A theoretical study of He₂ICI van der Waals cluster

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The structure, energetics, and dynamics of He₂ICI complex in its ground state are studied by means of *ab initio* electronic structure and quantum-mechanical calculations. Interaction energies for selected He₂ICI configurations are calculated at the coupled-cluster [CCSD(T)] level of theory using a large-core pseudopotential for the I atom and the aug-cc-pVTZ and aug-cc-pV5Z basis sets for the Cl and He atoms, respectively. The surface is characterized around its lower five minima and the minimum energy pathways through them. The global minimum of the potential corresponds to a “police-nightstick (1)” configuration, the second one to a linear, the next one to tetrahedral configuration, and the following two to “bifork” and “police-nightstick (2)” structures, with well depths of −99.12, −97.42, −88.32, −85.84, and −78.54 cm^{−1}, respectively. An analytical form based on the sum of the three-body parametrized HeICI interactions plus the He–He interaction is found to represent very well the tetra-atomic CCSD(T) results. The present potential expression is employed to perform variational five-dimensional quantum-mechanical calculations to study the vibrational bound states of the van der Waals He₂ICI complex. Results for total angular momentum $J=0$ provide the binding energy D_0 and the corresponding vibrationally averaged structure for different isomers of the cluster. Comparison of these results with recent experimental observations further justifies the potential used in this work. © 2006 American Institute of Physics.
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I. INTRODUCTION

Small rare gas-dihalogen van der Waals (vdW) complexes have proven to be ideal systems for studying the nature of long-range intermolecular forces, photodissociation dynamics, and energy transfer mechanisms. During the last decades, with the development of experimental techniques, such as supersonic beam expansion, and by performing more accurate *ab initio* electronic structure calculations, we are able to study the structure and dynamics of such complexes in detail.^{1,2} Considerable attention has been paid both by theory and experiment to the structure and interactions of systems with a single rare gas atom, i.e., of Rg-XY complexes where Rg is He, Ne, or Ar atom and X, Y=F, Cl, Br, or I. In particular, the assignment of the two-band structure of the $B \leftarrow X$ excitation spectrum turned out to be interesting and several theoretical studies have been carried out to explore it.^{3–5} A necessary condition for understanding the vibrational dynamics and for interpreting the spectra is an accurate description of the potential energy surfaces involved. Up to now accurate potentials for triatomic systems have been obtained either by fitting the potential parameters to experimental data obtained from high resolution spectroscopic methods^{6–10} or by performing state-of-the-art electronic structure calculations.^{8,11–18} For all Rg-XY cases studied, both experimental and theoretical studies support a double-minima topology for the ground state potential, corresponding to linear- and T-shaped configurations.^{4,19–22}

Studies of larger species are more complex and the difficulty in evaluating their potential surfaces increases with

the cluster size. Janda and co-workers^{23–25} were the first to obtain rotationally resolved excitation spectrum of complexes containing more than one rare gas atom. An interesting example is their experimental studies on Rg₂Cl₂ clusters, where difficulties in fitting the observed excitation spectrum by means of rigid rotor analysis led them to conclude that He₂Cl₂ is an extremely floppy, liquidlike cluster without any average structure and the dynamics of He_nCl₂ complexes will be quite different from their Ne_nCl₂Ar_n and Cl₂ analogs. Similar conclusions have been reported by several theoretical studies performing quantum Monte Carlo²⁶ or variational^{27,28} calculations, where the importance of performing exact calculations for such liquidlike systems is emphasized. In all the above mentioned dynamical studies for the tetra-atomic Rg_nCl₂ systems, pairwise atom-atom potential energy surfaces (PESs) have been employed. Even though the atom-atom potentials have been widely used, they have not been able to reproduce the high anisotropy of van der Waals complexes and to describe accurately enough all details of their dynamics.

The construction of *ab initio* potential energy surfaces for polyatomic molecular systems (including heavy atoms in our case) is a computationally prohibitive task. Thus, given the high quality *ab initio* PESs calculated for triatomic species, attempts are made using pairwise three-body interaction potentials to represent PESs of larger Rg_nXY complexes. *Ab initio* results have been presented for He₂Br₂ system, indicating that pairwise atom-atom interactions are not able to describe the complex, while a sum of three-body He–Br₂ terms,¹⁷ plus the He–He interaction can accurately represent the interaction energies for this cluster.²⁹ Such surfaces are of

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particular interest in the study of both the solvent properties of superfluid helium³⁰ and the relaxation dynamics of impurities embedded in helium droplets. Rotational and infrared spectroscopic studies for helium droplets doped with a variety of molecules are currently conducted in order to answer new and challenging questions on the role of the “quantum environment.”^{31–35} In this sense, our current studies on the interaction of helium with dihalogen molecules for the case of two helium atoms serve to bridge the gap between the small cluster and the large cluster limits.

In the present study the validity of the pairwise additivity of the three-body potentials for the He_2ICl is investigated. Comparison with the He_2Br_2 complex will allow us to evaluate the effect of changing the dihalogen upon the vdW bond. The electric dipole moment of ICl molecule and the larger reduced mass of the complex lead to a further stabilization of the linear triatomic He-I-Cl isomer. By analyzing the topology of the He_2ICl PES, we were able to rationalize the trends within the Rg_nXY family and relate them to properties of the trimers.

The plan of this paper is as follows. The next section outlines the methodology used to perform the *ab initio* calculations together with the computed optimal structures for He_2ICl . The analytical representation of PES is given in Sec. III. The CCSD(T) interaction energies are examined and compared with the potential values obtained by the sum of the three-body terms. Trends in topology of He_2XY are also investigated in Sec. III. The variational method to calculate the vibrational states of He_2ICl is briefly described in Sec. IV. The wave functions of the lower states are analyzed in terms of probability distributions of the internal coordinates and the dissociation energy of the vdW cluster is evaluated and compared to experiment. Finally, a summary is given in Sec. V.

II. AB INITIO CALCULATIONS

The *ab initio* calculations are performed using the Gaussian 98 package.³⁶ Computations are carried out at the CCSD(T) level of theory. The $\text{He}_2\text{-ICl}$ system is described using the $(r, R_1, R_2, \theta_1, \theta_2, \gamma)$ coordinate system. r is the bond length of ICl, R_1 and R_2 are the intermolecular distances of each He atom from the center of mass of I-Cl, θ_1 is

FIG. 1. Schematic representation of coordinate system for He_2ICl complex.

the angle between the $\mathbf{R}_1$ and $\mathbf{r}$ vectors, while θ_2 is the one between $\mathbf{R}_2$ and $\mathbf{r}$, and γ is the angle between the $\mathbf{R}_1$ and $\mathbf{R}_2$ vectors (see Fig. 1).

The supermolecular approach is used for the determination of the intermolecular energies, ΔE :

$$\Delta E = E_{\text{He}_2\text{ICl}} - E_{\text{BSSE}} - 2E_{\text{He}} - E_{\text{ICl}}, \quad (1)$$

where $E_{\text{He}_2\text{ICl}}$, E_{He} , and E_{ICl} are the energies of $\text{He}_2\text{-ICl}$, He, and ICl, respectively. The correction, E_{BSSE} , for the basis-set superposition error is calculated using the standard counterpoise method.³⁷

We performed CCSD(T) calculations for several configurations fixing the ICl bond length at its equilibrium value $r_e = 2.321 \text{ \AA}$.³⁸ For the present calculation we used for I atom the Stuttgart-Dresden-Bonn (SDB) large-core energy-consistent pseudopotential³⁹ in conjunction with the augmented correlation consistent triple zeta (SDB-aug-cc-pVTZ) valence basis set.⁴⁰ This basis set is of cc-pVTZ quality and has been optimized for use with the SDB pseudopotential. For the Cl atom we employed the aug-cc-pVTZ basis set while for the He atoms we used the aug-cc-pV5Z from EMSL library.⁴¹ In all calculations here 6d and 10f Cartesian functions are used.

TABLE I. CCSD(T) interaction energies, ΔE [Eq. (1)], for the He_2ICl molecule for different structures and at the indicated coordinate values with r fixed at $2.321 \text{ \AA}$ (see Fig. 2). Energies in cm^{-1} and distances in $\text{\AA}$.

Linear				Police nightstick (1)				Tetrahedral		Police nightstick (2)			
R_1	ΔE	R_2	ΔE	R_1	ΔE	R_2	ΔE	$R_1=R_2$	ΔE	R_1	ΔE	R_2	ΔE
3.4	30.88	4.5	98.06	3.4	31.36	3.3	-15.32	3.3	48.35	3.3	-4.15	4.5	109.28
3.6	-51.36	4.7	-24.47	3.6	-50.74	3.5	-60.07	3.5	-39.68	3.5	-48.90	4.7	-12.93
3.7	-68.45	4.9	-67.88	3.7	-67.82	3.7	-75.81	3.7	-70.03	3.7	-64.59	4.9	-56.16
3.8	-76.71	5.1	-78.62	3.8	-76.05	3.8	-78.02	3.8	-74.16	3.8	-66.83	5.1	-66.79
4.0	-78.77	5.3	-77.12	4.0	-78.15	4.0	-77.06	4.0	-71.70	4.0	-65.84	5.3	-65.23
4.2	-72.80	5.7	-66.50	4.2	-72.19	4.5	-65.75	4.5	-48.48	4.5	-54.47	5.7	-54.54
4.5	-61.52	6.0	-59.74	4.5	-60.93	5.0	-56.71	5.0	-30.29	5.0	-45.43	6.0	-47.76
5.0	-48.15	7.0	-49.32	5.0	-47.54	6.0	-48.88	6.0	-14.62	6.0	-37.53	7.0	-37.29
6.0	-37.90	8.0	-46.57	6.0	-37.27	8.0	-45.67	8.0	-8.30	8.0	-34.24	8.0	-34.50
8.0	-34.24			8.0	-33.60

FIG. 2. Optimal CCSD(T) structures for (a) police nightstick (1), (b) linear, (c) tetrahedral, (d) bifork, and (e) police-nightstick (2) He₂ICl configurations.

The results for the CCSD(T) supermolecular interaction energies at selected geometries are listed in Table I, while the geometries for the five optimal structures are shown in Fig. 2. According to the CCSD(T) results the linear configuration [see Fig. 2(b)] has the lowest energy -79.58 cm^{-1} with $R_1 = 3.922$ and $R_2 = 5.152 \text{ \AA}$. The next equilibrium structure is found at energy -78.99 cm^{-1} and corresponds to a “police-nightstick (1)” configuration [see Fig. 2(a)] with one helium in a near T-shaped orientation ($\theta_2 = 110.6^\circ$), while the second one is located in side of the iodine atom ($R_1 = 3.924$ and $R_2 = 3.858 \text{ \AA}$). In turn, a tetrahedral configuration [see Fig. 2(c)] with $R = 4.123 \text{ \AA}$, $\theta = 110.6^\circ$, and the He–He distance $2.9506 \text{ \AA}$ is located at energy of -74.58 cm^{-1} . A “bifork” configuration [see Fig. 2(d)] with one helium atom at linear $\theta_1 = 0^\circ$ and the other one at $\theta_2 = 39.73^\circ$ with R_1 and R_2 to be 3.863 and $4.537 \text{ \AA}$, respectively, at energy of -67.59 cm^{-1} is the fourth minimum, and the last one corresponding to a “police-nightstick (2)” configuration [see Fig. 2(e)] with one helium in the near T-shaped position and the other one in the side of Cl ($R_1 = 5.151$ and $R_2 = 3.858 \text{ \AA}$) is found at energy of -67.18 cm^{-1} .

For weakly bound systems it has been demonstrated that an efficient way to saturate the dispersion energy is the use of midbond functions.^{42–44} In particular, studies on triatomic dispersion-bound complexes have shown an improvement of $\approx 5\%$ in the interactions energies.^{15,43,44} Thus, in order to investigate the role of using bond functions in tetra-atomic

He₂XY clusters and to account for their effect in the interaction energies of the complex, test runs are carried out for specific configurations around the optimal structures, namely, linear, police nightstick, tetrahedral, and bifork (see Fig. 2 and Table II). We choose the same set of bond functions that has been employed in the study of the triatomic He–ICl system, namely, $(3s3p2d2f1g)$.^{22,45}

As for a polyatomic vdW system the location for such midbond functions is not clearly defined, and calculations are carried out in order to evaluate their influence in the interaction energies for the different configurations. For the linear and police-nightstick structures we compare results obtained by placing two sets of the $(3s3p2d2f1g)$ functions, each of them at the midpoints of the two R_1 and R_2 bonds and at the middle of the He–I and Cl–He distances, respectively. Very small differences, accounting 0.02 cm^{-1} , are obtained in the CCSD(T) interaction energies for these structures (see values in square brackets in Table II). For the tetrahedral and bifork configurations calculations are performed by using one or two sets of the $(3s3p2d2f1g)$ functions. The one set of midbond functions is placed at the middle of the intermolecular distance R for both tetrahedral and bifork structures, while the two sets of midbond functions are located, as for the linear and police-nightstick configurations at the midpoints of the two R_1 and R_2 bonds (see Fig. 2). As it was expected, CCSD(T) interaction energies obtained using two sets of midbond functions are lower, by about 3 cm^{-1} , compared with the ones from the one set calculations.

The MP4(SDTQ) and CCSD(T) results for all the above mentioned cluster structures, with and without the use of bond functions, are presented in Table II for different intermolecular distances. Similar differences in the interaction energies are obtained at both levels of theory, and the improvement in the interaction energies by using bond functions is calculated to be more than 10%, around the equilibrium geometries. In particular, the importance of midpoint functions is larger for structures containing linear He–I configuration than He–Cl one; as a major dispersion component comes from the He–I interaction, e.g., for the police-nightstick (1), a difference of 22.21 cm^{-1} is obtained in the CCSD(T) interaction energy, due to the absence of midpoint functions, while for the police-nightstick (2) this difference accounts 11.36 cm^{-1} . However, as a single point CCSD(T)+bf calculation requires an additional computational cost, five times more compared with a CCSD(T) one, we choose to perform such calculations for selected points of the He₂ICl PES.

Thus, CCSD(T)+bf calculations are carried out around the above mentioned configurations, and the computed optimal energies and geometries for He₂ICl are as follows: the police-nightstick (1) ($R_1 = 3.863$ and $R_2 = 3.821 \text{ \AA}$, $\theta_2 = 110.6^\circ$) is found at energy of -99.12 cm^{-1} , the linear ($R_1 = 3.860$ and $R_2 = 5.151 \text{ \AA}$) with energy -97.43 cm^{-1} , the tetrahedral ($R = 4.079 \text{ \AA}$, $\theta = 110.6^\circ$, and He–He distance of $2.9504 \text{ \AA}$) at energy of -88.32 cm^{-1} , the bifork ($R_1 = 3.863$ and $R_2 = 4.482 \text{ \AA}$, $\theta_2 = 39.73^\circ$) at energy of -85.84 cm^{-1} , and police-nightstick (2) ($R_1 = 5.152$ and $R_2 = 3.821 \text{ \AA}$) at -78.54 cm^{-1} . As can be seen, the police-nightstick (1) configuration is energetically favored (by only about 1.69 cm^{-1}) as compared to linear one. The difference is very sensitive to

TABLE II. MP4(SDTQ)/CCSD(T) interaction energies for the He_2ICl obtained with and without bond functions at the indicated configurations. bf stands for the $(3s3p2d2f1g)$ set of bond functions. Values in square brackets are obtained for different locations of the bf (see in the text), while values in parentheses are computed using one set of bf. Energies in cm^{-1} and distances in Å.

Configuration	R_1/R_2	MP4(SDTQ)/CCSD(T)	MP4(SDTQ)+bf/CCSD(T)+bf
Police	3.70/...	-68.39/-67.82	-93.15/-92.64
nightstick (1)	3.80/...	-76.51/-76.05	-98.63[-98.85]/-98.26[-98.28]
$R_2=3.82$	4.00/...	-78.44/-78.15	-96.35/-96.10
$\theta_2=110.6^\circ$	4.20/...	-72.40/-72.19	-87.24/-87.09
Linear	4.90/...	-64.46/-67.88	-89.79/-88.29
$R_2=3.86$	5.10/...	-79.84/-78.62	-98.21[-98.28]/-97.05[-97.03]
	5.30/...	-78.13/-77.12	-95.10/-94.20
Tetrahedral	3.70/3.70	-69.46/-70.03	-86.01(-82.81)/-86.58(-83.40)
$\theta_1=110.6^\circ$	3.80/3.80	-73.63/-74.16	-87.79(-85.05)/-88.32(-85.62)
	4.00/4.00	-71.29/-71.70	-81.62(-79.65)/-82.04(-80.09)
Bifork	.../4.30	-64.48/-64.09	-84.23(-80.64)/-83.91(-80.37)
$R_1=3.86$	.../4.46	-67.66/-67.27	-86.17(-82.72)/-85.81(-82.43)
$\theta_2=39.7^\circ$	.../4.55	-67.99/-67.58	-85.92(-82.52)/-85.57(-82.24)
	.../4.70	-67.12/-66.72	.../...
Police	.../4.90	-57.11/-56.16	-70.36/-69.31
nightstick (2)	.../5.10	-67.38/-66.79	-78.84/-78.15
$R_1=3.82$	.../ 5.30	-65.60/-65.23	-75.76/-75.35

TABLE III. Summary of the supermolecular calculations of the nonadditive effects around the lower five equilibrium He_2ICl structures. Results for each method without/with bond functions are presented. Energies in cm^{-1} and distances in Å.

Police-nightstick (1) structure, $R_2=3.82$, $\theta_2=110.6$					
R_1	HF	MP2	MP3	MP4(SDQ) (MP4(SDTQ))	CCSD (CCSD(T))
3.8	79.58/79.03	-71.11/-88.36	-67.42/-85.97	-62.31/-81.18 (-76.51/-98.63)	-61.10/-79.78 (-76.05/-98.26)
4.0	51.53/51.27	-73.85/-87.72	-70.45/-89.11	-66.37/-65.69 (-78.44/-96.35)	-65.56/-80.66 (-78.15/-96.10)
4.2	39.18/39.04	-68.43/-79.93	-65.36/-77.89	-61.94/-74.64 (-72.40/-87.24)	-61.34/-73.90 (-72.19/-87.09)
Linear structure, $R_1=3.86$					
R_2	HF	MP2	MP3	MP4(SDQ) (MP4(SDTQ))	CCSD (CCSD(T))
4.9	116.56/116.19	-63.14/-79.58	-57.85/-75.26	-50.26/-67.69 (-64.46/-89.79)	-48.68/-65.89 (-67.88/-88.29)
5.1	73.57/73.15	-74.78/-89.52	-70.26/-85.88	-64.15/-79.91 (-79.84/-98.21)	-62.90/-78.53 (-78.62/-97.05)
5.3	53.66/53.22	-74.01/-87.53	-69.95/-84.32	-64.81/-79.36 (-78.13/-95.10)	-63.76/-78.11 (-77.12/-94.20)
Tetrahedral structure, $R_1=R_2$, $\theta_1=110.6$					
R_1	HF	MP2	MP3	MP4(SDQ) (MP4(SDTQ))	CCSD (CCSD(T))
3.7	101.35/101.33	-59.94/-72.98	-59.32/-73.28	-55.09/-69.18 (-69.46/-86.01)	-54.23/-68.19 (-70.03/-86.58)
3.8	74.25/74.25	-65.32/-76.38	-64.64/-76.53	-61.01/-73.04 (-73.63/-87.79)	-60.36/-72.27 (-74.16/-88.32)
4.0	40.87/40.89	-64.79/-72.82	-64.15/-72.82	-61.47/-70.28 (-71.29/-81.62)	-61.04/-69.77 (-71.70/-82.04)
"Bifork" structure, $R_1=3.863$, $\theta_2=39.73$					
R_2	HF	MP2	MP3	MP4(SDQ) (MP4(SDTQ))	CCSD (CCSD(T))
4.3	78.09/77.69	-56.91/-72.03	-56.65/-73.13	-51.93/-68.74 (-64.48/-84.23)	-50.57/-67.20 (-64.09/-83.91)
4.46	62.35/61.96	-61.10/-75.28	-60.38/-75.83	-56.08/-71.83 (-67.66/-86.17)	-54.91/-70.47 (-67.27/-85.81)
4.55	55.99/55.59	-61.98/-75.65	-60.99/-75.92	-56.87/-72.16 (-67.99/-85.92)	-55.77/-70.87 (-67.58/-85.57)
Police-nightstick (2) structure, $R_1=3.82$, $\theta_1=110.6$					
R_2	HF	MP2	MP3	MP4(SDQ) (MP4(SDTQ))	CCSD (CCSD(T))
4.9	111.56/111.56	-50.13/-60.84	-46.29/-57.61	-39.94/-51.01 (-57.11/-70.36)	-38.83/-49.82 (-56.16/-69.31)
5.1	68.63/68.56	-61.63/-70.82	-58.56/-68.32	-53.73/-63.34 (-67.38/-78.84)	-52.96/-62.48 (-66.79/-78.15)
5.3	48.77/48.79	-60.77/-68.85	-58.16/-66.79	-54.32/-62.86 (-65.60/-75.76)	-53.75/-62.24 (-65.23/-75.35)

the basis set used, due to the importance of the dispersion energy of the complex. It is necessary to saturate this component in order to correctly predict the ordering of the minima, which is achieved in our case by supplementing the basis set with two sets of midbond functions. We should note that interaction energies as well as equilibrium distances of the above structures are very close to the ones obtained by CCSD(T)+bf calculations for the three optimized geometries of the triatomic HeICl complex.²² In particular, the interaction energies and equilibrium R_e distances have been predicted to be 58.62 cm⁻¹ and 3.86 Å for the linear well, 38.96 cm⁻¹ and 3.82 Å for the near T shaped ($\theta=110.9^\circ$), and 38.03 cm⁻¹ and 5.12 Å for the antilinear one. These results are compared very well with experimental data on He-ICl (Ref. 22) and their quality has been also demonstrated by dynamical simulations for the $B \leftarrow X$ excitation spectrum.⁴

In order to extract information on nonadditive interactions in He₂ICl we examine the above tetra-atomic equilibrium structures based on the *ab initio* calculations by partitioning the interaction energy into components, as given in Ref. 46. Therefore, we show in Table III the summary of supermolecular calculations of the entire nonadditivity in the different He₂ICl equilibrium structures using the results of the Møller-Plesset perturbation theory (MPPT) up to fourth order along with the ones of the CCSD(T) method. As can be seen in Table III, the use of bond functions clearly affects the interaction energies of the complex at the MP2 level, where the second-order dispersion term appears in the analysis of the contents of the two- and three-body supermolecular interaction energies.¹³ In turn, the total three-body interaction for different intermolecular configurations around the lower five equilibrium geometries computed through the MP3 amounts to -70.45/-89.11, -70.26/-85.88, -64.64/-76.53, -60.99/-75.92, and -58.56/-68.32 cm⁻¹, respectively. These energies neglect completely the effects of intramonomer correlation on three-body dispersion. The major effect of the intrasystem correlation on dispersion appears in MP4 level and is specially sensitive to the presence of triple excitations. For all configurations studied the MP4(SDQ) calculations reduce this effect to -66.37/-65.69, -64.15/-79.91, -61.01/-73.04, -56.87/-72.16, and -53.73/-63.34 cm⁻¹, respectively, while the inclusion of triples enhances both MP4(SDQ) and CCSD interaction energies [see MP4(SDTQ) and CCSD(T) values without/with bond functions in Table III]. The MP4(SDQ) results seem to be well converged with respect to the CCSD calculations. For a consistent treatment of two- and three-body correlation effects, the three-body potentials should be summed to a level of theory one order higher than the one corresponding to the two-body ones. The MP4(SDTQ) reproduces quantitatively the dominant contributions to the two-body interaction energy, while to achieve a similar level of correlation for the three-body terms one needs to advance to the next order of theory, i.e., MP5. However, it is more practical and accurate to turn to the CCSD(T) theory. Our calculations indicate that the total nonadditive effect in He₂ICl originating from supermolecular CCSD(T) calculations amounts to 0.46/0.37, 1.22/1.16, -0.53/-0.53, 0.39/0.36, and 0.59/0.69 cm⁻¹ for configurations nearby its equilibrium structures. We should mention that the same be-

havior was observed in the results of the MPPT energies for the HeICl complex²² around its linear and near T-shaped equilibrium configurations.

Further, the ordering of the minima for the He₂ICl complex discussed above is an element of the general trend in this matter in the set of He₂-dihalogen complexes. After studying the He₂Br₂ cluster,²⁹ together with the new insights from the current He₂ICl calculations and the decomposition of their interaction energies, it is worthwhile to discuss the whole set of such complexes. Both of the He₂XY complexes studied appear to have four different types of minima, namely, police nightstick, linear, tetrahedral, and bifork. The position of their global minimum is opposite and the energetic distance between this minimum and the secondary one varies for these complexes, but general trends are clearly visible. The relations between various components of intermolecular forces that lead to the ordering of the potential minima are found to be similar between the tetra-atomic and triatomic complexes. Thus, we may conclude that for He₂-homopolar dihalogen complexes the global minimum is expected to be for linear configurations, as all HeX₂ complexes studied appear to have linear global minimum. In contrast, for heteropolar ones, the location of their global minimum depends from the energy difference balance of the corresponding three triatomic potential wells. Such findings indicate a similar nature of binding in triatomic and tetra-atomic complexes of such type, and thus information on intermolecular interactions available for triatomic species might serve to study larger systems.

III. ANALYTICAL REPRESENTATION OF THE PES

We used one functional form for the He₂-ICl potential energy function based on the sum of three-body HeICl interactions and the He-He one, which has been used in previous tetra-atomic calculations for the He₂-Br₂.²⁹

$$V(r_e, R_1, R_2, \theta_1, \theta_2, \gamma) = \sum_i V_{\text{He}_i\text{ICl}}(r_e, R_i, \theta_i) + V_{\text{HeHe}}(R_1, R_2, \gamma), \quad (2)$$

where the corresponding $V_{\text{He}_i\text{ICl}}(r_e, R_i, \theta_i)$ terms with $i=1$ and 2 are the CCSD(T) parametrized potential of the HeICl complex²² and $V_{\text{HeHe}}(R_1, R_2, \gamma)$ term is the potential function for He₂ given in Ref. 48.

Configuration energies are determined by optimizing different structures with respect to atomic positions using the functional expressions given in Eq. (2). In Fig. 3 we plot the potential curves obtained and compare them with the tetra-atomic CCSD(T)/CCSD(T)+bf *ab initio* results. We should note that triatomic HeICl CCSD(T)/CCSD(T)+bf calculations were performed employing the same above mentioned basis sets. In Fig. 3 open circles indicate the CCSD(T) *ab initio* values, while crosses represent the sum of the three-body CCSD(T) HeICl interaction potential at the same points. Solid lines are for the potential curves obtained using the three-body CCSD(T)+bf HeICl interaction potential from Ref. 22 and filled circles are for the CCSD(T)+bf *ab initio* data. Figure 3(a) corresponds to police-nightstick (1) structures [see Fig. 2(a)] and represents the potential energy

FIG. 3. Comparison of potential values for (a) police-nightstick (1), (b) linear, (c) tetrahedral, and (d) police-nightstick (2), configurations He_2ICl . Solid lines are for the sum of three-body CCSD(T)+bf HeICl interaction potentials, while the $\text{CCSD(T)/CCSD(T)+bf}$ *ab initio* values are indicated by open and filled circles, respectively. The sum of three-body CCSD(T) HeICl terms is also indicated by crosses.

curves as a function of the distance R_1 between the center of mass of ICl and one He atom. In Figs. 3(b) and 3(c) representations of the potential energy curve are given for linear and distorted tetrahedral structures, respectively, as a function of R_2 distance. At the end, Fig. 3(d) corresponds to police-nightstick (2) configurations. As can be seen, the model potential based on the sum of the three-body CCSD(T) HeICl interactions with and without bond functions plus the He-He interaction reproduce very well the corresponding *ab initio* data with an average absolute deviation of 1.1 cm^{-1} for the CCSD(T)+bf values. Once we check the validity of the analytical form using the triatomic CCSD(T) and CCSD(T)+bf interactions we decide for our later calculations to employ the CCSD(T)+bf HeICl parametrized potential given in Ref. 22, that includes an additional set of bond functions in the middle of the triatomic van der Waals bond.

Figure 4 shows two-dimensional contour plots of the $V(r_e, R_1, R_2, \theta_1, \theta_2, \gamma)$ surface in XY or ZX Cartesian plane. The equipotential curves are shown for He moving around a triatomic HeICl molecule fixed at specific linear [see Fig. 4(a)] and T-shaped [see Figs. 4(b) and 4(c)] configurations. In this case the lowest five wells of the potential are found at energies of -97.72 , -96.67 , -86.38 , -85.64 , and -77.40 cm^{-1} , for the police-nightstick (1), collinear, bifork, tetrahedral, and police-nightstick (2) structures, respectively. The equilibrium distances and angles are at $R_1^e = 3.860 \text{ Å}$, $R_2^e = 3.811 \text{ Å}$, and $\theta_2 = 110.4^\circ$ for the police nightstick (1), $R_1^e = 3.861$ and $R_2^e = 5.124 \text{ Å}$ for the linear one, $R_1^e = 3.863 \text{ Å}$, $R_2^e = 4.458 \text{ Å}$, $\theta_1 = 0^\circ$, and $\theta_2 = 39.73^\circ$ for the bifork, $R^e = 4.087 \text{ Å}$ and $\theta = 110.5^\circ$ for the tetrahedral well, and $R_1^e = 5.121 \text{ Å}$, $R_2^e = 3.817 \text{ Å}$, and $\theta_2 = 110.75^\circ$ for the police-nightstick (2). These results compare very well with the values obtained from the *ab initio* CCSD(T)+bf interaction energies and structures calculations. Both studies predict a police-nightstick (1) structure as the global minimum, with the linear one, to lie above by only 1.0 – 1.7 cm^{-1} , as local minimum of the He_2ICl surface, together with the next three equilibrium structures. One can see that the analytical form predicts the bifork configuration to be energetically favored

by 0.76 cm^{-1} , compared to the tetrahedral one. This ordering of the minima is opposite to that found by the *ab initio* CCSD(T)+bf calculations, and such small differences are due to accidental accumulation of errors involved in the parametrization procedure of the HeICl potential surface. In particular, *ab initio* CCSD(T)+bf calculations are performed at the two different HeICl geometries corresponding to the

FIG. 4. Contour plots of the He_2ICl potential energy surface, $V(r_e, R_1, R_2, \theta_1, \theta_2, \gamma)$, Eq. (2) in the XY [(a) and (b)] or ZX (c) plane. The ICl distance is fixed at 2.321 Å along the Z axis, while the geometry of the triatomic molecule is fixed to a linear configuration with $R_1 = 3.86 \text{ Å}$ (a) and to a near T-shaped configuration with $R_1 = 3.82 \text{ Å}$, $\theta_1 = 110.6^\circ$ [(b) and (c)]. Contour intervals are of 5 cm^{-1} and for energies from -70 to -95 cm^{-1} (a), -55 to -90 cm^{-1} (b), and -45 to -85 cm^{-1} (c).

FIG. 5. Minimum energy path, V_m in cm^{-1} as a function of angle γ , for planar (a) and nonplanar with $\theta_1 = \theta_2 = 110.6^\circ$ (b) configurations. The probability $\int |\Psi|^2 \sin \gamma dR$ distributions for $n=0$ [police nightstick (1), solid line], $n=1$ (linear, dotted line), $n=2$ (tetrahedral, dashed line), $n=3$ (tetrahedral, long-dashed line), and $n=4$ [police-nightstick (2), dotted-dashed line] vdW levels of He₂ICl are also depicted.

bifork and tetrahedral structures. By comparing them with the values of the HeICl parametrized potential terms used in the Eq. (2), total errors of 0.624 and -1.93 cm^{-1} are obtained in the interaction energies for the bifork and tetrahedral minima, respectively. The major error of 0.96 cm^{-1} is found for the HeICl geometries with angle value close to one of the near-T-shaped well of the molecule. Taking into account these deviations the order of the two minima changes, in accord now with the *ab initio* CCSD(T)+bf results, and with energies of -85.76 and -87.55 cm^{-1} for the tetrahedral and bifork configurations, respectively. We should stress that similar analysis carried out for the other three potential minima shows no change in their ordering. However, an energetic distance of about 2.0 cm^{-1} , that is closer to the *ab initio* CCSD(T)+bf data, is obtained between the police-nightstick (1) and linear minima.

One-dimensional representations of the potential are shown in Fig. 5, where minimum energy paths are plotted as a function of the angle γ for planar [see Fig. 5(a)] and nonplanar with $\theta_1 = \theta_2 = 110.6^\circ$ [see Fig. 5(b)] configurations. The isomerization barrier between the police nightstick (1) $\leftrightarrow$ linear wells is found at energy of -81.46 cm^{-1} and an angle θ_2 of 139.75° , while the one between police nightstick (1) $\leftrightarrow$ bifork at energy of -75.24 cm^{-1} and $\theta_2 = 64.43^\circ$. In Fig. 6 we plot at indicated geometries, selected along to a minimum energy path [HeICl molecule is fixed at linear configuration, $\theta_1 = 0^\circ$ and $R_1 = 3.86 \text{ \AA}$ (see Fig. 2), while the R_2 distance is optimized for each θ_2 value], the *ab initio* CCSD(T) values and compare them with the corresponding $V(r_e, R_1, R_2, \theta_1, \theta_2, \gamma)$ ones, given by the Eq. (2) using CCSD(T) and CCSD(T)+bf three-body HeICl interactions. The above data and their comparison with MP4(SDTQ) values are available in an EPAPS document.⁴⁷ As can be seen, the differences obtained in the CCSD(T) results are fully

FIG. 6. *Ab initio* CCSD(T) interaction energies (open circles) and potential values obtained using the sum of three-body (3B) CCSD(T) HeICl terms (crosses), at selected points along the minimum energy path of He₂ICl cluster. Solid line is for the potential values obtained by the sum of CCSD(T) +bf HeICl potential interaction given in Ref. 22.

justified due to the different basis sets used, whether or not including bond functions, in the *ab initio* calculations of the triatomic and tetra-atomic complexes, respectively. Note that MP4(SDTQ)/CCSD(T) and MP4(SDTQ)+bf/CCSD(T)+bf results are within the difference of 10% in the interaction energies, attributed from the test runs to the use of bond functions (see Table I).

IV. BOUND STATE CALCULATIONS

The Hamiltonian operator in the coordinate system shown in Fig. 1 has the form^{27,49}

$$\hat{H} = -\frac{\hbar^2}{2\mu_1} \left(\frac{\partial^2}{\partial R_1^2} + \frac{2}{R_1} \frac{\partial}{\partial R_1} \right) - \frac{\hbar^2}{2\mu_2} \left(\frac{\partial^2}{\partial R_2^2} + \frac{2}{R_2} \frac{\partial}{\partial R_2} \right) + \frac{\hat{j}^2}{2\mu_3 r_e^2} + \frac{\hat{l}_1^2}{2\mu_1 R_1^2} + \frac{\hat{l}_2^2}{2\mu_2 R_2^2} - \frac{\hbar^2}{m_I + m_{\text{Cl}}} \nabla_1 \nabla_2 + V(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2), \quad (3)$$

where $\mu_1^{-1} = \mu_2^{-1} = m_{\text{He}}^{-1} + (m_I + m_{\text{Cl}})^{-1}$ and $\mu_3^{-1} = m_I^{-1} + m_{\text{Cl}}^{-1}$ are the reduced masses, $m_{\text{He}} = 4.0026 \text{ amu}$, $m_I = 126.904 473 \text{ amu}$, and $m_{\text{Cl}} = 34.968 852 721 \text{ amu}$ are the atomic masses of ⁴He, ¹²⁷I, and ³⁵Cl isotopes, and $\hat{l}_1$, $\hat{l}_2$, and $\hat{j}$ are the angular momenta associated with the vectors $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{r}$, respectively, leading to a total angular momentum $\hat{J} = \hat{l}_1 + \hat{l}_2 + \hat{j} = \hat{L} + \hat{j}$. r is fixed at the equilibrium I–Cl bond length (r_e), and the potential for He₂ICl complex is given by the expansion in Eq. (2).

For a total angular momentum J , the Hamiltonian of Eq. (3) is represented in a set of basis functions consisting of linear combinations of products of bidimensional radial functions by angular functions, which incorporate the whole symmetry of the system.²⁷ For the R_1 and R_2 coordinates numerical $\{\xi_n(R_i)\}$ with $i=1, 2$ and $n=1, \dots, N_R$ functions are used. We evaluate them as follows: First, the two-dimensional Schrödinger equation is solved in $(R, \theta; r_e)$ variables for a triatomic He–ICl system at total angular momentum zero. The employed PES was the CCSD(T) *ab initio* surface given in Ref. 22, and a discrete variable representation (DVR) basis set⁵⁰ is used. It consists of functions given by

$$f_l(R) = [2/\sqrt{\mathcal{L}(N+1)}] \times \sum_{k=1}^N \sin[k\pi(R-R^{\min})/\mathcal{L}] \sin(k\pi l)/N+1,$$

where N is the total number of DVR points, $\mathcal{L}$ is $R_i^{\max} - R_i^{\min}$, and the DVR points in the R coordinate are $R^l = (l\mathcal{L}/N+1) + R^{\min}$ for $l=1, \dots, N$. Second, considering a set of the N_R lowest eigenstates, their corresponding radial distributions are orthonormalized through a Gram-Schmidt procedure, and constitute the radial basis set, $\{\xi_n(R_i)\}$, for the tetra-atomic calculations.

For the angular basis functions, we consider the following linear combinations, which are eigenfunctions of the parity of total nuclear coordinates inversion p ,

$$\mathcal{F}_{l_1 l_2 L \Omega}^{(JM p)} = \sqrt{\frac{1}{2(1+\delta_{\Omega|0})}} [\mathcal{W}_{l_1 l_2 L \Omega}^{(JM)} + p(-1)^{J+l_1+l_2+L} \mathcal{W}_{l_1 l_2 L -\Omega}^{(JM)}], \quad (4)$$

with

$$\mathcal{W}_{l_1 l_2 L \Omega}^{(JM)} = \sqrt{\frac{2J+1}{4\pi}} \mathcal{D}_{M\Omega}^J(\phi_r, \theta_r, 0) \mathcal{Y}_{l_1 l_2}^{\Omega}(\mathbf{R}_1, \mathbf{R}_2), \quad (5)$$

M is the projection of J on the space-fixed (SF) z axis, Ω its projection on the body-fixed (BF) z axis, which is chosen here along the $\mathbf{r}$ vector. The $\mathcal{D}_{M\Omega}^J$ are Wigner matrices⁵¹ and $\mathcal{Y}_{l_1 l_2}^{\Omega}$ are angular functions⁵² in the coupled BF representation.

In turn, taking into account the fact that in the case of He_2ICl the Hamiltonian is also invariant under $\mathbf{R}_1 \leftrightarrow \mathbf{R}_2$ inversion, then a well-defined parity, p_{12} , basis set is built up as follows:

$$\Phi_{l_1 l_2 L \Omega | nm}^{JM p p_{12}} = \sqrt{\frac{1}{2(1+\delta_{nm}\delta_{l_1 l_2})}} [\Phi_{l_1 l_2 L \Omega | nm}^{JM p} + p_{12}(-1)^{l_1+l_2+L} \Phi_{l_1 l_2 L \Omega | mn}^{JM p}], \quad (6)$$

where $\Phi_{l_1 l_2 L \Omega | nm}^{JM p} = \phi_{nm} \mathcal{F}_{l_1 l_2 L \Omega}^{(JM p)}$ and $\phi_{nm}(R_1, R_2) = \xi_n(R_1) \xi_m(R_2) / R_1 R_2$.

For the evaluation of the Hamiltonian matrix elements, the numerical set of the radial basis functions $\{\xi_n(R_i)\}$ mentioned above is represented as linear combinations of the f_l DVR functions, $\xi_n(R_i) = \sum_{l=1}^N \langle \xi_n | f_l \rangle f_l(R_i) = \sum \xi_n(R_i^l) f_l(R_i)$, $i=1,2$ and $n=1, \dots, N_R$. The matrix elements of the Hamiltonian are given in Ref. 27.

In our calculations at $J=0$, $N_R=5$ radial numerical functions, represented at 50 DVR points over the range of 2.5–8 Å, for each R_1 and R_2 coordinates are used. In turn, values of $L=j=0-12$ with $l_1^{\max}=l_2^{\max}=12$ for even ($p_{12}=(-1)^{l_1+l_2+L}=+1$) and $p=(-1)^{J+L+l_1+l_2}$ parity symmetries were enough to achieve convergence in the variational calculation.

The five lowest vibrational states of He_2ICl are found at energies of -33.51 , -31.60 , -30.46 , -29.19 , and -28.03 cm⁻¹ (see Table IV and Fig. 5). In Fig. 5, together with the minimum energy path, we plot the angular probability density of the angle γ for the $n=0$ (solid line), $n=1$ (dot-

TABLE IV. Binding energies (D_0) and vibrationally averaged structures ($R_{1,2}^0$) for the five lower states of the He_2ICl . Energies in cm⁻¹ and distances in Å.

Energy level	Configuration	D_0 (cm ⁻¹)	$R_{1,2}^0$ (Å)
$n=0$	Police nightstick (1)	33.51	4.38
$n=1$	Linear	31.60	4.86
$n=2$	Tetrahedral	30.46	4.38
$n=3$	Tetrahedral	29.19	4.37
$n=4$	Police nightstick (2)	28.03	4.87

ted line) $n=4$ (dashed-dotted line) [see Fig. 5(a)], $n=2$ (dashed line), and $n=3$ (long-dashed line) [see Fig. 5(b)] eigenfunctions, while in Fig. 7 the radial $R_{i=1,2}$ and angular $\theta_{i=1,2}$ distributions for these states are shown. As can be seen, $n=0$ state is localized in the police-nightstick (1) well and its distributions show peaks at $\theta_{1,2}=10.26^\circ$, 109.83° , $R_{1,2}=4.197$ Å, and $\gamma=109.97^\circ$. The $n=1$ state corresponds to linear configurations, with maxima at $\theta_{1,2}=9.60^\circ$ and $105.13^\circ/166.05^\circ$, and at $R_{1,2}=4.170$ and 5.328 Å, and only one peak at $\gamma=164.46^\circ$ [see Fig. 5(a)], while the $n=2$ and $n=3$ states exhibit tetrahedral structures with maximum values at $\theta_{1,2}=109.87^\circ$ and 109.56° , and $R_{1,2}=4.188$ and 4.193 Å, respectively. The $n=2$ presents a broad distribution in γ , except small peak at $\gamma \approx 60^\circ$, where the He–He attractive interaction is maximum, while the $n=3$ state has one more peak at $\gamma \approx 134^\circ$. We should also note that around $\gamma=0$ there is a forbidden area, where the two helium atoms are collided [see Fig. 5(b)]. At the end the $n=4$ state is mainly localized in the police-nightstick (2) well, with peaks at $\theta_{1,2}=109.58^\circ$ and 166.01° , $R_{1,2}=4.169$ and 5.312 Å, and $\gamma=67.17^\circ$. Here, we should stress that the analysis of the above vibrational wave functions shows that the tetrahedral configuration is favored over the bifork configuration despite the reverse ordering of the minima predicted by the analytical form. This is due to the greater volume of the well in the

FIG. 7. Radial (a) and angular $\int |\Psi|^2 \sin \theta_{1,2} dR$ (b) probability densities for the lowest five vdW levels of He_2ICl for $J=0$ calculated using the $V(r_e, R_1, R_2, \theta_1, \theta_2, \gamma)$ PES. Solid line is for $n=0$ [police nightstick (1)], dotted line for the $n=1$ (linear), dashed line for $n=2$ (tetrahedral), long-dashed line for $n=3$ (tetrahedral), and dotted-dashed line for $n=4$ [police nightstick (2)] states.

former case. The radial expectation values for each of the above structures, R_i^0 with $i=1,2$, obtained by averaging R_i over the corresponding distributions, are listed in Table IV. To our knowledge, for the first time such results on the vibrationally averaged structures of He₂ICl are presented. In contrast with previous studies^{23,26,27} on He₂Cl₂ cluster, in the present work localized structures are determined for the lowest two He₂ICl vdW states. Traditional models based on a He₂Cl₂ tetrahedron frozen structure have failed to reproduce the experimental absorption spectrum, suggesting a quite delocalized structure for its vibrationally ground state.²³ Here, based on *ab initio* calculations we propose different structural models, such as police nightstick or linear, in order to fit the rotationally resolved excitation spectrum of He₂Cl₂ or similar species.

In addition, recent experimental observations have shown the existence of two different isomers for He₂ICl complex. The police nightstick has been found to be the most strongly bound one, while a second one has been assigned to a distorted tetrahedral structure, with both He atoms in the near T-shaped well.⁵³ Unfortunately, more experimental data are not yet available. Our CCSD(T) results support the police-nightstick (1) structure as the most stable one in agreement with experimental observations. As it can be seen, the energy differences between the above mentioned isomers are small, with the larger one to account for 1.91 cm⁻¹ between the police nightstick (1) and linear isomer, while the smaller value (1.14 cm⁻¹) corresponds to the difference of the linear and tetrahedral ones (see EPAPS document⁴⁷). In turn, we should note that the lack of the r dependence in the potential form might influence their relative stability. It has been shown that for the triatomic vdW complexes of He atom with homopolar/heteropolar halogens, the energy difference between the linear and T-shaped wells increases when the r bond is lengthened,^{11,15,17,54} and such behavior should be reflected in the properties of the corresponding tetra-atomic complexes. However, in order to justify our assertions for such tetra-atomic species, further experimental data are needed for He₂ICl or similar clusters, and their comparison with our results would finally contribute to evaluate the present CCSD(T) potential.

V. SUMMARY AND CONCLUSIONS

A ground potential energy surface is presented for the He₂ICl complex, where the ICl molecule is frozen at its equilibrium bond length. CCSD(T) calculations are carried out at selected configurations and the existence of five different minima, namely, police nightstick (1), linear, bifork, tetrahedral, and police nightstick (2), is found for the He₂ICl. The ordering of the minima is confirmed by single point calculations in larger basis sets, including midbond functions and also using both MP4(SDTQ) and CCSD(T) levels of theory, with the police-nightstick (1) structure to be energetically more favored than the linear one.

An analytical expression based on a sum of three-body HeICl CCSD(T)+bf potentials and He-He interaction is used to represent the tetra-atomic CCSD(T) *ab initio* data. A very good agreement is found between the analytical poten-

tial values and the computed CCSD(T) interaction energies for the He₂ICl system. Further, by analyzing the behavior of individual components of the interaction energy, and by comparing with the He₂Br₂ case,²⁹ we were able to rationalize the trends within the He₂XY family and to relate them to the properties of He-XY trimers. Accurate PESs for small molecules interacting with He atoms continue to be in demand since these molecules are probes of superfluidity in He nanodroplets. Thus, we propose such analytical form to accurately describe the intermolecular interactions for He₂-dihalogen complexes. This finding may also contribute to fit the rotationally resolved excitation spectrum of He₂Cl₂ or similar species, where the traditional tetrahedral structural models, based on atom-atom pairwise potentials, have failed.

The above surface is used to perform variational bound state calculations, and vdW energy levels and eigenfunctions for $J=0$ are evaluated for He₂ICl. Radial and angular distributions are computed for the five lower vibrational vdW states. All of them are well localized in configuration space, with an exception of the broad angular γ distributions for the $n=2$ and $n=3$ states. The ground state corresponds to police-nightstick (1) isomer, while the linear isomer lies above in energy by only 1.91 cm⁻¹. The next two excited vdW levels are assigned to tetrahedral configurations and the fifth one to a police-nightstick (2) isomer. The binding energies and the average structures for these species are determined to be $D_0=33.51$ cm⁻¹ with $R_{1,2}^0=4.38$ Å, $D_0=31.60$ cm⁻¹ with $R_{1,2}^0=4.86$ Å, $D_0=30.46$ cm⁻¹ with $R=4.38$ Å, and $D_0=28.03$ cm⁻¹ with $R_{1,2}^0=4.87$ Å, respectively. For the first time results on energetics and vibrationally averaged structures of He₂ICl are presented. Comparison of these results with recent experimental predictions attributes to evaluate the quality of the present surface, at least in an area nearby the different isomeric configurations, and to justify our predictions on their relative stability.

Whether the properties of the weak bonding in such systems can be predicted by the sum of atom-diatom interactions deserve further investigation. Such model might be applicable to a broad class of Rg₂XY vdW clusters. In the present study, the importance of introducing a heteropolar dihalogen, as well as changing the reduced mass of the complex, is evaluated. However, it is particularly interesting to investigate the intermolecular interactions and structural properties of similar clusters consisting of heavier Rg atoms, e.g., argon, where the Ar-Ar interaction is stronger. Thus additional interactions terms should be included for representing the global PES. Further, calculation and analysis of bound states for $J>0$ are also useful, as it could be indicative for infrared experimental studies. Extension of the present work in these lines is in progress.

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