/ha(Q 1 d)Z	4032	2158	3874	289
CCSD(T)/ha(5 1 d)Z	MP2/ha(5 1 d)Z	4031	2159	3872	289
CCSD(T)/ha(Q 1 d)Z	CCSD(T)/ ha(Q 1 d)Z	4032	2159	3873	290
CCSD(T)/ha(5 1 d)Z	CCSD(T)/ ha(Q 1 d)Z	4031	2159	3872	291
Experiment [15]				3867	294

frequency. Interestingly, the corresponding MP2/ha(Q 1 d)Z and MP2/ha(5 1 d)Z anharmonic frequencies are quite similar and lie within 5 cm^{21} of the experimental value. These deviations from the experimental HF stretching frequency are somewhat larger when HF donates the hydrogen bond in the FH ClH configuration. The CCSD(T)/ha(Q 1 d)Z result is still within 6 cm^{21}, but the differences grow as large as 18 cm^{21} for the anharmonic MP2 frequencies computed with the ha(Q 1 d)Z and ha(5 1 d)Z basis sets.

To shed more light on this situation, the harmonic (x_e) and anharmonic (d^{anh}) components of the VPT2 frequencies have been listed separately in Table 4. With the ha(Q 1 d)Z basis set, the MP2 and CCSD(T) anharmonic contributions to the HF stretching frequencies are nearly identical. For the more challenging HF donor, the d^{anh} terms differ by only 1 cm^{21} which indicates the large MP2 deviations from experiment in the FH ClH configuration can be attributed to the harmonic component of the vibrational frequency. In fact, the same good agreement with the experimental HF stretching frequencies and frequency shifts can be obtained by combining the CCSD(T) harmonic frequencies with the anharmonic corrections from MP2 VPT2 computations.

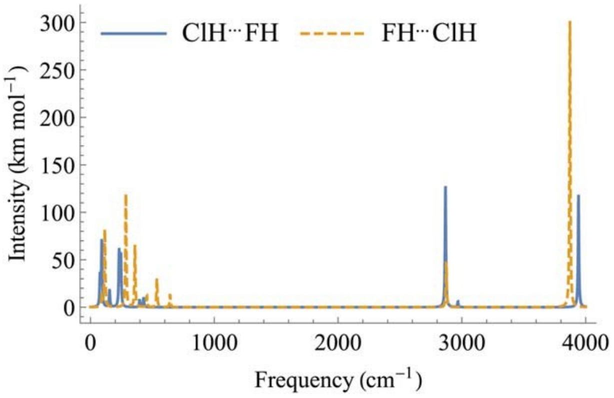

Figure 2. Simulated anharmonic vibrational spectra of both the ClH FH and FH ClH configurations at the CCSD(T)/ha(Q 1 d)Z level of theory. [Color figure can be viewed at wileyonlinelibrary.com]

The CCSD(T)/ha(Q 1 d)Z anharmonic vibrational spectra for both configurations can be seen in Figure 2. Overtones and combination bands with up to three vibrational quanta (m_i 1 m_j 5 3) are included in the spectra and also tabulated in the supporting information. However, most do not have sufficient IR intensity to be visible on this scale. The m_6 overtone at 537 cm^{21} has the greatest intensity, but is still only 30 km mol^{21}. Both configurations have numerous low-energy fundamental modes under 500 cm^{21} with more significant IR intensities on the order of 100 km mol^{21}. However, the HF and HCl stretching modes between 2800 cm^{21} and 4000 cm^{21} have the largest intensities for both configurations (100–300 km mol^{21}). For the ClH FH configuration the HF and HCl stretching modes have similar intensities, where the FH ClH configuration showcases the HF stretching mode as the most intense peak which is three times larger than any other peak in either spectrum. It is important to note that the peaks in the simulated spectra shown in Figure 2 were generated by overlapping Lorentzian functions with a full width half maximum value of 4 cm^{21} whereas the experimental peaks exhibit significant broadening from vibrational predissociation as discussed in detail in the last section of Ref. [15]

Conclusions

This work provides the first thorough characterization of this system (via full geometry optimizations and vibrational frequency analyses) with correlated ab initio methods and large basis sets. Both configurations of the mixed HF/HCl dimer are bound by almost 3 kcal mol^{21} near the CCSD(T)/CBS limit. The CCSD(T)/ha(5 1 d)Z electronic dissociation energies are 2.76 kcal mol^{21} for the ClH FH minimum and 2.95 kcal mol^{21} for the FH ClH minimum. The values decrease by 0.05 and 0.07 kcal mol^{21} respectively, when the CP procedure is applied. The relative CCSD(T)/ha(5 1 d)Z electronic energies show that the FH ClH configuration is lower than the ClH FH configuration by 0.19 kcal mol^{21} and that the transition state is 0.40 kcal mol^{21} higher than the ClH FH configuration. However, the inclusion of either the harmonic or anharmonic ZPVE makes both minima isoenergetic (within 0.03 kcal mol^{21} of each other according to the CCSD(T) results obtained with the two largest basis sets). The ZPVE corrections also decrease the barrier height by approximately 0.1 kcal mol^{21}. The CCSD(T)/ha(Q 1 d)Z D_0 for the ClH FH configuration deviates from the experimental value[16] by 20.03 kcal mol^{21}. The CCSD(T)/ha(Q 1 d)Z anharmonic frequencies and complexation induced frequency shifts differ by no more than 26 cm^{21} from the experimental values.[15] To conclude, these computations indicate that there is a slight electronic preference for HF to donate and HCl to accept a hydrogen bond in this mixed dimer. That proclivity vanishes, however, when the

ZPVE is included which suggests giving and receiving are equally virtuous in this context. The relative energetics indicate both configurations of the mixed HF/HCl dimer should be present in experiments conducted at extremely low temperatures and pressures. The CCSD(T)/ha(Q+d)Z anharmonic frequencies reported here from VPT2 computations will greatly facilitate more complete assignment of the vibrational spectra of these two minima, both of which have multiple fundamentals with appreciable IR intensities as well as overtones and combination bands below 600 cm^{-1} that will likely be discernible in their IR spectra.

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Keywords: hydrogen bonding · dissociation energies · coupled cluster method (CCSD(T)) · complete basis set (CBS) limit · second-order vibrational perturbation theory (VPT2)

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Additional Supporting Information may be found in the online version of this article.

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