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An approximate quantal treatment to obtain the energy levels of tetra-atomic $X \cdots I_2 \cdots Y$ van der Waals clusters ($X, Y = \text{He, Ne}$)

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The structure of tetra-atomic $X \cdots I_2 \cdots Y$ van der Waals (vdW) clusters, where $X, Y = \text{He, Ne}$, is studied using an approximate quantal treatment. In this model the above complexes are treated as like diatomic molecules with the rare-gas atoms playing the role of electrons in conventional diatomics. Then a H_2 -like molecular-orbital formalism is applied, choosing the discrete states of triatomic systems $I_2 \cdots X(Y)$ as molecular orbitals. Calculations at fixed configurations as well as including vdW bending motions restricted to the plane perpendicular to the I_2 axis have been carried out for the sake of comparison with previous results. Finally, the restrictions are relaxed and the vdW bending motions are incorporated in a full way within the framework of a configuration interaction. The structure of these clusters is also studied through the probability density function.

I. INTRODUCTION

A great deal of research effort has been addressed to the problem of understanding the structure and dynamics of atomic and molecular clusters in the past 15 years.¹⁻⁴ Several studies have been performed on van der Waals (vdW) clusters composed of only rare-gas atoms bound by vdW forces, using Monte Carlo and molecular-dynamics simulation techniques, and other approaches.⁵⁻⁷ Clusters of rare-gas atoms weakly bound to molecules with one or more chemical bonds have also been treated from both experimental⁸⁻¹⁰ and theoretical¹¹⁻¹³ points of view. In particular, considerable attention has been focused on triatomic vdW systems as $BC \cdots X$,¹⁴⁻¹⁶ where X is a rare-gas atom and BC is a conventional diatomic molecule. The reliability of various theoretical models has been tested by applying them to this type of complexes, since they provide excellent systems to study the processes and mechanisms of predissociation through which the internal energy of BC is transferred to the vdW bond leading to its fragmentation.¹⁷⁻¹⁹ Thus, we may consider the predissociation process as a simple unimolecular reaction along the vdW bond, where the vdW molecule would play the role of an activated complex that breaks up to form products with several different possible internal states.

Recently, some complexes with two weak bonds as $X \cdots BC \cdots Y$, where Y is a rare-gas atom too, and $BC = I_2$, have been studied regarding stretching motions^{20,21} as well as some restricted bending ones²² in order to consider some questions, such as the importance of correlation between different dissociative steps and the competition in the flow of energy from BC to each vdW bond.

In this work we propose a model that yields energy levels and associated wave functions of vdW clusters with two or more vdW bonds $BC \cdots X_n$. The aim is, at the end, to use these results to generate initial conditions and study the dynamics of vibrational predissociation of these complexes in a quasiclassical trajectory formalism.²³

In our model we take the BC internuclear axis as a quantization axis, and so the vdW molecules are treated as diatomic ones in which BC would be the nuclear structure, and

the rare-gas atoms would play the role of the electrons in ordinary diatomic molecules. Then, a molecular-orbital (MO) method, where the states of the triatomic systems are chosen to be the MO's, is used in order to get energy levels. We may write the Hamiltonian for a $BC \cdots X_n$ system, where $BC = I_2$, in the following way²⁵:

$$H = H_{BC} \sum_i^n h_i + \sum_{i < j}^n V_{X_i - X_j} + \Theta \left(\frac{1}{m_B + m_C} \right),$$

where

$$H_{BC} = T_{BC} + \frac{1}{2\mu_{BC}} r^2 j^2 + V_{BC}$$

and

$$h_i = T_i + \frac{1}{2\mu_{BC,X}} R_i^2 + V_{BC-X_i},$$

μ_{BC} and $\mu_{BC,X}$ being the reduced masses of BC and $BC \cdots X$, respectively, r and R the stretching coordinates of the diatom, and the vdW bond; the T terms are the radial kinetic energy operators, j^2 and I^2 are the angular momentum operators associated to the BC diatom rotation and the vdW bending motion, respectively, and V_{BC} , V_{BC-X_i} , and $V_{X_i-X_j}$ are the potential-energy interactions between the two atoms of BC , the X_i atom and the diatom, and between the X_i and X_j atoms, respectively. As can be observed, the Hamiltonian H is quite similar to that of a diatomic molecule in a self-consistent-field (SCF) formalism. So, we can recognize the first term as the diatomic Hamiltonian that accounts for the nuclear motion of BC ; the second one, h_i , takes into account the motion of the $BC \cdots X_i$ vdW bond (equivalent to the one-electron Hamiltonian in the Hartree-Fock equations), and finally, the third term consists of the interactions among rare-gas atoms (which in this case play a role similar to the interelectronic repulsions).

The $\Theta(1/m_B + m_C)$ term symbolizes the series of kinetic coupling terms between the vdW modes, which are multiplied by $1/m_B + m_C$. Since we are mainly interested in the lower energy levels and due to the big mass of the iodine diatom, we neglect those terms and take $\Theta(1/$

$m_B + m_C) \approx 0$. So, we hope that this approximation works reasonably well for the low excitation region of the spectrum.

For the study of the nuclear motion of BC, we only consider here the diatom stretching vibration, neglecting the rotational term $B_{BC} j^2$ in H_{BC} , and then averaging the remaining total Hamiltonian H between the eigenfunctions of H_{BC} to obtain a vibrational averaged Hamiltonian H_v . This approach is justified for low and intermediate vibrational excitations, $v < 40$, and our calculations have been performed for $v = 28$. For the BC rotation, we consider that due to the smallness of the rotational constant of I_2 , and the weakness of the coupling between I_2 rotation and bending motions of the two vdW bonds, it may be treated, as a first approximation, in the same way as the electronic motion–nuclear-rotation interaction in top symmetric molecules.²⁴ In fact, calculations carried out in a previous work,²⁵ taking into account the interaction between the I_2 rotation and the bending motion of the vdW bond in $I_2 \cdots X$ systems, yielded energy values quite similar to those obtained in calculations which neglect this interaction. These results support our decision of considering that these motions are weakly coupled. Therefore, the rotational energy of I_2 could be added to the energy of the eigenstates of H_v in a perturbative way later.

In this paper, the structure and stability of the $\text{He} \cdots I_2 \cdots \text{He}$, $\text{He} \cdots I_2 \cdots \text{Ne}$, and $\text{Ne} \cdots I_2 \cdots \text{Ne}$ systems have been studied considering every motion—both stretching and bending—of the vdW bonds without restrictions. Bond coordinates have been used to write the Hamiltonian. Besides, calculations were performed at certain fixed configurations—the T-shaped one among them—and including bending motions of the vdW bonds restricted to move in the perpendicular plane to the interdiatomic axis, in order to compare our results with previous treatments.

This paper is organized as follows. In Sec. II the theoretical approach and its approximations are presented, and in Sec. III the computational details are outlined and the results obtained are shown and discussed.

II. THEORY

The method that yields the discrete state of $\text{BC} \cdots \text{X}(\text{Y})$ systems, which constitute the MO basis set used in our model, has been already described elsewhere.²⁵ There are only two differences: cofocal elliptic coordinates were employed in Ref. 25, while we have chosen bond coordinates in the present work; on the other hand, the treatment given to the stretching vibrations of the I_2 diatom is different too. We will briefly review this method in Sec. II A. In Sec. II B, the treatment restricted to the plane perpendicular to the I_2 axis is presented, and, finally, the formalism to study these systems no longer restricted is developed in Sec. II C.

A. Finding the molecular orbitals

After separation of the whole system center of mass, we can write the Hamiltonian for the nuclear motion of a $\text{BC} \cdots \text{X}$ triatomic system as

$$h_{\text{BC-X}} = -\frac{\hbar^2}{2\mu_{\text{BC}}} \frac{\partial^2}{\partial r^2} + \frac{1}{2\mu_{\text{BC}} r^2} j^2 + V_{\text{BC}}(r) - \frac{\hbar^2}{2\mu_{\text{BC,X}}} \frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_{\text{BC,X}} R^2} l^2 + V_{\text{BC-X}}(r, R, \theta), \quad (1)$$

where all the symbols have been already defined but θ , which is the bending angle between the BC axis and the vdW bond.

The j^2 term will not be considered here, as was mentioned before. So, we treat the BC stretching vibration by means of a diabatic distorted-wave approach finding the vibrational states of

$$H_{\text{BC}}(r) = -\frac{\hbar^2}{2\mu_{\text{BC}}} \frac{\partial^2}{\partial r^2} + V_{\text{BC}}(r)$$

for a given v of BC. Then the remaining $h_{\text{BC-X}}$ is averaged between the v -dependent eigenfunctions of H_{BC} , $\chi_v(r)$. A Taylor-series expansion up to third order is used for $V_{\text{BC-X}}$.

Since the vdW stretching motions in the case $\text{X} = \text{He}, \text{Ne}$ are much faster than the bending ones,^{11(b)} the latter may be considered as adiabatic, taking θ as a parameter. So then, once the vibration of BC is separated, the adiabatic approximation is applied to the total wave function of the vdW bond motion and it takes the expression

$$\Psi_{n,l,\lambda}^{(v)}(R, \theta, \phi) = \psi_n^{(v)}(R; \theta) F_{l,\lambda}^{(v,n)}(\theta, \phi), \quad (2)$$

ϕ being the azimuthal angle around the BC internuclear axis. The meaning of the indexes n , l , and λ will be given later. The wave function ψ , depending parametrically on θ , describes the vdW stretching motion and is a solution of

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC,X}}} \frac{\partial^2}{\partial R^2} + V_{\text{BC-X}}^{(v)}(R; \theta) \right] \psi_n^{(v)}(R; \theta) = E_n^{(v)}(\theta) \psi_n^{(v)}(R; \theta), \quad (3)$$

where the superscript (v) in $V_{\text{BC-X}}^{(v)}$ stands for $\langle \chi_v(r) | V_{\text{BC-X}}(r, R, \theta) | \chi_v(r) \rangle$ and n is the corresponding stretching vibrational quantum number.

In order to calculate the angular part F we now solve the angular equation

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC,X}}} \langle 1/R^2 \rangle_n l^2 + E_n^{(v)}(\theta) \right] F_{l,\lambda}^{(v,n)}(\theta, \phi) = \epsilon_{l,\lambda}^{(v,n)} F_{l,\lambda}^{(v,n)}(\theta, \phi), \quad (4)$$

where λ is the quantum number associated to the projection on the BC axis of the vdW bending angular momentum, and l labels the energy position of the bending states. The $\langle 1/R^2 \rangle_n$ factor is the average of $1/R^2$ between the $\psi_n^{(v)}(R; \theta)$ functions. Note that both $\langle 1/R^2 \rangle_n$ and l^2 operators depend on θ and therefore do not commute. A proper symmetrization of their product is needed, and it is reached by the replacement

$$\langle 1/R^2 \rangle_n l^2 \rightarrow \frac{1}{2} (\langle 1/R^2 \rangle_n l^2 + l^2 \langle 1/R^2 \rangle_n).$$

The solutions of Eq. (4) are obtained by expanding $F_{l,\lambda}^{(v,n)}(\theta, \phi)$ in a spherical harmonic basis set

$$F_{l,\lambda}^{(v,n)}(\theta, \phi) = \sum_k a_{k,l,\lambda}^{(v,n)} Y_k^\lambda(\theta, \phi),$$

and diagonalizing. All of the spherical harmonics that take

part in the expansion of each angular state $F_{l,\lambda}^{(v,n)}$ are chosen to have the same projections λ as $F_{l,\lambda}^{(v,n)}$.

B. Treatment of X ... BC ... Y clusters restricted to move in the plane perpendicular to the BC axis

In this case we have two bending angles θ_1 and θ_2 , each related with a vdW bond, which are fixed at their equilibrium configuration, the T-shaped one, with $\theta_1 = \theta_2 = \pi/2$ (from now on, and for the sake of shortness, we will write $\bar{\theta}_1$ and $\bar{\theta}_2$ instead of $\theta_1 = \pi/2$ and $\theta_2 = \pi/2$). It implies that the two vdW bonds are allowed to have stretching and bending motions but only inside a plane perpendicular to the BC internuclear axis.

So, the Schrödinger equation for the nuclear motion can be written in the following way:

$$\left\{ H_{BC}(r) + h_X(r, R_1; \bar{\theta}_1) + h_Y(r, R_2; \bar{\theta}_2) - \frac{\hbar^2}{2\mu_{BC,X} R_1^2 \sin^2 \bar{\theta}_1} \frac{\partial^2}{\partial \phi_1^2} - \frac{\hbar^2}{2\mu_{BC,Y} R_2^2 \sin^2 \bar{\theta}_2} \frac{\partial^2}{\partial \phi_2^2} + V_{X-Y}[R_1, R_2; \bar{\theta}_1, \bar{\theta}_2, \cos(\phi_1 - \phi_2)] \right\} \times \Phi(r, R_1, R_2; \bar{\theta}_1, \bar{\theta}_2, \phi_1, \phi_2) = \epsilon \Phi(r, R_1, R_2; \bar{\theta}_1, \bar{\theta}_2, \phi_1, \phi_2), \quad (5)$$

where the angles ϕ_1 and ϕ_2 are the rotation angles of X and Y, respectively, around the BC internuclear axis, taken as the quantization axis. The term V_{X-Y} is the potential interaction between the two rare-gas atoms. The terms h_X and h_Y symbolize the Hamiltonians for the BC ... X and BC ... Y vdW bonds, respectively, and they are equal to that appearing in Eq. (3) [except that $V_{BC-X(Y)}(r, R; \theta)$ still has not been v averaged] with $\theta = \pi/2$ in the present case.

Now, assuming that the BC vibration has been already separated, we use the adiabatic approximation to write the total wave function as

$$\Phi_{v,\kappa,j}(r, R_1, R_2; \bar{\theta}_1, \bar{\theta}_2, \phi_1, \phi_2) = \chi_v(r) \rho_\kappa^{(v)}(R_1, R_2; \bar{\theta}_1, \bar{\theta}_2; \cos \phi) \mathcal{F}_j^{(v,\kappa)}(\phi_1, \phi_2), \quad (6)$$

where $\rho_\kappa^{(v)}$ is the tetra-atomic stretching function, depending parametrically on $\cos \phi$ (we have defined here $\phi = \phi_1 - \phi_2$), and \mathcal{F} is the bending one. The indexes κ and j are the quantum numbers corresponding to the tetra-atomic stretching and bending motions, respectively. Thus, Eq. (5) is adiabatically solved by finding, in the first place, the solutions of the equation

$$\left[h_X^{(v)}(R_1; \bar{\theta}_1) + h_Y^{(v)}(R_2; \bar{\theta}_2) + V_{X-Y}(R_1, R_2; \bar{\theta}_1, \bar{\theta}_2; \cos \phi) \right] \rho_\kappa^{(v)}(R_1, R_2; \bar{\theta}_1, \bar{\theta}_2; \cos \phi) = E_\kappa^{(v)}(\cos \phi) \rho_\kappa^{(v)}(R_1, R_2; \bar{\theta}_1, \bar{\theta}_2; \cos \phi), \quad (7)$$

for several different fixed configurations in the angle ϕ (taken as a parameter) within the range $0 \leq \phi \leq \pi$ (it should be noted that V_{X-Y} is an even function with respect to $\phi = \pi$ because of its $\cos \phi$ dependence). So, the stretching wave function $\rho_\kappa^{(v)}$ is written as

$$\rho_\kappa^{(v)}(R_1, R_2; \bar{\theta}_1, \bar{\theta}_2; \cos \phi) = \sum_{n,m} a_{n,m}^{(v,\kappa)}(\cos \phi) \phi_n^{(v)}(R_1; \bar{\theta}_1) \varphi_m^{(v)}(R_2; \bar{\theta}_2), \quad (8)$$

where $\phi_n^{(v)}$ and $\varphi_m^{(v)}$ are the eigenfunctions of the Hamiltonians h_X and h_Y .

Now we solve the equation

$$\left[-\frac{\hbar^2}{2\mu_{BC,X} \sin^2 \bar{\theta}_1} \left\langle \frac{1}{R_1^2} \right\rangle_{\phi_0} \frac{\partial^2}{\partial \phi_1^2} - \frac{\hbar^2}{2\mu_{BC,Y} \sin^2 \bar{\theta}_2} \left\langle \frac{1}{R_2^2} \right\rangle_{\phi_0} \times \frac{\partial^2}{\partial \phi_2^2} + E_\kappa^{(v)}(\cos \phi) \right] \mathcal{F}_j^{(v,\kappa)}(\phi_1, \phi_2) = \epsilon_j^{(v,\kappa)} \mathcal{F}_j^{(v,\kappa)}(\phi_1, \phi_2), \quad (9)$$

the terms with angular brackets labeled with ϕ_0 and φ_0 represent averages between these functions. Actually, in a more rigorous way, these averages should be calculated using the functions of (8). But in order to avoid consuming too much computer time, we only consider the first term in the expansion (8), which is the dominant one for all the configurations in ϕ [so we take $a_{0,0}^{(v,\kappa)}(\cos \phi) \simeq 1$ for all the ϕ], and then we write

$$\rho_\kappa^{(v)}(R_1, R_2; \bar{\theta}_1, \bar{\theta}_2) \simeq \phi_0^{(v)}(R_1; \bar{\theta}_1) \varphi_0^{(v)}(R_2; \bar{\theta}_2).$$

That approximation should hardly affect the first tetra-atomic states (the ones in which we are interested).

The function $\mathcal{F}_j^{(v,\kappa)}$ is expanded in a basis set built up with the product functions $e^{i\lambda_1 \phi_1} e^{i\lambda_2 \phi_2}$ as

$$\mathcal{F}_j^{(v,\kappa)}(\phi_1, \phi_2) = \sum_{\lambda_1, \lambda_2} b_{j,\lambda_1,\lambda_2}^{(v,\kappa)} e^{i\lambda_1 \phi_1} e^{i\lambda_2 \phi_2},$$

where λ_1 and λ_2 are the quantum numbers corresponding to the projections of the two X and Y bending angular momenta on the BC axis. By diagonalizing Eq. (9), we finally find the tetra-atomic energies $\epsilon_j^{(v,\kappa)}$ and wave functions $\Phi_{v,\kappa,j}$.

The potential $E_\kappa^{(v)}(\cos \phi)$ is previously expanded in a Fourier series

$$E(\cos \phi) \simeq a_0 + \sum_{n=1}^M a_n \cos n\phi, \quad (10)$$

M being the number of anisotropic terms included in the series. As $E(\cos \phi)$ is an even function of ϕ , only $\cos n\phi$ terms appear in the expansion. In this way, all the necessary quadratures involving $E_\kappa^{(v)}(\cos \phi)$ become analytical.

C. Treatment of X ... I₂ ... Y systems with nonrestricted vdW bending motions

When all the bending motions of both vdW bonds are allowed to take place, the θ_1 and θ_2 coordinates are no longer fixed at any equilibrium position and they can vary with freedom. Then, the Hamiltonian for the X ... I₂ ... Y systems is the one that was mentioned in the Introduction, taking $n = 2$, i.e.,

$$H = H_{BC}(r) + h_X(r, R_1, \theta_1, \phi_1) + h_Y(r, R_2, \theta_2, \phi_2) + V_{X-Y}(R_1, R_2, \theta_1, \theta_2, \phi_1, \phi_2). \quad (11)$$

In order to obtain the eigenstates of H , first of all, the vibration of BC is separated as it was done in previous sections. Then, the Ψ functions are used as MO's to build up configurations as the products of these MO's,

$$\Xi_{n,l,\lambda}^{(v)}(R_1, R_2, \theta_1, \theta_2, \phi_1, \phi_2) = \Psi_{n,l,\lambda}^{(v)}(R_1, \theta_1, \phi_1) \Psi_{m,j,v}^{(v)}(R_2, \theta_2, \phi_2), \quad (12)$$

in an equivalent way as the MO treatment of the electronic motion in the H_2 case. Now, the discrete states of H are obtained by using a configuration-interaction (CI) method. So, the eigenfunctions of H are expanded in the basis made up with those configurations

$$\Phi_{v,k}(r, R_1, R_2, \theta_1, \theta_2, \phi_1, \phi_2) = \chi_v(r) \sum_{\substack{n,l,\lambda \\ m,j,v}} a_{n,l,\lambda}^{(k)} \Xi_{n,l,\lambda}^{(v)}(R_1, R_2, \theta_1, \theta_2, \phi_1, \phi_2), \quad (13)$$

and the coefficients $a_{n,l,\lambda}^{(k)}$ are found variationally by diagonalizing the representation of H in that basis set.

The main difficulty one finds when evaluating the matrix elements of H is related to the calculation of the quadratures concerning the $V_{X-Y}(R_{X-Y})$ potential term, which involves six variables. Therefore, now we will focus our attention on the explanations of the method we have employed to calculate these quadratures. By using the cosine law, we can express the distance between X and Y, R_{X-Y} , as

$$R_{X-Y} = (R_1^2 + R_2^2 - 2R_1R_2 \cos \gamma)^{1/2},$$

with

$$\cos \gamma = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)$$

(in the same way as in Sec. II B, we use $\phi = \phi_1 - \phi_2$ for shortness). The integrals that have to be computed have the

form

$$\begin{aligned} \langle V_{X-Y} \rangle &= \langle \Xi_{n,l,\lambda}^{(v)} | V_{X-Y} | \Xi_{n',l',\lambda'}^{(v)} \rangle \\ &= \langle \psi_n^{(v)}(R_1; \theta_1) F_{l,\lambda}^{(v,n)}(\theta_1, \phi_1) \psi_m^{(v)}(R_2; \theta_2) \\ &\quad \times F_{j,v}^{(v,m)}(\theta_2, \phi_2) | V_{X-Y} | \psi_{n'}^{(v)}(R_1; \theta_1) F_{l',\lambda'}^{(v,n')} \\ &\quad \times (\theta_1, \phi_1) \psi_{m'}^{(v)}(R_2; \theta_2) F_{j',v'}^{(v,m')}(\theta_2, \phi_2) \rangle, \quad (14) \end{aligned}$$

and we begin by numerically carrying out the calculation of the integral of $V_{X-Y}(R_{X-Y})$ over the R_1 and R_2 variables, which involves the four ψ functions. As a result, we obtain a new function depending only on the four angular variables

$$\langle V_{X-Y} \rangle_{n,m} = f(\cos \gamma) = f(\theta_1, \theta_2, \phi_1, \phi_2).$$

It would be very convenient to find an expansion for f such that the integration over the angular coordinates becomes analytical. It is possible if we expand $f(\cos \gamma)$ in Legendre polynomials

$$f(\cos \gamma) = \sum_{\alpha=v}^N C_\alpha P_\alpha(\cos \gamma), \quad (15)$$

since by using the addition theorem of spherical harmonics²⁶

$$P_\alpha(\cos \gamma) = \frac{4\pi}{2\alpha + 1} \sum_{\mu=-\alpha}^{+\alpha} Y_\alpha^{\mu*}(\theta_1, \phi_1) Y_\alpha^\mu(\theta_2, \phi_2),$$

the integrals related to the angular variables become products of two integrals, each one involving three spherical harmonics

$$\begin{aligned} &\langle F_{l,\lambda}^{(v,n)}(\theta_1, \phi_1) F_{j,v}^{(v,m)}(\theta_2, \phi_2) | f(\cos \gamma) | F_{l',\lambda'}^{(v,n')}(\theta_1, \phi_1) F_{j',v'}^{(v,m')}(\theta_2, \phi_2) \rangle \\ &= \sum_\alpha C_\alpha \frac{4\pi}{2\alpha + 1} \sum_{\mu=-\alpha}^{+\alpha} (-1)^\mu \sum_{i,\kappa} a_{i,l,\lambda}^{(v,n)} a_{\kappa,j,v}^{(v,m)} \langle Y_i^\lambda(\theta_1, \phi_1) | Y_\alpha^{-\mu}(\theta_1, \phi_1) | Y_\kappa^\nu(\theta_1, \phi_1) \rangle \\ &\quad \times \sum_{i',\kappa'} b_{i',l',\lambda'}^{(v,n')} b_{\kappa',j',v'}^{(v,m')} \langle Y_{i'}^{\lambda'}(\theta_2, \phi_2) | Y_\alpha^\mu(\theta_2, \phi_2) | Y_{\kappa'}^{\nu'}(\theta_2, \phi_2) \rangle, \quad (16) \end{aligned}$$

and these three spherical harmonic integrals are analytical,²⁶ since

$$\begin{aligned} &\int_0^{2\pi} \int_0^\pi Y_i^{m_i}(\theta, \phi) Y_\lambda^\mu(\theta, \phi) Y_{i'}^{m_i'}(\theta, \phi) \sin \theta d\theta d\phi \\ &= \left[\frac{(2l'+1)(2\lambda+1)}{4\pi(2l+1)} \right]^{1/2} \\ &\quad \times C(l'\lambda 00; l'\lambda l 0) C(l'\lambda m_i' \mu; l'\lambda l m_i), \end{aligned}$$

where the C factors are the Clebsch-Gordan coefficients. We have used in (16) the property

$$Y_\lambda^{\mu*}(\theta, \phi) = (-1)^\mu Y_\lambda^{-\mu}(\theta, \phi).$$

At the beginning, we tried to expand $f(\cos \gamma)$ directly in Legendre polynomials, obtaining the C_α coefficients by conventional methods. However, the expansion of $f(\cos \gamma)$ in $P_\alpha(\cos \gamma)$ functions is very slowly convergent in the case of our systems, and too much computation time is needed to reach convergence. To overcome that difficulty we first expand $f(\cos \gamma)$ in a Fourier series, which has proved to be much more quickly convergent than the Legendre poly-

nomial expansion in our case,

$$f(\cos \gamma) = a_0 + \sum_{n=1}^M a_n \cos n\gamma. \quad (17)$$

Thus, by using the following relationship between the Legendre polynomials and $\cos n\gamma$ ²⁷:

$$\begin{aligned} \cos n\gamma &= \frac{2^{n-1}n!}{(2n-1)!!} P_n(\cos \gamma) \\ &\quad - \sum_{\kappa=1}^{E(n/2)} (2n-4\kappa+1) \\ &\quad \times \frac{2^{n-2\kappa-1}(n-\kappa-1)!(2\kappa-3)!!}{(2n-2\kappa+1)!!\kappa!} \\ &\quad \times P_{n-2\kappa}(\cos \gamma), \quad (18) \end{aligned}$$

where $E(n/2)$ means the integral part of $n/2$, we can transform the Fourier expansion (17) in a Legendre polynomial one as in (15), obtaining an analytical form for the integral of $f(\cos \gamma)$ [see Eq. (16)].

III. CALCULATIONS AND RESULTS

A. Potential-energy surface

The potential-energy surface (PES) is represented as an addition of pairwise atom-atom interactions in the following way:

$$V = V_{BC} + V_{BC-X} + V_{BC-Y} + V_{X-Y},$$

with

$$V_{BC-X} = V_{B-X} + V_{C-X},$$

and a similar expression for V_{BC-Y} , where each atom-atom interaction is a Morse function that worked fairly well in previous studies,^{11(c)}

$$V_i(R_i) = D_i [e^{-2\alpha_i(R_i - \bar{R}_i)} - 2e^{-\alpha_i(R_i - \bar{R}_i)}],$$

$i = BC, B-X, C-X, B-Y, C-Y, X-Y$, and

$$R_{BC} = r,$$

$$R_{B-X} = (R_1^2 + r^2/4 + 2R_1r \cos \theta)^{1/2},$$

$$R_{C-X} = (R_1^2 + r^2/4 - 2R_1r \cos \theta)^{1/2},$$

with R_{B-Y} and R_{C-Y} taking similar expressions, and

$$R_{X-Y} = (R_1^2 + R_2^2 - 2R_1R_2 \cos \gamma)^{1/2}.$$

The proper Morse parameters used in this work are listed in Table I.^{20,28-30} In the case of the V_{He-Ne} potential two different sets of parameters have been used. Set (a) is the same as Ref. 22 and it was used in order to obtain results comparable with those of this reference. In the restrictionless treatment we use the parameters of set (b) because we consider they are better.

B. Computational details

Discrete stretching energy levels have been calculated for both $I_2 \cdots He$ and $I_2 \cdots Ne$ triatomic systems by numerically solving Eq. (3) by means of a Truhlar procedure further improved by a Numerov method. A grid of $N = 3000$ points was used with $R_{in} = 4.0$ a.u. and $R_{fin} = 30.0$ a.u. for $I_2 \cdots He$, and $R_{in} = 6.5$ a.u. and $R_{fin} = 23.5$ a.u. for $I_2 \cdots Ne$. The solutions of the angular equation (4) were obtained by expanding $F(\theta, \phi)$ in a 32 spherical harmonic basis set. All the nonanalytical integrals were calculated using a Simpson $h/3$ quadrature, where h is the integration step.

In the treatment of Sec. II B, tetra-atomic stretching

energy levels are calculated at 160 different fixed configurations in the angle $\phi = \phi_1 - \phi_2$ within the range $0 \leq \phi \leq \pi$ for all the systems under study. We take this range since V_{X-Y} is symmetrical with respect to $\phi = \pi$. These energy levels yield the potential-energy curves $E(\cos \phi)$, depending parametrically on ϕ , that will be used to solve Eq. (9) later. The averages appearing in this equation have been evaluated with a Simpson $h/3$ quadrature. The potential curves $E(\cos \phi)$ are expanded in a Fourier series [Eq. (10)], and expansions up to 135 terms lead to a good convergence for the three systems.

The integration of V_{X-Y} over the R_1 and R_2 coordinates, necessary for the solution of Eq. (7) as well as for the evaluation of the integral (14), is carried out by using a Gauss-Legendre quadrature. This method of integration provides a very good accuracy with few quadrature points, which implies low computer-time consumption. It makes the Gauss-Legendre integration procedure specially suitable for our purposes, since in this work a large number of double integrals (over R_1 and R_2) have to be calculated. As it is known, this method presents a small inflexibility in the sense that the points of the different quadratures are fixed, that is, they are the zeros of Legendre polynomials. Then, the functions to be integrated have to be calculated in these specific points. However, it does not mean any difficulty to our model to calculate the integrals using these fixed points. Ninety-six quadrature points for each coordinate are used (e.g., the integration over R_1 and R_2) is evaluated using 9216 points), which provides a good ratio between accuracy and time consumption.

Fourier expansions consisting of 470 terms have been needed to fit the angular part of V_{X-Y} , $f(\cos \gamma)$ and, therefore, the same number of terms have been used in the Legendre polynomial expansion (15).

All the necessary diagonalizations were performed by using a standard Jacobi method.

C. RESULTS AND DISCUSSION

1. Triatomic systems

In this paragraph we are going to discuss some points related to the states of the $BC \cdots X$ systems, which are used as molecular orbitals in the treatment of $X \cdots BC \cdots Y$ systems. We have calculated those states for the systems $I_2 \cdots He$ and $I_2 \cdots Ne$, for fixed values of the quantum number λ , by taking the same exponential factor, $e^{i\lambda\phi}$, for all the spherical harmonics in the expansion of each state. In Table II, the energy levels for each fixed value of λ (up to $|\lambda| = 4$) are collected for the stretching ground state. The energy levels with the same absolute value of λ are degenerate. We have found seven, six, five, four, three, and two states for $\lambda = 0, \pm 1, \pm 2, \pm 3, \pm 4$, and ± 5 , respectively, and no bound states for $|\lambda| \geq 6$ for the $I_2 \cdots He$ case. For the sake of shortness only the first energy levels are presented for each λ value for this system as well as for the $I_2 \cdots Ne$ one. A larger number of bound states is obtained for each value of λ , including $\lambda = \pm 6$ and higher, in the $I_2 \cdots Ne$ case, as a consequence of its much deeper potential-energy well. All of these results are for the value $\nu = 28$ for the stretching vibrational quantum number of I_2 .

TABLE I. Morse potential parameters.

	D (cm ⁻¹)	α (Å ⁻¹)	R_{eq} (Å)
I-I	5168.72	1.834	3.0247
I-Ne	44.0	1.9	4.36
I-He	16.5	1.5	4.0
He-He	7.61	2.126	2.963
He-Ne	9.94 ^a	1.45 ^a	3.21 ^a
	14.73 ^b	2.10 ^b	3.029 ^b
Ne-Ne	36.41	2.105	3.087

^a Parameters from Ref. 22.

^b Parameters from Ref. 30(b).

TABLE II. Energies (in cm^{-1}) of the first $I_2 \dots X$ states ($X = \text{He}, \text{Ne}$) for some λ values (up to $|\lambda| = 4$) for the stretching ground state. These states are used as MO's in the CI treatment of Sec. II C. The symmetry of each MO is given in the second column of the table. These energies are for $\nu = 28$.

	λ	Symmetry	ϵ (cm^{-1})
$I_2 \dots \text{He}$	0	σ_g	-14.2056
		σ_u	-8.6484
		σ_g	-6.7397
	± 1	π_u	-13.9400
		π_g	-8.3877
		π_u	-6.2876
	± 2	δ_g	-13.1434
		δ_u	-7.6174
		δ_g	-5.3059
	± 3	φ_u	-11.8163
		φ_g	-6.3446
		φ_u	-3.8274
± 4	γ_g	-9.9594	
	γ_u	-4.5731	
	γ_g	-1.8615	
$I_2 \dots \text{Ne}$	0	σ_g	-67.2165
		σ_u	-57.7686
		σ_g	-50.2758
	± 1	π_u	-67.1645
		π_g	-57.7188
		π_u	-50.2315
	± 2	δ_g	-67.0074
		δ_u	-57.5661
		δ_g	-50.0853
	± 3	φ_u	-66.7455
		φ_g	-57.3109
		φ_u	-49.8380
	± 4	γ_g	-66.3787
		γ_u	-56.9531
		γ_g	-49.4901

Next, we will study some important symmetry properties of these molecular orbitals. Following the analogy already stated between our case and a MO treatment of the H_2 system, we may correspondingly classify our MO's by their value of λ . So, $\lambda = 0$ would imply a σ molecular orbital, $|\lambda| = 1$ a π MO, $|\lambda| = 2$ a δ MO, and so on. Also, since our diatomic molecule is homonuclear ($\text{BC} = \text{I}_2$), it possesses a center of symmetry or center of inversion. Thus there exists an additional symmetry operator which commutes with the Hamiltonian of the system: the inversion of the coordinates of all the particles. The triatomic eigenfunctions must either remain unchanged or only change sign by such an inversion. In the functions of our MO's, only the angular part, $F(\theta, \phi)$, is affected by this inversion operator, and, in the $F(\theta, \phi)$ expansion corresponding to each state, only spherical harmonics with either even or odd parity appear. Therefore, these MO's have a defined symmetry with respect to the inversion operator. The even or odd symmetry behavior will be indicated by a subscript g or u, respectively.

These symmetry properties (pointed out in Table II) are employed to select configurations with a determined symmetry to be used in the CI treatment of $X \dots \text{BC} \dots Y$ systems, as will be discussed later.

2. Tetra-atomic systems restricted to move in a perpendicular plane to the BC axis

As it was pointed out above, in this case we fix the θ_1 and θ_2 coordinates at $\theta_1 = \theta_2 = \pi/2$. Then, stretching energy levels have been calculated at the T-shaped conformation ($\theta_1 = \theta_2 = \pi/2$, $\phi = \pi$), in order to compare our results with those of previous works. These energies for the three systems are collected in Table III. Only the first levels are shown for the $\text{He} \dots \text{I}_2 \dots \text{Ne}$ and $\text{Ne} \dots \text{I}_2 \dots \text{Ne}$ systems. We also present in this table the results reported in Ref. 21 for the $\text{He} \dots \text{I}_2 \dots \text{Ne}$ complex. The model used in Ref. 21 is similar to ours except for two points. On the one hand, in Ref. 21 the I_2 diatom is considered as a rigid body fixed at its equilibrium bond distance. On the other hand, a kinetic coupling term is taken into account in the Hamiltonian. Comparison of both calculations shows the small influence of the I_2 vibration on the energy levels, as can be seen in Table III.

Now Eq. (7) is also solved for several other ϕ angles within the range $[0, \pi]$, using an adiabatic approach. The stretching energy levels thus obtained at these angles give rise to the potential-energy curves $E_{\kappa}^{(\nu)}(\cos \phi)$ that appear later in Eq. (9). We have only used the potential curve corresponding to the stretching ground energy level to solve this equation. It was found that the most stable conformation in the ϕ coordinate is about $\phi = \pi/4$ for the three complexes. The same result has been obtained in the calculations about

TABLE III. Stretching energy levels (in cm^{-1}) for the $X \dots \text{I}_2 \dots Y$ systems at the T-shaped conformation. These results are for the quantum number $\nu = 28$.

	E_{stret}^a	E_{stret}^b
$\text{He}-\text{I}_2-\text{He}$	-37.1419	
	-20.5349	
	-20.5346	
	-3.9280	
$\text{He}-\text{I}_2-\text{Ne}$	-91.1176	-91.384
	-74.4974	-74.725
	-65.2544	-65.254
	-48.6366	-48.616
	-44.9712	-44.810
	-30.3512	-30.194
	-28.3559	-28.138
$\text{Ne}-\text{I}_2-\text{Ne}$	-145.0550	
	-119.1953	
	-119.1949	
	-98.9154	
	-98.9153	
	-93.3352	
	-84.2991	
-84.2990		

^a This work.

^b Reference 21.

He \cdots I₂ \cdots Ne reported in Ref. 22. No calculations about He \cdots I₂ \cdots He and Ne \cdots I₂ \cdots Ne systems are available in the literature for comparison with ours.

The solution of Eq. (7) for several different ϕ angles yields a potential curve $E_{\kappa}^{(v)}(\cos \phi)$ that consists of a table of numerical values. In order to solve Eq. (9) it would be better to turn these numerical values into a functional form which would allow us to evaluate the integrals involving $E_{\kappa}^{(v)}(\cos \phi)$ analytically rather than numerically. Taking into account the basis functions used to represent Eq. (9) (e.g., exponential products $e^{i\lambda_1\phi} e^{i\lambda_2\phi_2}$), a suitable choice is a Fourier-series expansion of $E_{\kappa}^{(v)}(\cos \phi)$. Moreover, since $E_{\kappa}^{(v)}(\cos \phi)$ is even because of its $\cos \phi$ dependence, the coefficients of the sine terms vanish, and the Fourier expansion reduces to a series only composed of cosine terms. Due to the particular form of these curves, with a very much repulsive part at short distances and narrow and little deep wells, which implies strong variations along the ϕ range, the Fourier series needs many terms to reach convergence. Then, a convergence test was necessary for each particular curve in order to obtain the number of terms in the expansion that leads to a reasonable convergence without spending too much computer time. We found that the expansion belonging to He \cdots I₂ \cdots Ne converges in a faster way since its repulsive part increases more slowly and, as a result, the variation of the curve from the repulsive to the attractive

part is smoother than in the other two cases.

Once we have the above potential-energy curves expanded in a Fourier series we can find the tetra-atomic bending energy levels and wave functions by variationally solving Eq. (9). It is reached by employing a basis set built up with 109 product functions $e^{i\lambda_1\phi} e^{i\lambda_2\phi_2}$, half of which are degenerate in energy with respect to the other half, except for the case $\lambda_1 = \lambda_2 = 0$. These functions are chosen in such a way that $|\lambda_1| = |\lambda_2|$, the sign of λ_1 being the opposite to that of λ_2 . With this basis set we obtain the states of X \cdots I₂ \cdots Y with $\Lambda = 0$, where Λ is the quantum number corresponding to the projection on the BC axis of the total angular momentum. According to the H_2 treatment, we will symbolize the terms corresponding to these states as Σ . In Table IV we show the first energy levels calculated with our model together with the ground level of Ref. 22 for He \cdots I₂ \cdots Ne, reaching an excellent agreement in this case.

As a consequence of fixing the θ_1 and θ_2 coordinates, discussing $g-u$ symmetry is not appropriate in this case. However, another symmetry operator commuting with the Hamiltonian appears in X \cdots I₂ \cdots Y systems, the reflection of all the particles upon a plane through the I₂ internuclear axis. This symmetry operation means in practice to change the azimuthal angles ϕ_1 and ϕ_2 by their negative values $-\phi_1$ and $-\phi_2$. The X \cdots I₂ \cdots Y wave functions remain either unchanged or only change sign under such a reflection. We will symbolize the character of the X \cdots I₂ \cdots Y states with respect to that reflection by a superscript $+$ or $-$ for the wave function remaining unchanged or changing sign, respectively. This symmetry property is pointed out in Table IV for the different energy terms.

TABLE IV. Bending energy levels (in cm^{-1}) for the three systems under study. The symmetry of the energy terms is indicated in the table. All these results are for $v = 28$.

	Symmetry	E_{bend}^a	E_{bend}^b	
He-I ₂ -He	Σ^+	-37.1942		
	Σ^-	-36.9782		
	Σ^+	-36.1996		
	Σ^-	-34.9463		
	Σ^+	-33.2394		
	Σ^-	-31.1006		
	Σ^+	-28.5480		
	Σ^-	-25.5973		
	Σ^+	-22.2624		
	He-I ₂ -Ne	Σ^+	-93.9262	-93.9746
		Σ^-	-93.9261	
		Σ^+	-90.9502	
		Σ^-	-90.4200	
Σ^+		-89.5248		
Σ^-		-88.3110		
Σ^+		-86.8104		
Σ^-		-85.0432		
Σ^+		-83.0229		
Ne-I ₂ -Ne	Σ^-	-167.7497		
	Σ^+	-167.7496		
	Σ^-	-150.7335		
	Σ^+	-150.7335		
	Σ^+	-145.0754		
	Σ^-	-145.0161		
	Σ^+	-144.7919		
	Σ^-	-144.4418		
	Σ^+	-143.9727		

^a This work.

^b Reference 22.

3. Energy terms of X \cdots BC \cdots Y systems without restrictions on the vdW bending motions

Here we will discuss the results obtained by means of the model described in Sec. II C, which incorporates all the motions concerning the two vdW bonds. So, the discrete states of the total Hamiltonian (11) have been calculated within the framework of a CI treatment.

Since our attention is mainly addressed to the ground state of X \cdots I₂ \cdots Y systems, only states with Σ symmetry (Σ_g and Σ_u) have been studied. In order to save computation time, a previous selection of the configurations with the suitable symmetry to be used in the CI expansion (13) was necessary. In our calculations we have used configurations composed of MO's only belonging to the stretching ground state of the I₂ \cdots X and I₂ \cdots Y systems, that is to say, $\Xi_{o,l,\lambda}^{o,j,v}$ ones. The configurations involving MO's of excited stretching states are far away in energy from those in which only stretching ground-state MO's take part. Including such configurations with $n, m \neq 0$ would have, therefore, a very small influence on the ground and first excited states of X \cdots I₂ \cdots Y systems, but, however, it would mean a great deal of calculation time. The energy terms associated with the discrete states thus calculated are shown in Tables V and VI for Σ_g and Σ_u symmetries, respectively. The symmetry with respect to reflection upon the plane through the I₂ axis

TABLE V. Energy terms (in cm^{-1}) calculated using a configuration-interaction method. There are no restrictions on bending motions of the vdW bonds in this case. The symmetry of the terms is also indicated in the table. All of these terms have Σ_g symmetry. Seventeen, eighteen, and twelve configurations have been used in the CI treatment for the $\text{He} \cdots \text{I}_2 \cdots \text{He}$, $\text{He} \cdots \text{I}_2 \cdots \text{Ne}$, and $\text{Ne} \cdots \text{I}_2 \cdots \text{Ne}$ systems, respectively.

	Symmetry	Energy
He-I ₂ -He	Σ_g^+	-28.9661
	Σ_g^-	-28.4699
	Σ_g^+	-28.1089
	Σ_g^-	-26.8851
	Σ_g^+	-26.3147
	Σ_g^-	-24.0141
	Σ_g^+	-23.8384
	Σ_g^-	-21.7305
	Σ_g^+	-21.6202
		Σ_g^+
He-I ₂ -Ne	Σ_g^+	-83.4179
	Σ_g^-	-82.0832
	Σ_g^+	-81.4180
	Σ_g^-	-80.9204
	Σ_g^+	-80.2996
	Σ_g^-	-79.1592
	Σ_g^+	-78.6735
	Σ_g^+	-77.1022
	Σ_g^+	-77.1022
	Σ_g^-	-76.7006
Ne-I ₂ -Ne	Σ_g^-	-147.2926
	Σ_g^+	-146.2225
	Σ_g^+	-136.4249
	Σ_g^-	-136.1271
	Σ_g^+	-134.9178
	Σ_g^-	-134.7717
	Σ_g^+	-134.5126
	Σ_g^-	-134.0110
	Σ_g^-	-134.0110
	Σ_g^+	-133.5854

(the \pm symmetry) has also been added to the term symbols. The number of configurations used in the calculations of the Σ_g symmetry energy terms was 17, 18, and 12 [that is, 42, 31, and 29 product functions (12), since each configuration may be composed of one or more than one product function], for the $\text{He} \cdots \text{I}_2 \cdots \text{He}$, $\text{He} \cdots \text{I}_2 \cdots \text{Ne}$, and $\text{Ne} \cdots \text{I}_2 \cdots \text{Ne}$ systems, respectively. These numbers become 12, 18, and 6 configurations (involving 40, 31, and 30 product functions) in the Σ_u symmetry case. The different number of configurations used for the three systems is due to a computation time limitation. In fact, the bottleneck of the calculation is caused by the size of the expansion of $F(\theta, \phi)$, and we only need six spherical harmonics to reach a converged expansion in the He case, while 12 terms are necessary in the Ne case. Therefore, the number of configurations included in the calculation is to be reduced as the number of Ne atoms increases in the system studied. The above sizes of the CI expansion lead us to an energy convergence of 10^{-3} cm^{-1} for the $\text{He} \cdots \text{I}_2 \cdots \text{He}$ system and 10^{-2} cm^{-1} for the other systems. We can observe, by comparing the results of Tables V and VI, that the lowest-energy state with Σ_u symmetry is above several states with Σ_g symmetry. Therefore,

TABLE VI. Energy terms (in cm^{-1}), all of them with Σ_u symmetry, calculated by means of a CI method in the same way as those of Table V. The \pm symmetry is also pointed out. Twelve, eighteen, and six configurations were used in the CI expansion for the $\text{He} \cdots \text{I}_2 \cdots \text{He}$, $\text{He} \cdots \text{I}_2 \cdots \text{Ne}$, and $\text{Ne} \cdots \text{I}_2 \cdots \text{Ne}$ systems, respectively, in this case.

	Symmetry	Energy	
He-I ₂ -He	Σ_u^-	-23.7241	
	Σ_u^+	-23.5057	
	Σ_u^-	-22.9246	
	Σ_u^-	-22.8608	
	Σ_u^-	-22.6533	
	Σ_u^+	-22.5967	
	Σ_u^-	-21.4026	
	Σ_u^-	-21.3708	
	Σ_u^-	-21.0634	
		Σ_u^+	-21.0634
		Σ_u^-	-21.0634
		Σ_u^-	-21.0634
He-I ₂ -Ne	Σ_u^+	-78.3775	
	Σ_u^-	-77.7879	
	Σ_u^+	-75.9749	
	Σ_u^+	-75.5704	
	Σ_u^-	-75.4773	
	Σ_u^+	-74.6152	
	Σ_u^-	-73.9653	
	Σ_u^+	-73.6656	
	Σ_u^+	-73.3958	
		Σ_u^+	-73.3958
Ne-I ₂ -Ne	Σ_u^-	-137.9095	
	Σ_u^+	-137.8938	
	Σ_u^+	-137.2199	
	Σ_u^-	-136.8243	
	Σ_u^-	-127.3893	
	Σ_u^+	-127.0490	
	Σ_u^-	-126.7530	
	Σ_u^+	-126.7293	
	Σ_u^-	-126.7293	
	Σ_u^-	-125.4943	

not only the ground state of these complexes but also the first excited states have Σ_g symmetry.

If we make a comparison between the results of Tables IV and V, we realize that the energies corresponding to the states including all the vdW bending modes are higher than those obtained when the vdW bending motion is only allowed to take place in a plane. It is due, in part, to the use of triatomic states in the restricted treatment with lower energies than those of the nonrestricted one including the bending motion. In addition, the CI procedure yields a higher stabilization energy in the restricted treatment. Both effects, acting in the same direction, give rise to a ground energy in the "full" treatment placed over that of the approximate one by amount of $\sim 8 \text{ cm}^{-1}$ in $\text{He} \cdots \text{I}_2 \cdots \text{He}$, $\sim 11 \text{ cm}^{-1}$ in $\text{He} \cdots \text{I}_2 \cdots \text{Ne}$, and $\sim 21 \text{ cm}^{-1}$ in $\text{Ne} \cdots \text{I}_2 \cdots \text{Ne}$. Although the energy positions of the levels change by using either Hamiltonian (5) or (11), the same sequence is obtained for the \pm symmetry in the $\text{He} \cdots \text{I}_2 \cdots \text{He}$ case, and almost the same one is found for the other two systems. The change in the relative positions of the eighth and ninth levels in the $\text{He} \cdots \text{I}_2 \cdots \text{Ne}$ case, and the third and fourth levels in the $\text{Ne} \cdots \text{I}_2 \cdots \text{Ne}$ one, may be due to the increasing of the symmetry of the systems in the more complete calcula-

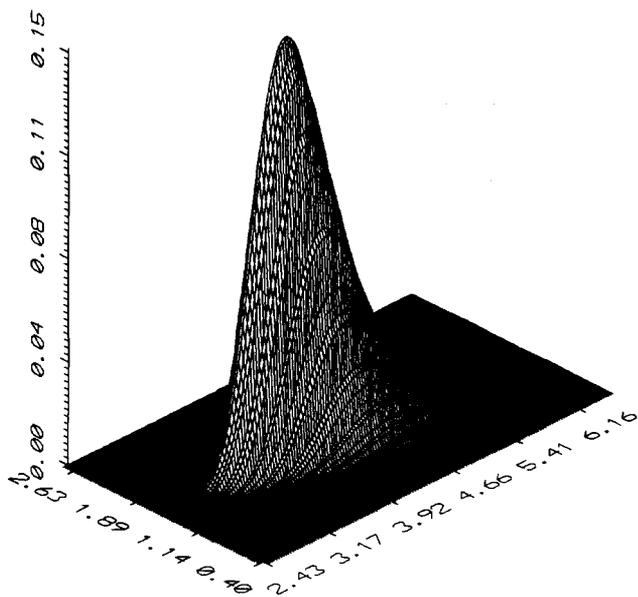


FIG. 1. Plot of the ρ_1 surface vs R (in Å) and θ (in radians) for the $I_2 \cdots He$ cluster. A grid of 9900 points (300 for R and 33 for θ) was used.

tion with respect to the restricted one. All of this makes us think that the energy levels belonging to both Tables IV and V can be correlated.

In the following, we will be concerned with the ground state of the vdW molecules studied in this paper, since it could be the starting point for a further quasiclassical trajectory treatment. In order to get some knowledge about the effect of using an CI formalism, we also performed calculations using only the ground-state configuration. Those calculations not using the CI method yield the results -28.7535 , -82.1067 , and $-136.6228 \text{ cm}^{-1}$ for the energies of the ground level of $He \cdots I_2 \cdots He$, $He \cdots I_2 \cdots Ne$, and $Ne \cdots I_2 \cdots Ne$, respectively. These energies are com-

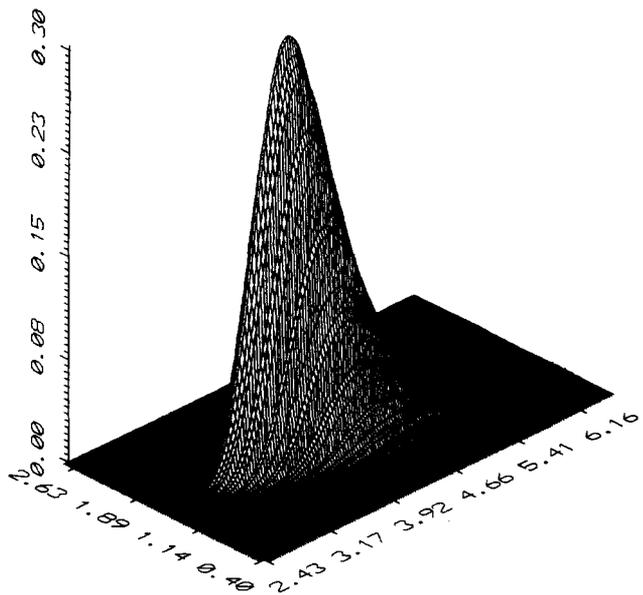


FIG. 2. Same as Fig. 1 for $I_2 \cdots He_2$.

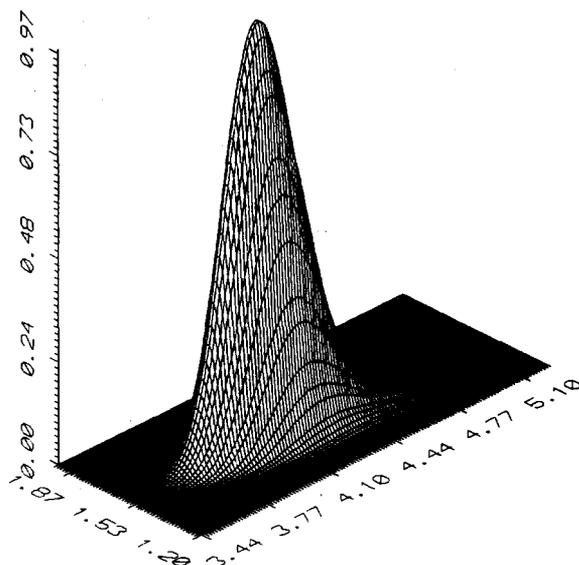


FIG. 3. Same as Fig. 1 for $I_2 \cdots Ne$.

posed of the sum of the triatomic energies corresponding to the systems $I_2 \cdots X$ and $I_2 \cdots Y$, plus the contribution of the potential term V_{X-Y} averaged between the triatomic wave functions. By subtracting the above ground level energies from those of Table V, where the CI method has been used, we can obtain the stabilization energy due to the use of the CI method. Those CI stabilization energies are -0.2126 , -1.3112 , and -10.6698 cm^{-1} for $He \cdots I_2 \cdots He$, $He \cdots I_2 \cdots Ne$, and $Ne \cdots I_2 \cdots Ne$, respectively. Comparison with the contributions of the potential term V_{X-Y} , which are -0.3423 , -0.6846 , and -2.1898 cm^{-1} , in the same order as above, shows that the CI method provides an energy contribution comparable to that of V_{X-Y} (for $He \cdots I_2 \cdots He$) or remarkably higher (for the other two cases).

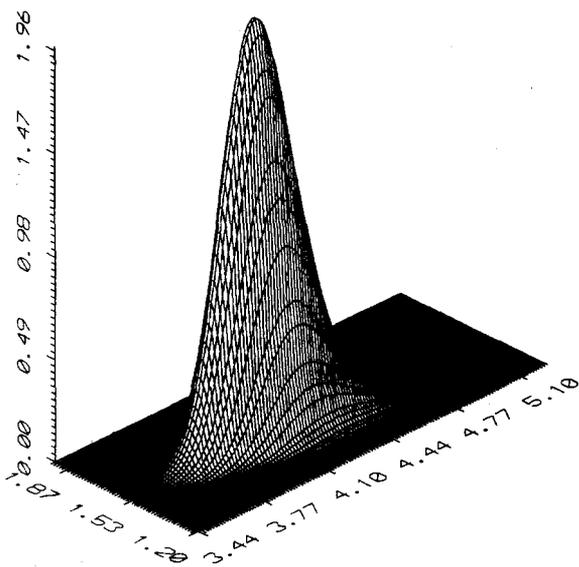


FIG. 4. Same as Fig. 1 for $I_2 \cdots Ne_2$.

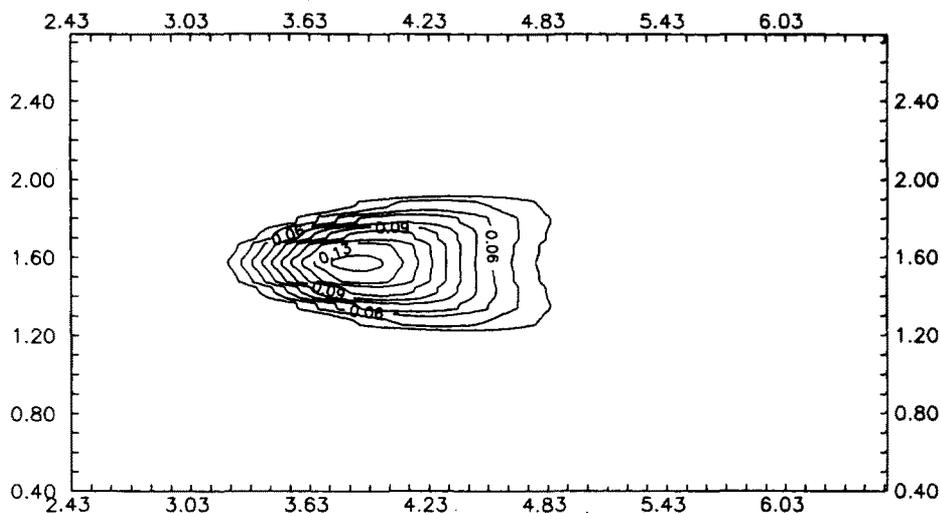


FIG. 5. Contour map of ρ_1 surface vs R (in Å) and θ (in radians) for the $I_2 \cdots He$ cluster. Intervals of 0.013 between the contours were used.

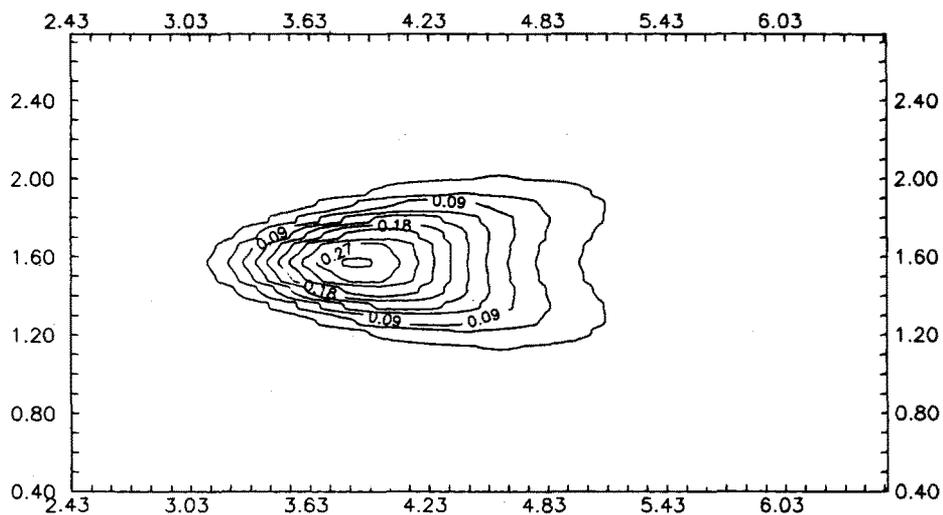


FIG. 6. Same as Fig. 5 for $I_2 \cdots He_2$. The intervals between the contours are 0.03 in this case.

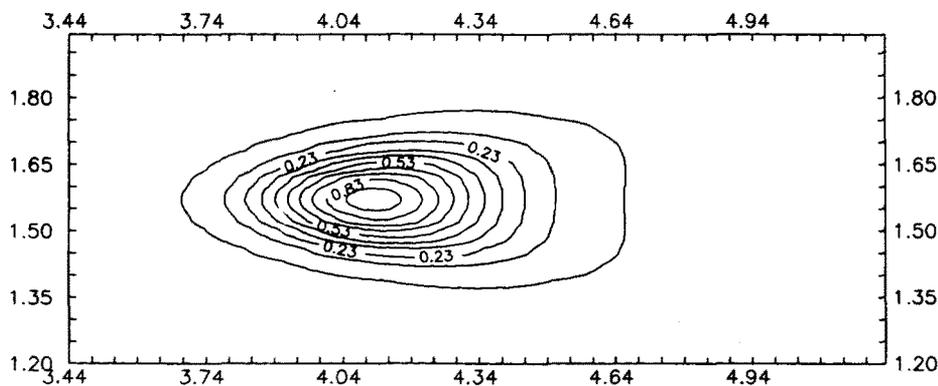


FIG. 7. Same as Fig. 5 for $I_2 \cdots Ne$ with intervals of 0.1 between the contours.

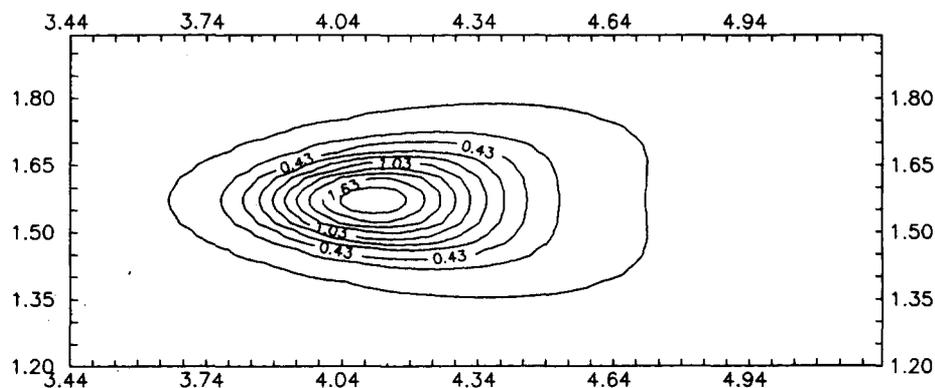


FIG. 8. Same as Fig. 5 for the $I_2 \cdots Ne_2$ cluster using intervals of 0.2.

In order to get some information about the structure of these clusters, we have studied the single-particle probability density function for the ground state of triatomic and tetra-atomic systems, excluding $He \cdots I_2 \cdots Ne$. This function, $\rho_1(R, \theta)$, is obtained in a similar way as the electron probability density,³¹ and provides the probability of finding a rare-gas atom in a volume element, dv (which depends on the coordinates of only one He atom) without taking into account the position of the other rare-gas atom. The function $\rho_1(R, \theta)$ has no dependence on the angular coordinate ϕ because it is symmetric with respect to this coordinate. Plots of the surfaces (Figs. 1–4) and the corresponding contour maps (Figs. 5–8) of ρ_1 vs R and θ are shown for the systems $I_2 \cdots He_n$ and $I_2 \cdots Ne_n$ ($n = 1, 2$). In all the cases we find the maximum of ρ_1 at $\theta = \pi/2$, ρ_1 decreasing quickly as we get far away from this angle in both directions (ρ_1 is symmetric with respect to $\theta = \pi/2$). It means that the vdW bending motion in the θ coordinate is localized in a small θ range centered at $\theta = \pi/2$. These results agree with those of previous works which have found the T-shaped conformation as the most stable one. An interesting point is the appearance in the plots of ρ_1 of two small “ribs” at large distances and only for a few θ angles, $\theta = \pi/2$ not being included among them. So, the motion of the rare-gas atoms presents a preference for these angles at large distances. We have found that this is due to the presence of two secondary wells (symmetric with re-

spect to $\theta = \pi/2$) in the potential-energy surface V_{1-x} at large distances for those angles.

Also, it is observed that the probability densities for the systems with Ne are more peaked and localized in R and θ ranges that are smaller than those corresponding to the clusters with He.

The study of the single-particle probability density does not show anything about the behavior of the tetra-atomic systems in the relative coordinate ϕ ($\phi = \phi_2 - \phi_1$). However, it can be studied through the two-particle probability density function, $\rho_2(R_1, R_2, \theta_1, \theta_2, \phi)$.³¹ So, we have plotted ρ_2 vs ϕ for the ground state of $I_2 \cdots He_2$ and $I_2 \cdots Ne_2$ clusters. Here, the rest of the coordinates ($R_1, R_2, \theta_1, \theta_2$) have been previously fixed to values randomly selected following the distribution $\rho_1(R, \theta)$. We performed several calculations for different fixed coordinate sets ($R_1, R_2, \theta_1, \theta_2$) and typical curves are shown in Fig. 9. We see in the figure that both curves reach a maximum at $\phi \approx 43^\circ$ for $I_2 \cdots He_2$ and $\approx 41^\circ$ for $I_2 \cdots Ne_2$ [the same angles were obtained for the other sets ($R_1, R_2, \theta_1, \theta_2$)], which correspond to the equilibrium ϕ angles for both systems. This results are in excellent agreement with those obtained with the restricted treatment in the above section, where we found that the most stable conformation in ϕ was around $\phi = 45^\circ$. As well as for $\rho_1(R, \theta)$, we find ρ_2 to be more peaked for $I_2 \cdots Ne_2$.

In conclusion, the formalism developed in the present

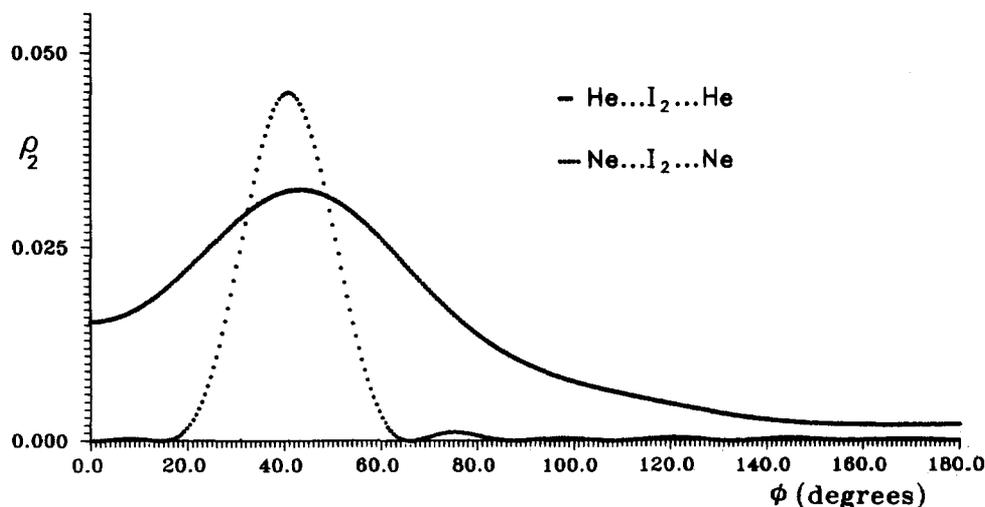


FIG. 9. Plot of ρ_2 vs ϕ for the $I_2 \cdots He_2$ and $I_2 \cdots Ne_2$ clusters. A grid of 300 points was used for ϕ . The maxima are placed at $\phi \approx 43^\circ$ for $I_2 \cdots He_2$ and $\approx 41^\circ$ for $I_2 \cdots Ne_2$. The values of the fixed coordinates are $R_1 = 3.76 \text{ \AA}$, $R_2 = 4.29 \text{ \AA}$, $\theta_1 = 94.2^\circ$, and $\theta_2 = 85.8^\circ$ for the $I_2 \cdots He_2$ curve; and $R_1 = 4.17 \text{ \AA}$, $R_2 = 4.27 \text{ \AA}$, $\theta_1 = 88.7^\circ$, and $\theta_2 = 103.3^\circ$ for the $I_2 \cdots Ne_2$ plot (see the text).

work constitutes a not very complicated procedure to study the structure of tetra-atomic vdW systems as $X \cdots I_2 \cdots Y$, incorporating all the degrees of freedom except the iodine rotation, which can be included as a perturbation later. Its relative simplicity, resting on the basic ideas of the MO model, encourages us to apply this type of treatment to more complicated systems $I_2 \cdots X_n$, with $n > 2$. The functions ρ_1 and ρ_2 appear to be promising tools that may be used as distributions in order to produce initial conditions for the R_i , θ_i , and ϕ_i coordinates, which are required in a quasiclassical trajectory treatment of the dynamics.

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