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***Ab initio* Study of Anharmonic Force Field and Spectroscopic Constants for Germanium Dichloride**

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Ab initio study of the equilibrium structure, spectroscopy constants, and anharmonic force field for several isotopomers of germanium dichloride ($^{70}\text{GeCl}_2$, $^{72}\text{GeCl}_2$, and $^{76}\text{GeCl}_2$) have been carried out at the MP2 and CCSD(T) levels of theory using cc-pVTZ basis set. The calculated geometries, rotational constants, vibration-rotation interaction constants, harmonic frequencies, anharmonic constants, quartic and sextic centrifugal distortion constants, cubic and quartic force constants are compared with experimental data. For small mass differences of the Ge isotopes, the isotopic effects for germanium dichloride are much weaker. The agreements are satisfactory for these two methods, but the deviations of CCSD(T) results are slightly larger than that of MP2, because of CCSD(T)'s inadequate treatment of electron correlation in hypervalent Cl atom.

Key words: Anharmonic force field, Spectroscopic constants, Germanium dichloride**I. INTRODUCTION**

Transient molecules containing silicon and germanium have attracted considerable attention recently because of their roles as important intermediates in the technologically important production of semiconductors. In order to optimize the manufacturing processes, it is crucial to establish sensitive methods for detecting and characterizing such intermediates in theory and experiment. High resolution infrared and microwave spectroscopy are the most important sources of information for molecular force fields. Given the anharmonic potential, the molecular vibrational and rotational energy levels are easily obtained using variational or perturbation theories. The most useful analytical methods for studying semiconductor growth processes are likely to be spectroscopic in nature. Since its first observation in the late 1960s, the electronic absorption spectrum [1, 2] of germanium dichloride has attracted several experimental [3–6] and theoretical [6–9] attention.

The potential function under the influence of which the nuclei are moving is the same for isotopic molecules, since these isotopologues have the same electronic structure. But because of the difference in the masses the vibrational frequencies are different. A study of isotope shifts in spectra of germanium dichloride may be helpful in ascertaining which molecule (or radical) is responsible for a given spectrum and it may also aid in the

spectrum. In addition, an accurate measurement of the isotope effect can be used to obtain a precise value for the ratio of the masses of the two kinds of isotopic atoms concerned. Under favorable conditions, the accuracy of the ratio of the masses so obtained is comparable with the accuracy of mass-spectrographic values. Apart from that, the study of the isotope effect in electronic band spectra has led to the discovery of new isotopes and an unambiguous confirmation of the quantum mechanical formula for the energy levels of the oscillator.

Employing the given force field, one can determine all spectroscopic constants of molecule, such as harmonic constants, anharmonic constants, rotational constants, centrifugal distortion constants, rotation-vibration interaction constants, *etc.* [10]. Recently, with the development of the method of analytic second derivatives of molecular energy, it has become possible to calculate the rovibrational spectra, harmonic or anharmonic force field of small or middle molecules by *ab initio* method [11–15]. It has been shown that spectroscopic constants from accurate, purely *ab initio* anharmonic force field are reliable [12–16].

As far as we know, there have been very few reports about the anharmonic force field and the isotopic effects of GeCl_2 . In 1995, Masaki *et al.* observed the millimeter-wave spectrum of GeCl_2 and its isotopic species in the ground and vibrationally excited states, ν_1 , ν_2 , $2\nu_2$, and ν_3 [17]. In 2000, Vast *et al.* presented a theoretical method to investigate the effects of isotopic disorder on the lattice dynamics of crystals [18]. Employing the method, they calculated the isotopic effect of Ge. In 2007, Pang *et al.* calculated spectroscopic constants of $^{74}\text{GeCl}_2$ using three levels of theory [19].

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To complete this series of germanium dichloride and the isotopic effects, it would be interesting to determine the anharmonic force field and spectroscopic constants of $^{70}\text{GeCl}_2$, $^{72}\text{GeCl}_2$, and $^{76}\text{GeCl}_2$.

In this work, we determined the equilibrium structure, and calculated the *ab initio* anharmonic force field at several levels of theories. Accuracy was checked by comparing the *ab initio* spectroscopic constants with their corresponding experimental values. We also discussed the isotopic effects on anharmonic force field and spectroscopic constants for four isotopologues.

II. COMPUTATIONAL METHODS

The geometry optimizations calculations presented below have been carried out with the Gaussian 03 program [20], and the second-order Møller-Plesset perturbation theory [21] (MP2) has been used. At the computed equilibrium geometries, harmonic force fields were evaluated analytically. No orbital has been kept frozen during these calculations. Cubic and semidiagonal quartic normal coordinate force constants have been evaluated using the ACESII [22] program package for the coupled cluster (CC) theory with single and double excitations augmented by a perturbational estimate of the effects of connected triple excitations (CCSD(T)) method [23], while the Gaussian 03 program for the MP2 calculations. Correlation consistent basis set has been used in the geometry optimizations and anharmonic force field, the standard valence cc-pVTZ basis has been employed for these isotopomers of germanium dichloride [24]. The electronic configuration describes the distribution of electrons of an atom in atomic orbitals. Considering the ground electronic configuration of Ge and Cl can be written as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$ and $1s^2 2s^2 2p^6 3s^2 3p^5$, respectively, the cc-pVTZ basis set is employed. The basis of Ge is the [6s5p3d1f] contraction of a (20s13p9d1f) primitive set [24]. The basis of Cl is the [5s4p2d1f] contraction of a (15s9p2d1f) primitive set [24]. This basis set has also been chosen as it was felt that the basis set enhancement beyond cc-pVTZ does not lead to major improvements in the computed anharmonic properties and that polarized triple-zeta basis sets should therefore be sufficient in such applications. For each isotopomer the cubic force field has been used to compute spectroscopic parameters using the usual second-order perturbation theory.

III. RESULTS AND DISCUSSION

For the main isotopic species the theoretical results for the molecular geometries, the spectroscopic constants, and the full quartic force fields are calculated. They are compared with the corresponding experimental or empirical data [6, 9, 17, 25] whenever these are

TABLE I Molecular equilibrium geometries including bond lengths R , bond angles A , and total energies E_T of GeCl_2 .

Method	$R/\text{Å}$	$A/(\text{°})$	$E_T/\text{Hartree}$
MP2	2.168758	99.9691	-2995.07
CCSD(T)	2.169999	100.22387	-2995.20
Theory [6]	2.177	100.3500	
Theory [9]	2.16876	99.9691	
Theory [25]	2.191	100.5000	
Expt. [17]	2.16945(2)	99.8825(15)	

available. While comparison of anharmonic force constants is possibly the most meaningful way to compare different force field representations of the PES of a molecule, it is more usual to compare the anharmonic force fields by their ability to predict standard rovibrational spectroscopic constants [26]. The isotopic composition for chlorine are 75.8% of ^{35}Cl and 24.2% of ^{37}Cl , and the major isotopic species for germanium have a more complex composition with 20.5% of ^{70}Ge , 27.4% of ^{72}Ge , 36.5% of ^{74}Ge , 7.8% of ^{76}Ge [27].

We calculated the *ab initio* structures and total energy for the optimized geometries of these molecules, at the MP2 and CCSD(T) level of theory using cc-pVTZ basis set. The computed equilibrium structures of GeCl_2 and experimentally derived [17] equilibrium structure are shown in Table I. The MP2 results are almost the same values for these isotopomers, due to the fact that the equilibrium internuclear distances are the same in these isotopic molecules but not the effective internuclear distances [10]. So we listed the equilibrium structures of $^{74}\text{GeCl}_2$ instead of other isotopomers. The previous computed results are also listed in Table I [6, 9, 25]. From Table I we can see that the total energy for the optimized geometries of GeCl_2 calculated by CCSD(T) method is slightly lower than that of MP2 method (about 0.13 Hartree), which means that the optimized structure by CCSD(T) method is more stable.

The refined rotational parameters can be used to determine an improved geometry for germanium dichloride. Table II lists the computed rotational constants for $^{70}\text{GeCl}_2$, $^{72}\text{GeCl}_2$, $^{74}\text{GeCl}_2$, and $^{76}\text{GeCl}_2$ at MP2 and CCSD(T) methods with cc-pVTZ basis set, along with the available experimental data [17]. The theoretical ground-state rotational constants (A_0 , B_0 , C_0) have been obtained from the associated equilibrium constants (A_e , B_e , C_e) by taking into account of the effects of vibration-rotation coupling via perturbation theory [28, 29]. As far as it goes, no experimental data of equilibrium rotational constants have been reported for $^{70}\text{GeCl}_2$, $^{72}\text{GeCl}_2$, and $^{76}\text{GeCl}_2$. The deviations between the experimental values and the computed values at the equilibrium geometry are within 0.02%–0.25% (in absolute value).

The calculated vibration-rotation interaction constants α_i^X (with $X=A, B, C$ and $i=1, 2, 3$) for these

TABLE II Rotational constants of equilibrium and ground states for GeCl₂.

Isotope	Method	A_e	B_e	C_e	A_0	B_0	C_0
⁷⁰ GeCl ₂	MP2	7429.28	2620.09	1936.98	7443.30	2612.54	1930.63
	CCSD(T)	7261.83	2606.50	1918.05	7271.73	2599.11	1911.56
	Expt. [17]				7430.47	2612.97	1929.91
⁷² GeCl ₂	MP2	7326.08	2620.09	1929.89	7339.92	2612.57	1923.60
	CCSD(T)	7261.83	2606.50	1918.05	7273.60	2599.05	1911.67
	Expt. [17]				7327.38	2613.00	1922.87
⁷⁴ GeCl ₂	MP2	7231.65	2619.22	1922.80	7245.38	2611.72	1916.57
	CCSD(T)	7261.82	2606.50	1918.05	7275.20	2599.00	1911.76
	Expt. [17]				7229.65	2613.04	1916.07
⁷⁶ GeCl ₂	MP2	7135.49	2619.22	1915.94	7149.04	2611.74	1909.76
	CCSD(T)	7261.83	2606.50	1918.05	7276.70	2598.96	1911.86
	Expt. [17]				7137.38	2613.06	1909.50

TABLE III Vibration-rotation interaction constants of GeCl₂.

Method	Isotope	α_1^A	α_2^A	α_3^A	α_1^B	α_2^B	α_3^B	α_1^C	α_2^C	α_3^C
MP2	⁷⁰ GeCl ₂	-2.494	-59.708	34.165	8.880	3.440	2.781	1.216	4.099	7.369
	⁷² GeCl ₂	-2.145	-58.842	33.311	8.8114	3.443	2.794	1.374	4.077	7.123
	⁷⁴ GeCl ₂	-1.861	-58.086	32.508	8.750	3.441	2.815	1.507	4.052	6.908
	⁷⁶ GeCl ₂	-1.550	-57.275	31.727	8.685	3.444	2.828	1.642	4.029	6.688
CCSD(T)	⁷⁰ GeCl ₂	1.208	-60.891	39.884	8.757	3.720	2.290	0.516	4.110	8.346
	⁷² GeCl ₂	-0.078	-59.914	36.449	8.757	3.559	2.590	0.887	4.068	7.807
	⁷⁴ GeCl ₂	-1.175	-58.996	33.412	8.742	3.400	2.860	1.205	4.029	7.339
	⁷⁶ GeCl ₂	-2.197	-58.115	30.561	8.733	3.256	3.082	1.496	3.996	6.895
Expt. [17]		-2.220(84)	-61.035(131)	31.926(64)	8.8454(40)	4.0190(179)	2.7932(50)	2.1307(12)	4.3142(16)	6.3037(13)
			-62.278(120)			3.9886(102)			4.3391(21)	

major isotopes are collected in Table III, together with the corresponding experimental data for ⁷⁴GeCl₂ [17]. Comparing the experimental data with the calculated data, the MP2 results generally yield vibration-rotation constants with the correct sign and with reasonable magnitude. It is easy to find that the error between the calculated value of α_i^C and the corresponding experimental data is very big. The reason is that there is an important Coriolis interaction between the vibrational states ν_1 and ν_3 in GeCl₂. The calculated value of α_i^C in Table III does not take this interaction into account. However, the experimental data have contained it [17]. For this reason, the direct comparison with the experimental α constants is not immediate. It is more informative to compare the values of $B_0^X - B_e^X = \frac{1}{2} \sum \alpha_i^X$ because the interaction was mostly cancelled out. As shown in Table III, good agreement with experimental values is obtained for the B and C rotational constants. However, for $A_0 - A_e$, the experimental value, -15.665 MHz, is smaller than the computed values (2.06 and 2.29 MHz). The deviations between CCSD(T) results and experimental values are somewhat larger than MP2 results, especially for α_1^A and α_1^C . A possible reason is that CCSD(T) theory

TABLE IV Harmonic and fundamental vibrational wavenumbers of GeCl₂ (in cm⁻¹).

Method	Isotope	ω_1	ω_2	ω_3	ν_1	ν_2	ν_3
MP2	⁷⁰ GeCl ₂	425.0	406.9	165.5	422.1	403.9	164.6
	⁷² GeCl ₂	423.2	404.8	165.0	420.3	401.9	164.2
	⁷⁴ GeCl ₂	421.4	402.8	164.6	418.5	399.9	163.2
	⁷⁶ GeCl ₂	419.7	400.8	164.1	416.8	398.0	162.8
CCSD(T)	⁷⁰ GeCl ₂	422.1	406.2	164.7	418.6	403.3	163.6
	⁷² GeCl ₂	420.3	404.1	164.2	417.3	401.5	163.8
	⁷⁴ GeCl ₂	418.6	402.1	163.8	415.7	399.1	163.0
	⁷⁶ GeCl ₂	416.9	400.2	163.4	413.7	397.9	162.2
Expt. [17]					399	372	159

has difficulties in describing electron correlation in the hypervalent Cl atom [30, 31].

Table IV presents the calculated harmonic and fundamental vibrational wavenumbers of the major isotopes of GeCl₂ without any scaling factor. The heavier isotopic molecule has the smaller frequency. For small mass differences the frequencies of the isotopic molecules are close to those of the ordinary molecule. The isotope shifts of ω_3 and ν_3 are very small because

TABLE V Vibrational anharmonicity constants X_{ij} of GeCl_2 .

Method	Isotope	X_{11}	X_{12}	X_{13}	X_{22}	X_{23}	X_{33}
MP2	$^{70}\text{GeCl}_2$	-0.629	-0.807	-2.499	-0.033	-0.760	-0.660
	$^{72}\text{GeCl}_2$	-0.623	-0.793	-2.489	-0.034	-0.751	-0.647
	$^{74}\text{GeCl}_2$	-0.617	-0.790	-2.477	-0.307	-0.754	-0.637
	$^{76}\text{GeCl}_2$	-0.610	-0.778	-2.464	-0.745	-0.305	-0.628
CCST(D)	$^{70}\text{GeCl}_2$	-0.745	-0.798	-3.283	-0.106	-0.878	-0.444
	$^{72}\text{GeCl}_2$	-0.634	-0.683	-2.845	0.145	-0.848	-0.387
	$^{74}\text{GeCl}_2$	-0.637	-0.787	-2.496	-0.025	-0.754	-0.688
	$^{76}\text{GeCl}_2$	-0.620	-1.097	-2.836	-0.086	-0.900	-0.182

TABLE VI Equilibrium quartic centrifugal distortion constants of GeCl_2 .

Isotope	Method	D_J	D_K	D_{JK}	d_J	d_K
$^{70}\text{GeCl}_2$	MP2	1.1523	37.6862	-7.4708	0.4194	1.6511
	CCSD(T)	1.0200	36.2468	-6.6220	0.4174	1.5627
	Expt. [17]	1.2254(19)	41.81(49)	-8.148(29)	0.44588(99)	1.760(26)
$^{72}\text{GeCl}_2$	MP2	1.1491	36.7096	-7.3563	0.4210	1.6096
	CCSD(T)	1.0200	36.2347	-6.6093	0.4174	1.5692
	Expt. [17]	1.2207(21)	40.35(57)	-7.834(36)	0.4468(11)	1.801(32)
$^{74}\text{GeCl}_2$	MP2	1.1459	35.8702	-7.2576	0.4224	1.5712
	CCSD(T)	1.0200	36.2218	-6.5966	0.4174	1.5755
	Expt. [17]	1.2254(12)	37.89(46)	-7.674(45)	0.45234(63)	1.834(31)
$^{76}\text{GeCl}_2$	MP2	1.1429	34.9819	-7.1525	0.4239	1.5318
	CCSD(T)	1.0200	36.2088	-6.5838	0.4174	1.5819
	Expt. [17]	1.21514(52)	38.20(35)	-7.324(21)	0.45234(fix)	1.834(fix)

the atom Ge which is replaced by its isotope moves very little in the particular normal mode, whereas the shifts of others are more larger because the atom Ge in question has a large amplitude in that normal mode. So the investigation of the isotope effects is invaluable in correlating the observed vibrational frequencies with the theoretical normal modes of GeCl_2 .

Table V presents the anharmonic constants X_{ij} of the major isotopes of GeCl_2 . The theoretical fundamental wave numbers were derived from the corresponding harmonic wave numbers and anharmonicity constants. For molecules containing two equivalent bonds of the general formula XY_2 , the relations [32–34] relate some of the vibrational anharmonicity constants as follows:

$$X_{11} \approx X_{33} \approx \frac{1}{4}X_{13} \quad (1)$$

These relations are based on an approximate model, but they provide a useful check on the calculations because it has been observed experimentally that they hold well for some of the XY_2 type molecule. As the appropriate entries of Table V testify, the interrelations presented in the Eq.(1). hold very well for the directly determined *ab initio* spectroscopic constants. So far, both the harmonic wave numbers and anharmonic constants of these molecules have not been deduced experimentally. In view of the limited experimental data on

these constants, *ab initio* predictions of them are expected to be useful for future experimental work.

The experimental ground-state values and computed equilibrium quartic centrifugal distortion constants (A reduction [35]) of $^{70}\text{GeCl}_2$, $^{72}\text{GeCl}_2$, $^{74}\text{GeCl}_2$, and $^{76}\text{GeCl}_2$ are compared in Table VI. This permits to check the quality of the harmonic force field. The deviations between the experimental and *ab initio* are only a few percent, the largest deviation (>10%) being for d_K as usual. It is worth noting that the deviations are almost the same (the percentage) as for $^{74}\text{GeCl}_2$. It is likely that a large part of these deviations could be explained by the difference between ground state and equilibrium constants which values are known to be a few percent. The effects for these quartic centrifugal constants are much weaker, and the shift between our results and experiment is still very satisfactory.

The equilibrium sextic centrifugal distortion constants (A reduction [35]) for these isotopomers of GeCl_2 calculated from the MP2/cc-pVTZ cubic force fields are shown in Table VII. It should be pointed out that the ACESII program used for the CCSD(T) calculations does not permit to calculate sextic centrifugal distortion constants and the comparison is thus restricted to the MP2/cc-pVTZ results for these isotopomers. The calculations generally yield the sextic centrifugal distortion constants with the correct sign and with rea-

TABLE VII Sextic centrifugal distortion constants of GeCl₂ (10⁻³ Hz) by MP2 method.

Isotope	H_J	H_K	H_{JK}	H_{KJ}	h_J	h_K	h_{JK}
⁷⁰ GeCl ₂	1.181158	1.947953	-165.466698	694.833678	0.602030	106.675057	-1.034999
⁷² GeCl ₂	1.181298	1.713581	-160.078247	667.797408	0.601960	102.635591	-1.087219
⁷⁴ GeCl ₂	1.181767	1.495866	-155.431472	645.148136	0.602045	99.160580	-1.137723
⁷⁶ GeCl ₂	1.181945	1.276156	-150.539331	621.092224	0.601957	95.531855	-1.186101

TABLE VIII Quadratic, cubic, and quartic force constants of GeCl₂ in normal coordinates (cm⁻¹).

Method	Isotope	111	211	222	331	1111	2111	2211	3311	3322	3333
MP2	⁷⁰ GeCl ₂	-67.676	-12.073	-21.873	-80.462	9.615	3.673	-2.071	13.527	-4.633	14.297
	⁷² GeCl ₂	-67.414	-11.839	-21.806	-79.866	9.590	3.596	-2.041	13.383	-4.584	14.186
	⁷⁴ GeCl ₂	-67.152	-11.629	-21.728	-79.300	9.572	3.524	-2.051	13.255	-4.582	14.089
	⁷⁶ GeCl ₂	-66.905	-11.409	-21.663	-78.743	9.566	3.453	-2.022	13.134	-4.535	13.988
CCSD(T)	⁷⁰ GeCl ₂	-71.932	10.907	22.650	-85.841	9.922	-3.249	-3.926	15.444	-3.529	21.607
	⁷² GeCl ₂	-69.869	11.179	22.090	-82.575	10.709	-3.596	-1.205	14.823	-2.172	20.373
	⁷⁴ GeCl ₂	-68.015	11.407	21.555	-79.711	9.783	-3.493	-2.073	13.574	-4.641	13.786
	⁷⁶ GeCl ₂	-66.294	11.614	21.053	-76.901	9.272	-3.023	-2.704	15.175	-4.945	20.206

sonable magnitude. Although no experimental sextic centrifugal distortion constants are found in references, we believe the results of MP2/cc-pVTZ are reliable.

The investigation of the vibrational frequencies of molecules isotopic with the one considered gives additional equations for the force constants. While the number of constants in the most general quadratic potential function is usually larger than the number of fundamental frequencies. Thus if only one isotopic species is observed not all the force constants can be evaluated unless simplifying assumptions are made. But with the help of the fundamental frequencies of one or more isotopic molecules a sufficient number of additional equations is in general obtained to determine all constants in the most general (quadratic) potential function. Table VIII lists complete *ab initio* quartic force fields in normal coordinates for GeCl₂. It includes the results of MP2 and CCSD(T) with cc-pVTZ basis set. From group theoretical arguments we find that, in its C_{2v} ground electronic state, the germanium dichloride molecule has two geometric variables, and 4 quadratic, 6 cubic, 9 quartic, 12 quintic, and 16 sextic force constants. By definition, the quadratic normal coordinate constants correspond to the harmonic wave numbers. All cubic force constants are predicted to be negative by MP2 level of theory. Therefore, the fact that f_{211} and f_{222} have been predicted to be positive in CCSD(T) results should be regarded as weaknesses in the CCSD(T) calculation rather than indications that there were problems in the MP2 calculations. It is also noteworthy that the cubic constants f_{221} and f_{233} are determined to be much smaller in absolute magnitude than other force constants. So, only the constants higher than 1 cm⁻¹ are reported in this Table. In the quartic part of the force field pronounced devia-

tions exist for some of the constants. First of all, it is noteworthy how different the calculated f_{3333} constants are. This is probably due not only to theory effects but also to higher-order contamination and truncation effects during the determination. Finally, it is interesting to note that the CCSD(T) results do not seem follow any simple rule.

IV. CONCLUSION

In conclusion, we present some results to the isotopic effects on GeCl₂. The isotopic effects for germanium dichloride are much weaker. All spectroscopic constants calculated with this approach are in good agreement with the available experimental results, proving the high quality of the underlying anharmonic force field and the viability of the perturbation-resonance approach at the same time. The MP2 results are in excellent agreement with the available experimental data for main isotopomers, so that the MP2 predictions for spectroscopic constants yet unknown are expected to be reliable.

Those isotopic molecules are also symmetrical, because the central atom is replaced by an isotope. As an asymmetric top molecule, the effective Hamiltonian in A reduction [35] can be written as

$$\begin{aligned} \hat{H}^A = & A_K J_z^2 + A_J J^2 + \frac{1}{2} a (J_+^2 + J_-^2) - D_K J_z^4 - \\ & D_{JK} J^2 J_z^2 - D_J J^4 + H_K J_z^6 + H_{KJ} J^2 J_z^4 + \\ & H_{JK} J^4 J_z^2 + H_J J^6 + \frac{1}{2} [-d_K J_z^2 - d_J J^2 + \\ & h_K J_z^4 + h_{JK} J^2 J_z^2 + h_J J^4, J_+^2 + J_-^2]_+ \quad (2) \end{aligned}$$

$$A_K = \frac{A - (B + C)}{2} \quad (3)$$

$$A_J = \frac{B + C}{2} \quad (4)$$

$$a = \frac{B - C}{2} \quad (5)$$

here $[\cdot, \cdot]_+$ represents the positive commutator. Submitting the parameters in Tables VI and VII into the above equation, one can obtain the computed rotational energy of molecule in the study, which is necessary to assign the observed rotational energy of molecule.

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