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Dissociation dynamics of $I_2 \cdots Ne_n$ van der Waals clusters ($n = 1-9$): A quasiclassical approach

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The dynamics of vibrational predissociation (VP) of van der Waals (vdW) $I_2 \cdots Ne_n$ clusters is studied by means of a quasiclassical trajectory approach. We assume a near-equilibrium geometry that accounts for the I_2 stretch and the stretching and bending modes of the rare gas atoms restricted to move along a plane perpendicular to the I_2 axis. A sharp increase of the halfwidth is observed for $n = 9$ together with certain stability of the $n = 8$ cluster size with respect to dissociation. It would indicate the existence of a first coordination shell for Ne around I_2 containing eight atoms. In addition, the dissociation results less and less efficient as n increases and statistical mechanisms become important for the cluster sizes studied.

I. INTRODUCTION

It has become a field of increasing interest to analyze the energetics and dynamics of van der Waals (vdW) clusters in recent years. In part, it has been due to the continuous progress of the experimental techniques capable of carrying out very accurate measurements. Also, it has greatly contributed to the development of several theoretical approaches such as Monte Carlo and molecular-dynamics simulations,^{1,2} the density functional formalism,^{3,4} self-consistent field,⁵ and wave packet^{6,7} treatments, among the most relevant ones. Both experimental and theoretical research efforts have been addressed to an extensive variety of vdW complexes. Most of these studies have been concerned with rare gas atom-diatomic clusters,⁸⁻¹² but systems with one vdW bond and several chemical bonds^{13,14} or only those composed by rare gas atoms^{1,4} have received great attention. Also, there has been the study of clusters with a diatomic molecule and two^{15(a),16-19} or more weak bonds ($I_2 \cdots He_n$ ($n = 1-3$),^{15(a)} $I_2 \cdots Ne_n$ ($n = 1-7$),^{15(b)} $Br_2 \cdots Ne_n$ ($n = 1-3$),²⁰ $ICl \cdots Ne_n$ ($n = 1-5$),²¹ $Cl_2 \cdots Ne_n$ ($n = 1-3$),²² $I_2 \cdots He_n$ ($n = 1-9$)²³), in order to elucidate the competition in the flowing of energy from the excited diatom to each vdW bond, and to explore the structure and possible coordination effects^{15(b),23} in these systems. Indeed, in some of the above references,^{15(b),20-22} it was experimentally found that a band shift rule^{15(b)} is fulfilled up to certain value of n (different for each cluster). In this light it was inferred that the corresponding n rare gas atoms occupy equivalent sites. A geometry consistent with these experimental results, proposed by some authors,^{15(b),22} is that in which the rare atoms are encircling the diatomic axis (a "belt" configuration). Kenny *et al.*^{15(b)} suggested the existence of a first coordination shell about the diatomic molecule, which would be composed of the rare gas atoms occupying equivalent positions (six atoms in the case of $I_2 \cdots Ne_n$).

In this work, we face the problem of studying the VP of $I_2 \cdots Ne_n$ clusters, with I_2 vibrationally excited in the $B^3\Pi_{0+}$ electronic state, from a theoretical point of view. A quantal treatment of such a system, with so many degrees of

freedom, becomes both very expensive and complicated. We thus chose a quasiclassical trajectory (QCT) approach as more appropriate to study these complexes. The QCT treatment has the advantage of providing a great deal of physical insight of the mechanisms that take place in the VP process, such as transference of energy among the different bonds involved, intramolecular vibrational relaxation (IVR), and so forth, which may be easily pursued along the trajectory evolution. Recently, we have applied a QCT model to $I_2 \cdots He_n$ clusters ($n = 1-9$),²³ assuming a near-equilibrium geometry that allows the vdW bonds to move along a plane perpendicular to the I_2 interdiatomic axis. Since the rotational constant associated to I_2 is very low ($B \sim 0.04$ cm⁻¹), this molecule was treated as a nonrotating body. Hence the following motions were taken into account: the stretch of I_2 , the stretching vibration with respect to the center of mass of I_2 , and the bending oscillation of each vdW bond along the plane perpendicular to I_2 , i.e., $2n + 1$ degrees of freedom. This near-equilibrium geometry is actually the same as that proposed by experimentalists (the rare gas atoms encircling the diatomic axis), but with one restriction, i.e., each vdW bending motion outside the perpendicular plane is "frozen" at its equilibrium configuration in our treatment. We observed for $I_2 He_n$ clusters a sharp increase of the halfwidth for VP from $n = 8$ to $n = 9$, and we inferred the existence of a first coordination shell for He atoms about I_2 containing eight atoms in equivalent sites. Also, we found the dissociation reaction of the first vdW bond to be less and less efficient as n increased, it being due to IVR mechanisms between the different bonds, despite the relatively small interaction He-He. In the light of these results, is interesting to study, from a theoretical point of view, the systems $I_2 \cdots Ne_n$ in order to search possible coordination effects already found experimentally,^{15(b)} but now analyzing other properties such as the halfwidth for VP, instead of the band shifts as in Ref. 15(b). These systems present another feature of interest due to the fact that the interactions $I_2 \cdots Ne$ and $Ne-Ne$ are stronger than the equivalent ones for the $I_2 \cdots He_n$ case. Hence, it would be expected that for $I_2 \cdots Ne_n$ clusters, statistical mechanisms will be enhanced and, therefore,

more evident than for the corresponding systems containing He atoms. In addition $I_2 \cdots Ne_n$ clusters with $n \geq 2$ allow to analyze dissociation pathways yielding Ne_2 products, which have been experimentally observed for $Cl_2 \cdots Ne_n$ ($n = 1-3$) clusters.²² The He_2 product is not possible for $I_2 \cdots He_n$ dissociation because of this diatomic molecule has no bound states.

In this paper we have assumed for $I_2 \cdots Ne_n$ clusters the same near-equilibrium geometry as for $I_2 \cdots He_n$, already mentioned above. We would like to stress the fact that previous results^{19,24} point out that this geometry is closer to the real situation for $I_2 \cdots Ne_n$ clusters than for $I_2 \cdots He_n$ ones.

The outline of the paper is the following. In Sec. II we describe the QCT treatment together with the potential energy surface used. In Sec. III details of the calculations and results obtained are given. Some concluding remarks are made in Sec. IV.

II. THEORY

A. The quasiclassical trajectory approach

The QCT formalism applied in this paper is the one already used in a previous work,²³ although some modifications have been introduced in order to analyze multiple continuum (MC) dissociation pathways^{22,25} producing simultaneous breaking up of $2Ne$, $3Ne$,... atoms, or those pathways yielding $I_2 \cdots Ne_{n-2} + Ne_2$ products. We will briefly describe the model, focusing our attention mainly on the modifications.

The classical Hamiltonian used in the present work for the $I_2 \cdots Ne_n$ clusters includes all the kinetic coupling terms as well as those via the potential between the vdW modes considered. This Hamiltonian has been showed elsewhere [see Eq. (17) in Ref. 23]. The corresponding Hamilton equations constitute a set of $4n + 2$ first order coupled differential equations to be solved once the initial conditions have been established. The initial conditions are calculated from previous quantal results²⁴ in the same way as in Ref. 23. Only a small difference remains. The range of 10° taken to randomly select the relative angles between adjacent rare atoms, from which the initial bending angles are calculated,²³ is centered in this work at 40° , instead of at 45° as for $I_2 \cdots He_n$. The reason is because in previous calculations¹⁹ it was found that the equilibrium value of this relative angle is $\sim 41^\circ$ for $I_2 \cdots Ne_2$ (while it is $\sim 43^\circ$ for $I_2 \cdots He_2$). For $I_2 \cdots Ne_9$, the Ne atoms are very close together and there begin to appear repulsions between them when they separate even a few degrees from their equilibrium angles. Then, in order to avoid the calculation of very repulsive initial conditions, we have restricted the range of selection from 10° to 4° , also centered at 40° .

A trajectory is considered as dissociated when one of the R_i distance (i.e., the distances from the rare gas atoms to the center of mass of I_2) becomes larger than a certain value R_{max} , for which the corresponding vdW interaction vanishes. The trajectories are also terminated when the time exceeds a given T_{max} .

We fitted the distribution of trajectories to an exponential law of decay²⁶

$$N_{ND} = N_T e^{-t/\tau}, \quad (1)$$

N_T being the total number of trajectories, N_{ND} the number of nondissociated ones at time t and τ the lifetime of the cluster. From the lifetime, the halfwidth is calculated as

$$\Gamma = \frac{\hbar}{2\tau}. \quad (2)$$

As regards the calculations related to MC dissociation, we consider a trajectory as a MC one, yielding $2Ne$, $3Ne$,... products, if at the end of the trajectory two or more rare gas atoms can be considered as dissociated. There is no problem to consider the first atom as dissociated, since it has reached the R_{max} value above mentioned (in fact, this is the condition that ends the trajectory evolution). In order to consider that the remaining atom (or atoms) also reached dissociation, two additional conditions must be fulfilled simultaneously at the end of the trajectory, that is to say, the corresponding $I_2 \cdots Ne$ bond distance and energy have to be greater than certain values such that it may be considered that the atom (or atoms) escapes. The above is concerned with dissociation of Ne atoms as free atoms, but these atoms also can dissociate as Ne_2 diatomic molecules. We will consider that the dissociation process produced a Ne_2 diatom if the above conditions are fulfilled, at least for two atoms, and in addition, these two atoms are bonded with a negative energy.

B. Potential energy surface (PES)

We represent the PES for these clusters as an addition of pairwise atom-atom interactions

$$V = V_{I_2} + \sum_i^n V_{I_2-Ne_i} + \sum_{i < j}^n V_{Ne_i-Ne_j}, \quad (3)$$

with

$$V_{I_2-Ne_i} = 2V_{I-Ne_i}, \quad (4)$$

where each atom-atom interaction is described by a Morse function. It should be pointed out that despite the $V_{I_2-Ne_i}$ interaction is expressed as a sum of I-Ne pairwise interactions, Eq. (4), the Morse parameters of the I-Ne interaction have been fitted in order to reproduce experimental data corresponding to the triatomic $I_2 \cdots Ne$ molecule.²⁷ So, some three-body effect would be accounted for by this potential.

The Morse potential parameters used for the I-I,²⁸ I-Ne,²⁷ and Ne-Ne²⁹ interactions are listed in Table I.

III. RESULTS AND DISCUSSION

A. Details of the calculations

Hamilton equations were numerically solved by means of an Adams-Moulton integrator initiated by a fourth order Runge-Kutta-Gill integrator with a time step $\Delta t = 0.4 \times 10^{-15}$ s. The greatest time used in the integration was taken depending on the number of Ne atoms n , i.e., $T_{max} = 50 \times 10^{-12}$ s/n. (equivalent to 125 000/ n cycles of integration). For higher values of n than six, this maximum total time was found to be short for a large number of trajectories, and it was enlarged by 10×10^{-12} s. The value chosen for R_{max} was 9.0 Å. With these parameters we obtain stable

TABLE I. Morse interaction parameters.

	$D(\text{cm}^{-1})$	$\alpha(\text{\AA}^{-1})$	$R_{eq}(\text{\AA})$
I-I	5168.72	1.834	3.0247
I-Ne	44.0	1.9	4.36
Ne-Ne	29.36	2.088	3.091

values of the final magnitudes, being the conservation in total energy of the order of 10^{-11} cm^{-1} .

For MC dissociation, the two additional conditions to be fulfilled by the atoms escaping (except by the first) are a bond distance larger than 8 Å and a bond energy above the dissociation limit.

All the calculations in this paper were carried out for the diatomic vibrational level $v = 28$.

B. Coordination effect

Taking as a starting point a set of previously calculated initial conditions, the Hamiltonian equations were integrated for each cluster $I_2 \cdots Ne_n$ being $n = 1, 9$. The distributions of trajectories obtained were then fitted to the exponential law of decay Eq. (1). In Table II we present the total number of trajectories calculated, N_T^{calc} for each value of n . In the third column of this table we report the number of trajectories actually used to carry out each linear fit N_T . This is the number of trajectories that remains after applying a usual box quantization procedure, i.e., after removing those trajectories for which the I_2 molecule has not lost at least one vibrational quantum. The correlation coefficients of the linear fits are shown in the fourth column. From these coefficients it can be assessed a good agreement with the assumed exponential law of decay, as well as the statistics of the distribution of trajectories is good enough. As was mentioned, several of the calculated initial conditions for $I_2 \cdots Ne_n$ are repulsive. The trajectories corresponding to these repulsive initial conditions dissociate so quickly that the iodine mole-

FIG. 1. Halfwidth for VP vs the cluster size up to $n = 8$. Error bars (standard deviations, are included). The value corresponding to $n = 9$, $\Gamma(9) = 4.334 \pm 1.107 \text{ cm}^{-1}$, is not displayed because it gets out of the figure scale.

cule has not enough time to transfer one vibrational quantum to some vdW bond. It, however, does not affect our final results for $n = 9$ because these trajectories have been removed by applying the box quantization procedure. Thus from 3891 trajectories calculated for $n = 9$, only 1585 remain valid after box quantization. In order to improve the linear fit, some trajectories corresponding to the extreme points (very short time and very long time trajectories) were still removed leaving the final number of 1316 showed in Table II.

Lifetimes τ were obtained for each cluster from the above linear fits. The fifth column of Table II show them together with their corresponding standard deviations $(SD)_\tau$. The lifetimes gradually decrease with increasing n up to $n = 7$. For $n = 8$ an increase of τ is observed, becoming more stable than other sizes, $5 \leq n \leq 7$, from the dissociation point of view. This behavior is not shown by $I_2\text{-He}_n$ clusters—see Table IV of Ref. 23—where the lifetime monotonically decreases with the size up to $n = 8$. Finally, a sharp decrease is found for $n = 9$.

From lifetimes we calculated the associated halfwidths by means of Eq. (2), and they are displayed in Fig. 1 vs n .

TABLE II. Different quantities depending on the cluster size n : (a) Total number of trajectories calculated. (b) Number of trajectories involved in the linear fits after quantization. (c) Correlation coefficients corresponding to each linear fit. (d) Lifetimes (picoseconds) including their standard deviations. (e) Estimated IVR times (picoseconds). (f) Percent of τ_{IVR} in the lifetime τ . (g) Percent of trajectories leading to multiple continuum ($2Ne$, $3Ne$, etc.) fragmentation. (h) Percent of trajectories giving rise to diatomic Ne_2 products.

n	N_T^{calc} (a)	N_T (b)	Correlation coefficient (c)	τ (d)	τ_{IVR} (e)	% IVR (f)	% MC (g)	% Ne_2 (h)
1	1000	991	-0.998	9.02 ± 0.06				
2	1000	999	-0.998	7.36 ± 0.07	2.85	39	3.7	1.1
3	1000	997	-0.994	6.70 ± 0.08	3.71	55	5.6	0.4
4	1000	998	-0.993	6.12 ± 0.08	3.87	63	6.5	0.9
5	1000	1000	-0.988	5.99 ± 0.09	4.19	70	7.4	0.5
6	1000	997	-0.987	5.72 ± 0.09	4.22	74	8.0	0.4
7	1000	999	-0.986	5.51 ± 0.09	4.22	77	9.5	0.9
8	1000	996	-0.993	6.08 ± 0.09	4.95	81	6.8	1.3
9	3891	1316	-0.946	0.61 ± 0.16				

The value of the halfwidth for $n = 9$, $\Gamma(9) = 4.335 \pm 1.107 \text{ cm}^{-1}$ has not been included in Fig. 1 since it gets out of the scale represented. The behavior of $\Gamma(n)$ is, correspondingly to that of τ , smoothly increasing up to $n = 7$ and decreasing from $n = 7$ to $n = 8$. The most relevant change in $\Gamma(n)$ is observed, however, for $n = 9$, where a sharp increase occurs. The error in $\Gamma(9)$ (its standard deviation, $\pm 1.107 \text{ cm}^{-1}$) is large, but not enough as to mask the abrupt jump from $\Gamma(8)$, 0.435 cm^{-1} , to $\Gamma(9)$, 4.335 cm^{-1} . This fact leads us to think of the existence of a first coordination shell for the Ne atoms about I_2 , as in the case of $I_2 \cdots He_n$ clusters.²³ That coordination shell would contain eight rare gas atoms, arranged in equivalent sites in a plane perpendicular to I_2 . The disagreement with the estimates of Kenny *et al.*^{15(b)}—they found six Ne atoms in the first coordination shell—may be due to the Ne–Ne potential used throughout our calculations, which does not take into account the presence of I_2 . In this sense, we may think of an effective Ne–Ne interaction within the cluster showing an equilibrium distance larger than the considered here, as has been pointed out for the $Ne_2 Cl_2$ cluster.²² This would lead, at least from a “static” point of view, to a lower number of atoms in the first shell.

C. Intramolecular vibrational relaxation mechanisms

Another interesting result is related to the intramolecular energy transfer that takes place in $I_2 \cdots Ne_n$ clusters. We can see from Fig. 1 that the halfwidths are very low (up to $n = 8$), which means that the reaction of dissociation is very inefficient, being less and less efficient as n increases. This behavior was already found for $I_2 \cdots He_n$ clusters.²³

It may be explained in terms of IVR mechanisms between the different bonds of the clusters. Such intramolecular energy transfer mechanisms increase the lifetime of each cluster more and more as the cluster size grows, because the number of modes available to store the initial energy from I_2 also increases. So with increasing n , statistical distribution of the initial energy is observed in our calculations, being necessary the loss of more than one quantum (several ones for the clusters with high n) from the I_2 stretch.

As in the precedent work on clusters containing He atoms,²³ the incidence of the IVR mechanism on the dissociation process is estimated assuming additive IVR and “expected” dissociation times yielding the calculated lifetimes. Indeed, in absence of direct interactions among the vdW modes, the expected lifetime of a cluster containing n Ne atoms would be nearly $1/n$ times the corresponding one to $n = 1$, the possible small difference arising from very inefficient indirect couplings through the I_2 molecule. However, the calculated size dependent lifetimes $\tau(n)$ become much larger than the expected values for noninteracting vdW modes, $\tau(1)/n$. Therefore, the corresponding delay may be identified as the time expended by the system interchanging energy among vdW modes, i.e., the IVR time,

$$\tau(n) = \tau(1)/n + \tau_{IVR}^{(n)}.$$

These estimates are reported in sixth column of Table II for $n = 2$ –9, as well as the percent of τ_{IVR} in the total lifetime τ (seventh column).

This percent is, except for $n = 2$, greater than 50 and increases monotonically with the size of the cluster, showing a growth in the degree of statistical mechanisms during the predissociation process. However, and in spite of “*a priori*” expectations, this behavior is nearly the same already found in $I_2 He_n$ clusters²³—see Table V in Ref. 23, the IVR percents being slightly higher in the present case. Only for $n = 9$ the deviation from the general behavior is now more evident and with the simple estimate currently used, $\tau_{IVR}(9)$ would become negative. It indicates that dissociation occurs for this cluster even more efficiently than a linear behavior would predict.

The effect of vibrational relaxation and energy redistribution can also be observed along the time evolution of the trajectories. As an example, in Fig. 2 we show the evolution of the stretching energies for a trajectory followed by a $I_2 \cdots Ne_3$ cluster. Those energies are labeled E_{BC} , E_{BC-X_1} , E_{BC-X_2} , and E_{BC-X_3} . In Fig. 2(a), E_{BC} vs time, the dashed line indicates the energy of the initial vibrational level, $v = 28$, of I_2 . During the first 0.3 ps, the I_2 stretch loses $\sim 40 \text{ cm}^{-1}$, as well as the $BC-X_1$ stretches, which lose $\sim 20 \text{ cm}^{-1}$ each, giving all this energy to the $BC-X_2$ stretch that becomes excited by $\sim 80 \text{ cm}^{-1}$, see Figs. 2(b), 2(d), and 2(c). Clearer evidence of energy redistribution occurs about 13 ps when the I_2 stretch transfers $\sim 100 \text{ cm}^{-1}$ to the $BC-X_1$ stretch, whose energy becomes positive by $\sim 70 \text{ cm}^{-1}$. However, this mode quickly relaxes giving energy to the $BC-X_2$ bond, which finally breaks up. This constitutes an example of single dissociation process, the time evolution of the trajectory having been enlarged to determine that the $BC-X_2$ bond was the dissociated one.

D. Multiple continuum and Ne_2 dissociation products

Observation of multiple dissociation pathways, i.e., finding not only a single Ne atom, but also $2Ne$, $3Ne$,... and Ne_2 products, is another aspect denoting statistical nature of dissociation, as was already suggested by Hair *et al.*²² These pathways have been observed to a relevant extent along our trajectory calculations. In Table II, again, we show the percent of trajectories for which we observed dissociation to two or more Ne atoms (eighth column), and to Ne_2 products, from $n = 2$ to $n = 8$ (ninth column). Most of the MC dissociations yielded $2Ne$ products (double continuum dissociation), but a number of trajectories dissociating to $3Ne$ products was also observed. As regards the trajectories dissociating to Ne_2 products, most of them followed the exiting channel $I_2 \cdots Ne_{n-2} + Ne_2$, being also detected in some cases $I_2 \cdots Ne_{n-3} + Ne + Ne_2$ products. We can see from Table II that the number of MC trajectories increases with n up to $n = 7$, slightly decreasing for $n = 8$. This decrease may be related to the stability of this cluster size with respect to dissociation, as discussed above. Also, the fact that the largest number of Ne_2 products was found for $n = 8$, is very likely to be a consequence of the Ne–Ne attractive interactions that occur in the $I_2 \cdots Ne_8$ cluster.

A pictorial view of a typical double continuum dissociation can be obtained from Fig. 3. In that figure we show the

FIG. 2. Time evolution of stretching energies corresponding to the different bonds for a $I_2 \cdots Ne_3$ cluster. (a) I_2 bond; (b), (c), and (d), I_2 -Ne bonds. Dashed line in (a) denotes the initial energy stored in the iodine molecule.

FIG. 3. The same as Fig. 2 for a $I_2 \cdots Ne_2$ cluster. This figure shows a double continuum dissociation ($I_2 \cdots Ne_2 \rightarrow I_2 + 2Ne$) about 8 ps.

energy evolution with time of the I_2 and the two vdW stretches for a trajectory corresponding to a $I_2 \cdots Ne_2$ cluster. It is clearly observed that by about 8 ps the I_2 stretch de-excites causing the simultaneous breaking up of the vdW bonds. The cluster completely dissociates, in this case, to $I_2 + Ne + Ne$ products.

The fact of observing Ne_2 dissociation products is a consequence of the strong coupling between the vdW bonds. Figure 4 displays an example of trajectory along which the reaction of dissociation $I_2 \cdots Ne_2 \rightarrow I_2 + Ne_2$ takes place. In Figs. 4(a)-4(c) the energy evolution with time of the three stretches involved is represented, and Fig. 4(d) shows the

FIG. 4. The same as Fig. 2 for a $I_2 \cdots Ne_2$ cluster. In Fig. (d) the evolutions of the Ne-Ne distance is pursued. This evolution from 6 ps shows that a dissociation to $I_2 + Ne_2$ products takes place.

variation of the Ne-Ne interatomic distance ($R_{x_1-x_2}$) along the trajectory. About 5 ps the first vdW bond (the BC- X_2 one) dissociates and by about 6 ps later the other vdW bond does. From that moment the two Ne atoms escape together forming a diatomic unit, as reflected by the oscillations of $R_{x_1-x_2}$ that correspond to a diatomic bond. The time evolution of this trajectory was enlarged for the sake of showing several $R_{x_1-x_2}$ oscillations.

IV. CONCLUDING REMARKS

The dynamics of $I_2 \cdots Ne_n$ clusters, $n = 1-9$, have been studied in this work by means of a QCT approach. Lifetimes and halfwidths for VP were calculated for all of the clusters. The behavior of the halfwidth vs n , gradually increasing up to $n = 7$, then decreasing for $n = 8$ and finally showing a sharp increase for $n = 9$, brings us to think of the existence of a first coordination shell for Ne atoms about I_2 . This coordination shell would contain eight equivalent Ne atoms, being $n = 8$ a possible magic cluster size.

From our calculations, this conclusion results more patent for Ne than He^{23} containing clusters. However, there is a disagreement with the experimental data, for which a six-atom coordination shell fits better with a band shift rule.^{15(b)} This discrepancy could be partially avoided by taking into account that the equilibrium Ne-Ne distance becomes larger within the complexes with I_2 than in the isolated diatomic molecule, an experimental fact already found in the $Ne_2 Cl_2$ complex.²²

On the other hand, the reaction of dissociation is observed to be less and less efficient as the cluster size grows, due to a intense energy transfer between the different modes. This behavior indicates that statistical nature dissociation mechanisms occur for this cluster size range. Observing alternative dissociation pathways, such as dissociation to $2Ne$, $3Ne, \dots$, and Ne_2 products, in addition to single Ne dissociation, is another criterion showing the statistical nature of the reaction in these clusters.

As regards to the efficiency of these different reaction channels, the single dissociation accounts for more than 90%, with the exception of $I_2 \cdots Ne_7$, followed by multiple continuum dissociations and, finally, by those fragmentations involving Ne_2 products with an incidence $\leq 1\%$.

The model proposed in the present work assumes a near equilibrium geometry, that leaves some vdW bending modes (the ones outward the plane perpendicular to the I_2 axis) fixed at their equilibrium positions. Including such modes in the dynamical study of these clusters may also have the effect of changing the number of atoms in the coordination shell. Further work on this line would be both valuable and interesting, as well as extending the calculations to clusters with other different diatomic molecules than I_2 .

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