



# Communication: Spectroscopic consequences of proton delocalization in $\text{OCHCO}^+$

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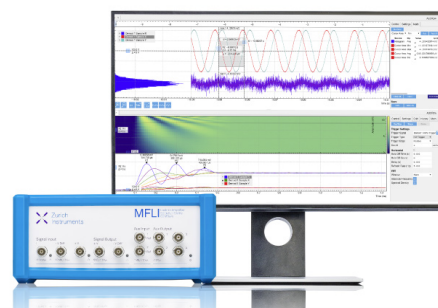
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## Communication: Spectroscopic consequences of proton delocalization in OCHCO<sup>+</sup>

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Even though quartic force fields (QFFs) and highly accurate coupled cluster computations describe the OCHCO<sup>+</sup> cation at equilibrium as a complex between carbon monoxide and the formyl cation, two notable and typical interstellar and atmospheric molecules, the prediction from the present study is that the equilibrium  $C_{\infty v}$  structure is less relevant to observables than the saddle-point  $D_{\infty h}$  structure. This is the conclusion from diffusion Monte Carlo and vibrational self-consistent field/virtual state configuration interaction calculations utilizing a semi-global potential energy surface. These calculations demonstrate that the proton “rattle” motion ( $\nu_6$ ) has centrosymmetric delocalization of the proton over the  $D_{\infty h}$  barrier lying only 393.6 cm<sup>-1</sup> above the double-well OCHCO<sup>+</sup>  $C_{\infty v}$  minima. As a result, this molecule will likely appear  $D_{\infty h}$ , and the rotational spectrum will be significantly dimmer than the computed equilibrium 2.975 D center-of-mass dipole moment indicates. However, the proton transfer fundamental, determined to be at roughly 300 cm<sup>-1</sup>, has a very strong intensity. This prediction as well as those of other fundamentals should provide useful guides for laboratory detection of this cation. Finally, it is shown that the two highest energy QFF-determined modes are actually in good agreement with their vibrational configuration interaction counterparts. These high-level quantum chemical methods provide novel insights into this fascinating and potentially common interstellar molecule. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929345>]

### I. INTRODUCTION

HCO<sup>+</sup> is one of the most useful molecules in the universe for exploring the structure of various astronomical bodies ranging from molecular clouds to distant galaxies. It was first observed in the interstellar medium (ISM) in 1970 by Buhl and Snyder<sup>1</sup> right on the tail of the first confirmed detection of the ubiquitous and highly significant related molecule, carbon monoxide.<sup>2</sup> HCO<sup>+</sup> is now known to be one of the most abundant interstellar molecules and is often used as a spectroscopic probe due to its large dipole moment ( $\sim 3.9$  D)<sup>3-5</sup> and shift of rotational lines as compared to CO. The high abundance of these molecules in the ISM leads one to wonder if a van der Waals complex could be formed between the two since both have enough internal charge separation to form such and proton exchange would be fairly rapid. Additionally, both species are probably present in the atmospheres of various planetary bodies within our solar system and beyond.

The gas phase reaction of CO and HCO<sup>+</sup> can lead to the creation of the OCHCO<sup>+</sup> complex,<sup>6</sup> a novel, proton-bound molecule whose near-centrosymmetric nature leads to fairly high stability.<sup>7</sup> However, the kinetic energy of one or

both of these reactants present in the interstellar medium would probably overcome the energy budget of the simple stoichiometric product, OCHCO<sup>+</sup>. Typically in gas phase interstellar reactions, the energy surplus over the activation energy of colliding reactants is dealt with by the presence of a leaving group that takes the excess energy away with it as kinetic energy.<sup>8</sup> Hence, the reaction of CO with the hydrogen molecule-formaldehyde cation (H<sub>2</sub>-H<sub>2</sub>CO<sup>+</sup>) complex is what probably gives rise to most of the OCHCO<sup>+</sup> that is likely present in the ISM.<sup>9-12</sup> Regardless, the potential presence of OCHCO<sup>+</sup> in the ISM<sup>11</sup> is a tantalizing astrochemical path to follow in the molecular physics of molecular clouds and circumstellar envelopes.

It was originally believed that OCHCO<sup>+</sup> is truly centrosymmetric belonging to the  $D_{\infty h}$  point group like its isoelectronic partner, N<sub>2</sub>-H-N<sub>2</sub><sup>+</sup>,<sup>7</sup> which is also of interest to interstellar chemistry.<sup>10,12</sup> However, subsequent high-level coupled cluster computations indicate that OCHCO<sup>+</sup> exhibits a double-well potential in the proton transfer motion and prefers, at any given instant, to exist as a  $C_{\infty v}$  structure.<sup>13</sup> However, the potential barrier at the  $D_{\infty h}$  configuration was reported to be only 358 cm<sup>-1</sup> above the global minimum.<sup>14</sup> The lack of an inversion center in the OCHCO<sup>+</sup> complex would allow it to be rotationally active and subsequently strongly dipolar if this  $C_{\infty v}$  arrangement can be conserved. In any case, the motion

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of the proton between the two carbon monoxide molecules<sup>7</sup> should also give rise to a strong vibrational signature for this motion making it a clear marker for this molecule.

Spectroscopic information regarding the rovibrational nature of the  $\text{OCHCO}^+$  complex is necessary in order to probe the ISM for its presence through the use of modern astronomical telescopes such as the Atacama Large Millimeter/submillimeter Array (ALMA), the Stratospheric Observatory For Infrared Astronomy (SOFIA), or the upcoming James Webb Space Telescope (JWST) in addition to high-resolution archival data like that from the Herschel Space Observatory (HSO). It is therefore the goal of this work to provide spectroscopic data for the  $\text{OCHCO}^+$  complex in order to allow for its potential observation in the ISM. Various theoretical methods are brought to bear to provide as much reliable spectroscopic data as possible. The fundamental chemical physics of this complex will also be explored from the perspective of the various theoretical approaches in order to provide a deeper understanding of this and related systems. Whether detected in the ISM or in the laboratory, the presence of this complex will greatly enhance the understanding of how the carbon monoxide and the isoelectronic formyl cation interrelate across potential energy surfaces (PESs) in gas phase reactions.

In this paper, a computational study producing the spectroscopic features of  $\text{OCHCO}^+$  is undertaken by generating a full-dimensional PES that spans the double-well region. Several sets of vibrational calculations are then undertaken using this surface with a focus on the proton transfer mode. High-level quartic force fields (QFFs) are also reported to determine the extent to which they are able to describe the chemical physics of the  $\text{OCHCO}^+$  cation. QFFs are fourth-order Taylor series expansions of the nuclear Hamiltonian, and they have recently provided exceptional comparison to experiment for rotational constants ( $<0.2\%$ ) and fundamental vibrational frequencies ( $\sim 0\text{--}5\text{ cm}^{-1}$ ).<sup>15–20</sup> However, the loose-association of atoms in this molecule, most notably the central proton, raises questions about the validity of a QFF in this case.<sup>20</sup> By applying multiple approaches to the analysis of this molecule, a complete picture emerges.

## II. COMPUTATIONAL DETAILS

The proton-bound nature of  $\text{OCHCO}^+$  makes this cation an excellent choice for high-level vibrational methods with larger potential surfaces. To that end, a semi-global PES is constructed. This PES spans both  $C_{\infty v}$  minima in  $\text{OCHCO}^+$  and the saddle point region in between them. In total, 8613 energies were calculated using coupled cluster singles, doubles, and perturbative triples  $[\text{CCSD(T)}]^{21}$  with the explicitly correlated  $\text{CCSD(T)-F12}$  method<sup>22,23</sup> and the aug-cc-pVTZ-F12 basis set.<sup>24</sup> These energies are fit using a basis of permutationally invariant polynomials, in Morse variables,<sup>25</sup> up to total polynomial order of five. This results in a fitting basis of 904 terms with the linear coefficients determined by standard least squares optimization. The root mean square fitting error of this fit is  $0.4\text{ cm}^{-1}$ . More details of this fit are given in the supplementary material.<sup>26</sup>

This PES is utilized in three sets of vibrational calculations. The first and most approximate one is a one-dimensional

description of the proton motion, using the so-called  $Q_{im}$ -path and the relaxed potential along it.<sup>27</sup> In brief, in this approach, the imaginary-frequency normal mode (which in this case describes the proton transfer) is varied from zero, the value at the saddle point, to large positive and negative values that span the saddle point and the two minima and beyond to the repulsive region of the PES.  $V(Q_{im})$  is the potential along this path, relaxed with respect to all other saddle point normal modes. The eigenvalues and eigenfunctions of this potential are then obtained numerically. Details of the present calculations are given in the supplementary material.<sup>26</sup> These calculations provide a fast description of the extent of localization/delocalization of the proton transfer mode. The second set of vibrational calculations is diffusion Monte Carlo (DMC) calculations. These are essentially exact for the zero-point wave function and energy but require a full dimensional PES. In addition, in favorable cases, fixed-node DMC can also provide accurate, if not exact, excited state energies. In the present case, this is used to obtain the energy of the proton transfer fundamental. Details of these calculations are also in the supplementary material.<sup>26</sup> Finally, approximate MULTIMODE (MM) calculations<sup>28,29</sup> are performed for this linear molecule. MM determines energies and eigenfunctions of the Watson Hamiltonian, using matrix diagonalization within a vibrational self-consistent field/vibrational configuration interaction (VSCF/VCI) formalism. However, the code has not been fully modified to describe the present case of a linear molecule. Thus, the code is run without vibrational angular momentum terms. An estimate of the error introduced by this approximation is provided by a comparison of the exact zero-point energy (ZPE), from DMC calculations, with the MM ones. MM makes use of a  $n$ -mode representation of the potential,<sup>28,29</sup> in the present case  $n$  varies from 4 to 6. An exact representation is for  $n = 9$ , which is the number of normal modes. More details of the MM calculations are given in the supplementary material;<sup>26</sup> however, note that the largest matrix diagonalized is of order 36 858. Finally, MP2/aug-cc-pVTZ double harmonic intensities are also computed from the  $D_{\infty h}$  structure utilizing Gaussian09.<sup>30,31</sup>

Higher-order electronic structure methods are also employed but are prohibitively expensive for the number of points needed for a full-dimensional PES. Even so, composite energy PESs in the form of QFFs<sup>32,33</sup> have, again, recently been shown to exhibit exceptional comparison to experiment<sup>15–20</sup> warranting their employment here. Restricted Hartree-Fock<sup>34,35</sup> reference wave functions and  $\text{CCSD(T)}$  combined with the cc-pV5Z basis set determine the reference geometry for this smaller QFF surface.  $\text{CCSD(T)}$  optimizations with the Martin-Taylor (MT) basis set designed for the treatment of core correlation<sup>36</sup> are also undertaken with and without the core electrons included. The differences in the bond lengths, as these are the only totally symmetric internal coordinates, are then added to the  $\text{CCSD(T)}/\text{cc-pV5Z}$  result to produce the reference geometry.

From this structure, the desired grid is created. For the  $\text{OCHCO}^+$  QFF, 2253 points are constructed from the necessary symmetry-internal coordinate system given in the supplementary material.<sup>26</sup> At each displaced geometry on the surface,  $\text{CCSD(T)}$  computations make use of a 3-point complete basis

set (CBS) limit extrapolation procedure<sup>37</sup> for aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z (Refs. 38 and 39) energies. This produces the initial CCSD(T) energy that is further corrected, again, for core correlation with the MT basis set as well as for corrections for Douglas-Kroll (DK) scalar relativistic considerations.<sup>40</sup> The CCSD(T)/CBS +  $\Delta_{MT}$ (MT core – MT without core) +  $\Delta_{DK}$ (DK with relativity – DK without) energies are computed at each point to produce the CcCR PES so named for the CBS (“C”), core correlation (“cC”), and relativistic (“R”) composite terms employed. A fitting of the energy points through a least-squares fit procedure to a sum of squared residuals on the order of  $10^{-16}$  produces the CcCR equilibrium geometry. A refit to this new minimum yields the force constants with zero gradients. Cartesian derivatives provided by the INTDER 2005 (Ref. 41) program are fed into the SPECTRO<sup>42</sup> program which utilizes second-order perturbation theory to generate the spectroscopic constants<sup>43</sup> and vibrational frequencies<sup>44,45</sup> through the so-called VPT2 approach.

### III. RESULTS AND DISCUSSION

CCSD(T)/aug-cc-pV5Z energies from the corresponding geometry optimizations show that the OCHCO<sup>+</sup> minima exist 4283 cm<sup>-1</sup> below the OC + HCO<sup>+</sup> dissociation limit in line with the 4900 cm<sup>-1</sup> estimate from Klemperer and Vaida.<sup>11</sup> However, the  $D_{\infty h}$  structure is only 0.049 eV or 393.6 cm<sup>-1</sup> above the degenerate  $C_{\infty v}$  true minima in line with previous work by Mladenović and Roueff.<sup>14</sup> The CcCR  $D_{\infty h}$  stationary point geometry exhibits 1.115 84 Å C–O and 1.387 93 Å C–H bond lengths. Hence, the  $C_{\infty v}$  VPT2 vibrationally averaged ( $R_v$ ) geometry, as provided in Table V of the supplementary material,<sup>26</sup> may not be what experiments may interpret as the observed geometry. The equilibrium values are similar and corroborate previous CCSD(T)/aug-cc-pV5Z results,<sup>13</sup> as well as the proposition by Klemperer and Vaida<sup>11</sup> that OCHCO<sup>+</sup> can be thought of as “a gas-phase” zwitterion where the interconversion between the two minima propagates a continuous hydrogen bond/covalent bond exchange. However, the low proton-motion barrier complicates such classifications especially when examining the vibrational frequencies of OCHCO<sup>+</sup>. The stationary point geometries obtained from the PES, given in the supplementary material,<sup>26</sup> agree well with the ones above, and the barrier height on the PES is 383 cm<sup>-1</sup>, in good agreement with the above benchmark value of 393.6 cm<sup>-1</sup>.

The CcCR harmonic frequencies at the minimum are given in the supplementary material<sup>26</sup> and are in good agreement with the CCSD(T)/aug-cc-pVQZ values provided earlier<sup>13</sup> as well as the CCSD(T)-F12/cc-pVTZ-F12 values also computed in the same study. The harmonic frequencies from the PES, given in the supplementary material,<sup>26</sup> agree well with the benchmark CcCR ones, although some differences as large as 20 cm<sup>-1</sup> are seen. Harmonic frequencies at the saddle point are also given in the supplementary material<sup>26</sup> and, as expected, there is one imaginary frequency, which corresponds to the proton transfer mode.

The first set of results using the PES are from the  $Q_{im}$ -model. These are shown in Figure 1, which contains a plot of

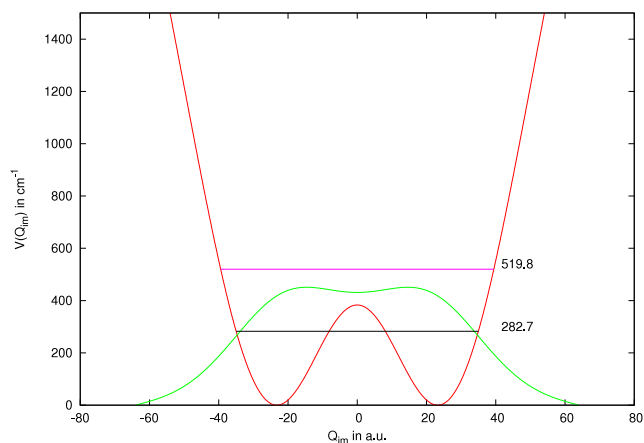


FIG. 1.  $V(Q_{im})$  potential, ground state wave function, and energies of ground and first excited states.

$V(Q_{im})$ , the ground and first excited wave functions and the corresponding energies. As seen, the ground-state energy (i.e., the zero-point level) is roughly 100 cm<sup>-1</sup> below the barrier height, but the wave function has a large amplitude at the barrier and is highly delocalized. This is a manifestation of significant tunneling owing to the light proton mass. The first excited state is roughly 140 cm<sup>-1</sup> above the barrier. So these results already indicate that the proton is highly delocalized over the two minima. The next set of results are from the full dimensional DMC and MM calculations. Figure 2 here and Figure 2 in the supplementary material<sup>26</sup> show isosurface plots of the ground state and fixed-node first excited state wave functions, respectively, from the DMC calculations. These indicate substantial delocalization for both states, providing rigorous confirmation of the conclusions of the  $Q_{im}$ -model.

The energies from the vibrational calculations are given in Table I. Only the MM calculations provide energies of all fundamentals. These are shown for 4 and 5-mode representations (MRs) of the PES. A 6MR of the PES was also done and the results are very close to the 5MR ones and so they are not shown in the table. First, note that the 5MR (and 6MR) MM zero-point energy is 9 cm<sup>-1</sup> above the rigorous DMC result. This error in the MM calculations is almost certainly due to the lack of vibrational angular momentum terms in the Hamiltonian. Next, consider the proton fundamental  $\nu_6$ . The larger MM 5MR calculations place this at 316.5 cm<sup>-1</sup>, roughly 21 cm<sup>-1</sup> above the fixed-node DMC result, which is not “exact.” The corresponding energy from the  $Q_{im}$ -model is 362 cm<sup>-1</sup>. Based on the MM and DMC results, an estimate of 300 cm<sup>-1</sup> for the proton transfer fundamental is reasonable, with an uncertainty of roughly  $\pm 15$  cm<sup>-1</sup>.

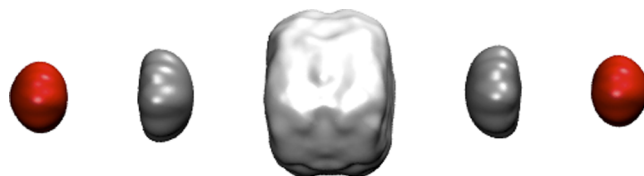


FIG. 2. Ground vibrational state wave function isosurface of OCHCO<sup>+</sup> from diffusion Monte Carlo calculations.

TABLE I. The OCHCO<sup>+</sup> CCSD(T)-F12/aug-cc-pVTZ-F12 PES harmonic frequencies at the saddle point, MULTIMODE VSCF/VCI zero point and fundamental energies for 4MR, 5MR, and 6MR cases, diffusion Monte Carlo zero-point and proton transfer fundamental and selected QFF results (in cm<sup>-1</sup>). Also MP2/aug-cc-pVTZ double harmonic intensities (in parentheses in km/mol).

	Harmonic	4MR	5MR	CcCR
$\nu_1 \sigma_g$ O–C symmetric stretch	2324.3	2308.2	...	2270.4 <sup>a</sup>
$\nu_2 \sigma_u$ O–C antisymmetric stretch	2291.4 (54)	2246.3	...	2239.6 <sup>a</sup>
$\nu_3 \sigma_g$ C–H symmetric stretch	394.5	285.7	272.3	...
$\nu_4 \pi_u \perp$ proton motion	1277.1 (8)	1199.6	1184.9	...
$\nu_5 \pi_g$ O–C–H symmetric bend	290.9	291.3	285.4	...
$\nu_6 \sigma_u$ C–H antisymmetric stretch	862.4i (5186)	338.4	316.5	362 <sup>b</sup> /295 <sup>c</sup>
$\nu_7 \pi_u$ O–C–H antisymmetric bend	143.7 (16)	157.0	148.1	...
Zero-point energy	...	4217.1	4214.6	4205 <sup>c</sup>

<sup>a</sup>VPT2 results.

<sup>b</sup>1D-DVR result.

<sup>c</sup>DMC results.

IR intensities of the active fundamentals are clearly desirable, and future calculations will give these based on a full dipole moment surface to be used with MM wave functions. For now, we estimate these from MP2/aug-cc-pVTZ double harmonic intensities obtained at the barrier reference configuration. These are also given in Table I for the four vibrationally active modes:  $\omega_2$ ,  $\omega_4$ ,  $\omega_6$ , and  $\omega_7$ . The antisymmetric  $\omega_6/\nu_6$  proton transfer motion is substantially brighter than any other frequency, nearly a factor of 100 $\times$  brighter at 5186 km/mol than the next-brightest O–C antisymmetric  $\omega_2/\nu_2$  stretch at 54 km/mol. This is to be expected since as the proton moves from one  $C_{\infty v}$  minimum to the other, the molecular dipole moment changes sign, or as the proton moves from the  $D_{\infty h}$  saddle point to a  $C_{\infty v}$  minimum, the molecular dipole moment goes from exactly zero to 2.975 D (all dipole moments calculated with respect to the center of mass). There are other examples of similar systems where the proton transfer mode yields a very large dipole moment (for example, see Ref. 46, specifically Table VII therein).

An instantaneous view of OCHCO<sup>+</sup>, as provided by equilibrium computations or single-reference vibrational methods like VPT2, may appear to be  $C_{\infty v}$ , but any observable interpretation for the structure of this molecule will be  $D_{\infty h}$ . Even though, the CcCR QFF VPT2 frequency for  $\nu_6$  is also real at 144.1 cm<sup>-1</sup>, the lack of inclusion of both, degenerate minima in the PES reduces its accuracy. Additionally, the fundamental mode descriptions have been redefined for the VCI results since the  $C_{\infty v}$  labels are misleading and improper for the  $D_{\infty h}$  structure that is produced in these computations. Another significant difference between the VPT2 and VCI results is the  $\nu_3$  mode. VPT2 puts this fundamental at 997.5 cm<sup>-1</sup> whereas 5MR VCI is 272.3 cm<sup>-1</sup>. This mode is hugely anharmonic in VPT2 but much better behaved in VCI. The main reason that the VPT2 results are higher is the improper description of the PES in the single-reference QFF. The VCI results should be much more trustworthy for this mode and probably for most of the other vibrational frequencies, as well. Most of the lower frequency VPT2 modes are within  $\sim 20\%$  of the 5MR results, but this is not good enough for experimental comparison.

It is very interesting to note that the  $\nu_1$  and  $\nu_2$  modes are actually quite consistent between the two vibrational methods

and PESs. VPT2  $\nu_1$  is 2270.4 cm<sup>-1</sup> while its 4MR counterpart is higher 37.6 cm<sup>-1</sup> at 2308.2 cm<sup>-1</sup>. The  $\nu_2$  frequencies are even closer at 2239.6 cm<sup>-1</sup> and 2246.3 cm<sup>-1</sup>, respectively. This indicates that the QFF is actually a fairly good description of these fundamentals. Such a result could be expected since these modes are well-above the centrosymmetric barrier. Hence, they are less likely to be influenced by the presence of the double well and could be appropriate for the description of such modes as has been observed previously.<sup>20</sup> However, the full vibrational spectrum for such a molecule without a clearly defined single minimum still requires more advanced approaches like VCI, DMC, and one-dimensional discrete variable representation (1D-DVR) utilized here.

#### IV. CONCLUSIONS

In this work, it is shown that at equilibrium the OCHCO<sup>+</sup> cation is a complicated system of note. Both constituent pieces are common and significant interstellar species suggesting that this cation may be common in the ISM and may be considered a gas-phase zwitterion.<sup>11</sup> The equilibrium OCHCO<sup>+</sup> minimum is not centrosymmetric and  $D_{\infty h}$  but is  $C_{\infty v}$ . However, the  $D_{\infty h}$  barrier between the two  $C_{\infty v}$  minima along the proton transfer motion coordinate is only 393.6 cm<sup>-1</sup> above the degenerate global minima. These global minima lie 4283 cm<sup>-1</sup> below the CO and HCO<sup>+</sup> dissociation limit. The tunneling of the proton rattle mode beneath the internal barrier and the resulting delocalized centrosymmetric space occupied by the proton makes this cation appear  $D_{\infty h}$  in the interpretation of most experimental observations. These conclusions are the result of a larger CCSD(T)-F12 PES coupled with DMC and VSCF/VCI calculations. Hence, the VCI vibrational frequencies provided in this work are more trustworthy than their VPT2 counterparts with the exception of the two highest-frequency modes that are in good agreement between the vibrational methods. The exceptionally bright ( $\sim 100\times$  that of any other) proton rattle frequency ( $\nu_6$ ) is determined to take place at 316.5 cm<sup>-1</sup> (31.6  $\mu\text{m}$ ) as described by the highest-level VSCF/VCI computations. From this, the frequencies provided here allow for laboratory and potential interstellar exploration as to the presence of this cation complex in relevant chemical environments.

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