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Citation: *J. Chem. Phys.* **109**, 9288 (1998); doi: 10.1063/1.477590

View online: <http://dx.doi.org/10.1063/1.477590>

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# Potential energy surface and spectroscopy of clusters of rare-gas atoms with cyclopropane

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(Received 6 July 1998; accepted 25 August 1998)

Analytical empirical potential energy surfaces describing the van der Waals interaction between rare-gas atoms and cyclopropane are presented. The functional form is based on pairwise Lennard-Jones-type potentials which have been widely used to describe rare-gas-benzene complexes, also studied in this work in order to check our theoretical method and for comparison. The parameters have been chosen in order to accurately fit the high resolution microwave spectra recently reported by Xu and Jäger [*J. Chem. Phys.* **106**, 7968 (1997)]. The observed splitting in the microwave spectra of Ne-cyclopropane, associated with rotational tunneling, is well reproduced. Moreover, such tunneling is also important for complexes of Ar and Kr in excited van der Waals states. These phenomena involve a high delocalization of the wave functions and, therefore, intermolecular spectroscopy techniques would provide a good check of the potential energy surface over a broad region of the configuration space. © 1998 American Institute of Physics.

[S0021-9606(98)00345-6]

## I. INTRODUCTION

In the last few years, the study of clusters involving aromatic molecules, particularly rare gas-benzene complexes, have received a renovated interest due to the development of several kinds of experimental techniques, such as high resolution and high sensitivity microwave spectroscopy,<sup>1-3</sup> ionization-detected stimulated Raman spectroscopies,<sup>4-6</sup> rotationally resolved ultraviolet (UV) spectroscopy<sup>7,8</sup> or high resolution coherent ion dip spectroscopy.<sup>9,10</sup>

Benzene is a prototype of aromatic systems, and because of its simplicity and high symmetry, its complexes with rare-gas atoms have been well studied theoretically.<sup>11-19</sup> One of the most interesting aspects of such theoretical studies is the determination of potential energy surfaces (PES) describing the van der Waals interaction. Recently, realistic PES's have been empirically obtained from microwave data.<sup>3</sup> These PES's provide a good description around the equilibrium configuration as has been confirmed by recent intermolecular spectroscopy studies.<sup>6,10</sup> The empirical potential energy surfaces for rare-gas atoms-benzene dimers<sup>3</sup> include three-body terms depending on the distances between the rare-gas atom and two carbon atoms of benzene. This is consistent with some theoretical treatments of the dispersion energy on these systems,<sup>13</sup> in which it is found that contributions arising from  $\pi$  electrons can not be expressed as simple sums of pairwise terms, especially at planar configurations.

On the other hand, high resolution microwave spectra have been recently obtained for complexes of rare-gas atoms with cyclopropane.<sup>20</sup> It was found that for clusters of Ne there was a splitting that could be explained by rotational tunneling of the Ne atom around the cyclopropane ring. In such a situation the ground van der Waals state of Ne-cyclopropane explores configurations in which the Ne is in

the carbon ring plane. In cyclopropane, the angle between two carbon-carbon bonds is of  $60^\circ$ , due to symmetry requirements, far from the expected  $120^\circ$  of a typical  $sp^3$  hybridization of the electronic orbitals of the carbon atoms. This situation yields a small overlap between the  $\sigma$  orbitals describing two carbon-carbon bonds, and originates a small aromatic character of cyclopropane. Even when cyclopropane is a pseudoaromatic system, this situation might help to understand how important these three-body terms are, mainly near the equilibrium configuration.

In this work, empirical potential energy surfaces which reproduce the high resolution microwave spectra of clusters of rare-gas atoms and cyclopropane<sup>20</sup> are proposed. Since the binding energy for these complexes is of the order of a few hundreds of  $\text{cm}^{-1}$ , it is necessary to achieve highly accurate energy levels in order to simulate the microwave spectra (of the order of thousands of MHz). The procedure is shown in Sec. II. The potential energy surfaces, based on Lennard-Jones-type functions, are described in Sec. III, together with an analytic Fourier expansion for the azimuthal angle describing the interaction of the rare-gas atom with benzene or cyclopropane. The resulting microwave and intermolecular spectra are discussed in Sec. IV and compared to those of benzene complexes. Finally, Sec. V is devoted to some conclusions.

## II. THEORETICAL TREATMENT

In the kind of complexes under study, benzene and cyclopropane can be considered as rigid rotors due to the large mismatch between the fast intramolecular frequencies and the slow intermolecular motions associated with the van der

TABLE I. Symmetry operations on the body-fixed coordinates and on the angular functions. Note that for  $C_2(x)$  operators the labels  $a, b, c$  correspond to a  $\pi$  rotation about an axis in the ring plane containing the first, second and third carbon atom, respectively. Analogously, for the  $C_2(y)$  operators. The rotation matrix is defined according to Refs. 25 and 26 which explains the differences with respect to Ref. 14 where another convention is used.

Symmetry operator	Euler angles	Body-fixed polar angles of $\mathbf{R}$	Transformed function
$E$	$\alpha, \beta, \gamma$	$\theta, \phi$	$W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_6(z)$	$\alpha, \beta, \gamma + \pi/3$	$\theta, \phi - \pi/3$	$e^{-i(\omega-\Omega)\pi/3} W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_6^{-1}(z)$	$\alpha, \beta, \gamma - \pi/3$	$\theta, \phi + \pi/3$	$e^{i(\omega-\Omega)\pi/3} W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_3(z)$	$\alpha, \beta, \gamma + 2\pi/3$	$\theta, \phi - 2\pi/3$	$e^{-2i(\omega-\Omega)\pi/3} W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_3^{-1}(z)$	$\alpha, \beta, \gamma - 2\pi/3$	$\theta, \phi + 2\pi/3$	$e^{2i(\omega-\Omega)\pi/3} W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2(z)$	$\alpha, \beta, \gamma + \pi$	$\theta, \phi - \pi$	$(-1)^{\Omega+\omega} W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2^a(x)$	$\alpha + \pi, \pi - \beta, -\gamma$	$\pi - \theta, -\phi$	$(-1)^{J+\ell} W_{-\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2^b(x)$	$\alpha + \pi, \pi - \beta, -\gamma - 2\pi/3$	$\pi - \theta, -\phi + 2\pi/3$	$(-1)^{J+\ell} e^{2i(\omega-\Omega)\pi/3} W_{-\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2^c(x)$	$\alpha + \pi, \pi - \beta, -\gamma + 2\pi/3$	$\pi - \theta, -\phi - 2\pi/3$	$(-1)^{J+\ell} e^{-2i(\omega-\Omega)\pi/3} W_{-\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2^a(y)$	$\alpha + \pi, \pi - \beta, \pi - \gamma$	$\pi - \theta, \pi - \phi$	$(-1)^{J+\ell-\Omega-\omega} W_{-\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2^b(y)$	$\alpha + \pi, \pi - \beta, -\gamma + \pi/3$	$\pi - \theta, -\phi - \pi/3$	$(-1)^{J+\ell-\Omega-\omega} e^{2i(\omega-\Omega)\pi/3} W_{-\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$C_2^c(y)$	$\alpha + \pi, \pi - \beta, -\gamma - \pi/3$	$\pi - \theta, -\phi + \pi/3$	$(-1)^{J+\ell-\Omega-\omega} e^{-2i(\omega-\Omega)\pi/3} W_{-\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$
$E^*$	$\alpha, \beta, \gamma + \pi$	$\pi - \theta, \phi$	$(-1)^{\ell+\omega+\Omega} W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi)$

Waals interactions. Within this approximation, since benzene and cyclopropane are oblate symmetric tops, the Hamiltonian takes the form

$$H = A\hat{\mathbf{J}}^2 + (C-A)\hat{j}_z^2 + \frac{\hat{\mathbf{I}}^2}{2\mu R^2} - \frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + V(R, \theta, \phi), \quad (1)$$

where  $\hat{\mathbf{J}}$  and  $\hat{j}_z$  are the angular momentum of the rigid rotor and its projection on the principal axis of largest inertia moment, respectively. The  $A$  and  $C$  rotational constants are obtained from high resolution microwave spectra for benzene<sup>21,22</sup> and for cyclopropane.<sup>23,24</sup>  $\mathbf{R}$  is the vector joining the rare-gas atom to the center of mass of the rigid rotor,  $\hat{\mathbf{I}}$ , and  $\mu$  being the corresponding angular momentum operator and reduced mass, respectively. Finally, in Eq. (1),  $V(R, \theta, \phi)$  is the intermolecular interaction potential depending on  $\mathbf{R}$ , expressed in polar coordinates in the rigid rotor body-fixed frame, in which the  $z$ -axis is perpendicular to the carbon ring plane and the  $x$ -axis is parallel to the vector that joins the rigid rotor center of mass with the first carbon atom of the ring.

The binding energy of the complexes under study is of several hundreds of  $\text{cm}^{-1}$ , while the rotational transitions searched are of some GHz, which involves the calculation of eigenvalues with high accuracy, and hence the use of highly converged basis sets. In order to minimize the number of such functions, a careful choice of the basis must be done, as is described in what follows.

### A. Angular basis functions

In the body-fixed frame, the angular basis set functions considered are of the form

$$W_{\Omega/\omega}^{JM}(\alpha, \beta, \gamma, \theta, \phi) = \sqrt{\frac{2J+1}{8\pi^2}} D_{M\Omega}^{J*}(\alpha, \beta, \gamma) Y_{\ell/\omega}(\theta, \phi), \quad (2)$$

where the Euler angles  $\alpha, \beta, \gamma$  determine the orientation of the symmetric top with respect to the space-fixed frame.  $D_{M\Omega}^{J*}$  are rotation matrices<sup>25,26</sup> corresponding to a total angular momentum  $J$  with projections  $M$  and  $\Omega$  on the  $z$ -axis of the space-fixed and body-fixed frames, respectively (the total angular momentum operator is, indeed,  $\hat{\mathbf{J}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$ ).  $Y_{\ell/\omega}$  are usual spherical harmonics for an angular momentum  $\ell$  with a projection  $\omega$  on the body-fixed  $z$ -axis.

It is convenient to use symmetry adapted angular basis functions, accounting for the permutation of identical nuclei and the inversion of all the spatial coordinates of the system. The possible permutation operators should be consistent with the rigid rotor approach and do not change the relative positions between the atoms in benzene or cyclopropane. Such permutations are equivalent, in the body-fixed frame, to rotations. For benzene the permutation group is isomorphic with  $D_6$  [formed by 2  $C_6(z)$ , 2  $C_3(z)$ ,  $C_2(z)$ , 3  $C_2(x)$ , 3  $C_2(y)$  and the identity], while for cyclopropane the group is  $D_3$  [formed by 2  $C_3(z)$ , 3  $C_2(x)$  and the identity]. The inversion of spatial coordinates,  $E^*$ , with the identity,  $E$ , form the group  $C_i$ , so that the final group of symmetry operators, obtained as the direct product between the permutation group and  $C_i$ , is  $D_{6h}$  for benzene and  $D_{3h}$  for cyclopropane. The action on the body-fixed coordinates and on the angular basis set of Eq. (2) is summarized in Table I. The action of the symmetry operators on the angular functions of Eq. (2) either is proportional to itself or generates a new one with the  $\Omega, \omega$  values changed of sign. As a consequence, symmetry adapted angular basis functions are of the form



$$\langle W_{\Omega'\ell'\omega'}^{JM} | \hat{I}^2 | W_{\Omega\ell\omega}^{JM} \rangle = \delta_{\ell'\ell'} \delta_{\Omega\Omega'} \delta_{\omega\omega'} \quad \hbar^2 \ell(\ell+1),$$

$$\begin{aligned} \langle W_{\Omega'\ell'\omega'}^{JM} | \hat{J}^2 | W_{\Omega\ell\omega}^{JM} \rangle \\ = \delta_{\ell'\ell'} \delta_{\Omega\Omega'} \delta_{\omega\omega'} \quad \hbar^2 [J(J+1) + \ell(\ell+1) - 2\Omega\omega] \\ - \delta_{\ell'\ell'} \delta_{\Omega\Omega'} \delta_{\omega\omega'} \delta_{\omega\omega' \pm 1} \\ \times \hbar^2 \sqrt{J(J+1) - \Omega\Omega'} \sqrt{\ell(\ell+1) - \omega\omega'} \end{aligned}$$

$$\langle W_{\Omega'\ell'\omega'}^{JM} | \hat{J}_z^2 | W_{\Omega\ell\omega}^{JM} \rangle = \delta_{\ell'\ell'} \delta_{\Omega\Omega'} \delta_{\omega\omega'} \quad \hbar^2 (\Omega - \omega)^2. \quad (7)$$

The potential term is expanded in spherical harmonics as

$$V(R, \theta, \phi) = \sum_{\Lambda, \lambda} V_{\Lambda, \lambda}(R) Y_{\Lambda, \lambda}(\theta, \phi), \quad (8)$$

where the expansion coefficients fulfill  $V_{\Lambda, |\lambda|}(R) = (-1)^\lambda V_{\Lambda, -|\lambda|}(R)$ . The potential is symmetric under the reflection through the ring plane, i.e.,  $V(R, \theta, \phi) = V(R, \pi - \theta, \phi)$ . In addition,  $V(R, \theta, \phi) = V(R, \theta, \phi + 2n\pi/N)$  ( $N$  being the number of carbon atoms of the ring) and  $\lambda = 0, \pm N, \pm 2N, \dots$ . Using this expansion, the potential matrix elements become

$$\begin{aligned} \langle W_{\Omega'\ell'\omega'}^{JM} | V | W_{\Omega\ell\omega}^{JM} \rangle = \delta_{\Omega'\Omega} \frac{(-1)^{\omega'}}{\sqrt{4\pi}} \sum_{\Lambda\lambda} V_{\Lambda\lambda}(R) \\ \times \sqrt{(2\ell'+1)(2\Lambda+1)(2\ell+1)} \\ \times \begin{pmatrix} \ell & \Lambda & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \Lambda & \ell' \\ \omega & \lambda & -\omega' \end{pmatrix}, \end{aligned} \quad (9)$$

with  $(\dots)$  being 3- $j$  symbols.

### C. Radial basis functions and matrix elements

The radial basis set functions,  $\Phi_v(R)$ , are eigenstates of a one-dimension Hamiltonian for some reference potential  $V_{\text{ref}}(R)$  and are numerically calculated. Thus, since the equilibrium configuration of these complexes corresponds to  $\theta = 0$  or  $\pi$ , the number of functions required to converge the calculation is greatly reduced choosing  $V_{\text{ref}} = V(R, \theta=0, \phi)$ .

It should be noted, however, that for complexes with Ne, the number of bound eigenstates supported by a single  $V_{\text{ref}}$  is not enough and one has to use several reference potentials. As an example, for Ne-cyclopropane a second reference potential for  $\theta = \pi/2$  and  $\phi = \pi/3$  is used, since the total eigenfunctions for this system can reach such a configuration, as it will be discussed in what follows. The corresponding eigenfunctions are further orthonormalized following a Schmidt procedure.<sup>27</sup>

Derivatives of radial numerical functions are evaluated using a fast Fourier transform method.<sup>28</sup> All the radial integrals required to evaluate the Hamiltonian matrix elements are calculated numerically. Such procedure involves an error. However, the same integrals are calculated for all the eigenvalues, which compensates errors when considering transitions.

### D. Diagonalization

The eigenstates of the total Hamiltonian of Eq. (1) belonging to the  $\Gamma_j$  irreducible representation are expanded as

$$\begin{aligned} \Psi_i^{JM\Gamma_j}(\alpha, \beta, \gamma, \mathbf{R}) \\ = \sum_{v\Omega'\omega} A_{v\Omega'\omega}^{JM\Gamma_j} \frac{\Phi_v(R)}{R} \mathcal{W}_{\Omega'\ell\omega}^{JM\Gamma_j}(\alpha, \beta, \gamma, \theta, \phi). \end{aligned} \quad (10)$$

In order to increase the number of accurate decimal figures through the diagonalization, the integer part of the ground eigenvalue, in  $\text{cm}^{-1}$ , is subtracted to every diagonal Hamiltonian matrix element. Thus, to get eigenvalues with an accuracy of the order of 1 kHz, eight significant figures are converged for the ground state with the basis set chosen as follows. In Eq. (10), basis functions are added up until weights for all different quantum numbers become smaller than  $10^{-10}$ , the weight of  $v$ , for example, being defined as  $w_v = \sum_{\Omega'\ell\omega} |A_{v\Omega'\omega}^{JM\Gamma_j}|^2$  (and similarly for  $\Omega$ ,  $\ell$  and  $\omega$ ).

The matrices required for such accuracy become very large as  $J$  increases (being of the order of  $40\,000 \times 40\,000$  for the largest  $J$ 's considered in degenerate representations) and a variational method was only possible for  $J=0$ . For the simulation of the microwave spectra only the ground van der Waals states for several  $J$  and  $\Gamma_j$  are required. These states are calculated using an iterative Lanczos method which has proven to be very efficient and accurate.<sup>29</sup> In this method, the initial guess is obtained in a diagonalization with a reduced basis set. In each iteration a subspace formed by  $\approx 50$  functions is generated from the initial guess following the Lanczos algorithm,<sup>30,31</sup> and the resulting tridiagonal Hamiltonian matrix is diagonalized. The resulting ground eigenvalue is used for the next iteration until the residue (overlap between the wave functions before and after each diagonalization) is smaller than a given criterion,  $10^{-12}$  in this case.

### III. POTENTIAL ENERGY SURFACES

Cyclopropane and benzene are formed by several rings of  $N$  identical atoms, all of them centered along the body-fixed  $z$ -axis. For the case of benzene, the equilibrium configuration corresponds to an arrangement of atoms in two circular and concentric rings in a plane, one of carbon atoms, with radius  $R_C = 1.395 \text{ \AA}$  and  $z_C = 0$ , and the second of hydrogen atoms, with radius  $R_H = 2.479 \text{ \AA}$  and  $z_H = 0$ . Cyclopropane is composed of three rings, a central ring of carbon atoms, with radius  $R_C = 0.874\,87 \text{ \AA}$ , and  $z_C = 0$ , placed between two parallel rings of hydrogen atoms, with radius  $R_H = 1.449\,24 \text{ \AA}$  with  $z_H = \pm 0.911\,52 \text{ \AA}$ . Thus, the interaction potential is a periodic function of the  $\phi$  variable, as we have already discussed. Assuming the knowledge of the PES which will be specified later on, and in order to obtain the  $V_{\Lambda\lambda}(R)$  coefficients appearing in Eq. (8), it is convenient first to account for the periodicity of the potential in the  $\phi$  variable and perform a Fourier expansion

$$V(R, \theta, \phi) = W_0(R, \theta) + 2 \sum_{g>0} W_g(R, \theta) \cos(gN\phi), \quad (11)$$

with

$$W_g(R, \theta) = \frac{N}{2\pi} \int_0^{2\pi/N} d\phi V(R, \theta, \phi) \cos(gN\phi). \quad (12)$$

The  $g=0$  coefficient describes the interaction between the rare-gas atom and a continuum ring, while the  $g>0$  coefficients account for the corrugation in the potential. Using the property  $V_{\Lambda|\lambda|} = (-1)^\lambda V_{\Lambda-|\lambda|}$ , ensuring that the potential is a real function, Eq. (8) can be rewritten as

$$V(R, \theta, \phi) = \frac{1}{\sqrt{2\pi}} \sum_{\Lambda} \left[ V_{\Lambda 0}(R) \Theta_{\Lambda 0}(\theta) + 2 \sum_{\lambda>0} V_{\Lambda\lambda}(R) \Theta_{\Lambda\lambda}(\theta) \cos(\lambda\phi) \right], \quad (13)$$

where  $\Theta_{\Lambda\lambda}$  are normalized associated Legendre functions.<sup>25</sup> Comparison of Eqs. (13) and (11) leads one to identify

$$W_g(R, \theta) = \frac{1}{\sqrt{2\pi}} \sum_{\Lambda} V_{\Lambda\lambda}(R) \Theta_{\Lambda\lambda}(\theta), \quad (14)$$

with  $\lambda = gN$ . Hence, the  $V_{\Lambda\lambda}$  are readily obtained through quadratures involving Fourier coefficients

$$V_{\Lambda gN}(R) = \sqrt{2\pi} \int_{-1}^1 d(\cos\theta) \Theta_{\Lambda gN}(\theta) W_g(R, \theta). \quad (15)$$

The rings of identical atoms of benzene and cyclopropane, denoted by  $\alpha$ , are characterized by a radius  $R_\alpha$  and by the position of its center on the  $z$ -axis,  $z_\alpha$ . The Fourier expansion is done independently for each ring  $\alpha$ , obtaining the corresponding  $W_g^\alpha$ , and the total Fourier coefficients of Eq. (12) are then obtained as the simple addition  $W_g = \sum_\alpha W_g^\alpha$ .

Assuming that the van der Waals interaction is described by a sum of Lennard-Jones pairwise potentials between each of the atoms of the ring and the rare-gas atom, the Fourier coefficients for each ring can be obtained analytically through the following expression:<sup>32</sup>

$$W_g^\alpha(R, \theta) = 4N\epsilon_\alpha \sum_{k=6,12} \sigma_\alpha^k \frac{(-1)^{k-1}}{b^{gN}(k/2-1)!} \times \frac{d^{k/2-1}}{da^{k/2-1}} \frac{(\sqrt{a^2-b^2}-a)^{gN}}{\sqrt{a^2-b^2}}, \quad (16)$$

where  $a = R_\alpha^2 + r_\alpha^2$  and  $b = -2R_\alpha r_\alpha \sin\theta_\alpha$  [with  $r_\alpha = \sqrt{R^2 + z_\alpha^2 - 2z_\alpha R \cos\theta}$  and  $\tan\theta_\alpha = R \sin\theta / (R \cos\theta - z_\alpha)$ ], and  $\sigma_\alpha$  and  $\epsilon_\alpha$  are the usual Lennard-Jones parameters associated with the interaction of the identical atoms of ring  $\alpha$  with the rare-gas atom. The Fourier expansion convergence depends on the matter density of the ring. Usually, as in the interaction of an atom with a planar surface<sup>33</sup> or with an helicoidal arrangement of atoms,<sup>34,35</sup> a maximum of three or four terms is required in the expansion to reproduce the standard pairwise sum procedure.

When the rare-gas atom is located on the  $N$  fold symmetry axis, the body-fixed  $z$ -axis, the zero-order coefficient takes the simple form

$$W_0^\alpha(R, \theta=0) = 4N\epsilon \sum_{k=6,12} (-1)^{k/2} \frac{\sigma^k}{(R_\alpha^2 + r_\alpha^2)^{k/2}}, \quad (17)$$

and the  $W_{g>0}^\alpha$  coefficients vanish. Therefore, the zero-order term (continuum ring approximation) becomes ‘‘exact’’ in such configurations. The equilibrium position  $z_e$  for the rare-gas atom is obtained analytically in such a symmetric configuration giving two equivalent minima at

$$z_e - z_\alpha = \pm \sqrt{2^{1/3} \sigma^2 - R_\alpha^2} \quad \text{when } R_\alpha < 2^{1/6} \sigma, \quad (18a)$$

or a single minimum at

$$z_e - z_\alpha = 0 \quad \text{when } R_\alpha \geq 2^{1/6} \sigma, \quad (18b)$$

with the minimum value of the potential given by

$$W_0^\alpha(z_e - z_\alpha, \theta=0) = -N\epsilon. \quad (19)$$

In summary, the expansion of the potential in spherical harmonics, Eq. (8), is done in two steps. First, a Fourier expansion is performed in the  $\phi$  variable, and the global  $W_g$  Fourier coefficients of the potential are obtained as the sum of the individual  $W_g^\alpha$  terms obtained analytically for each ring, as explained above. This analytical expansion is faster than a numerical procedure and, what is more important, reduces the error. In the second step, for each Fourier component  $W_g(R, \theta)$ , the  $V_{\Lambda,\lambda}(R)$  ( $\lambda = \pm gN$ ) coefficients are evaluated numerically using a Gauss-Legendre quadrature.

## A. Benzene

There are several *ab initio* calculations on the potential energy surfaces (PES) of complexes of rare-gas atoms with benzene.<sup>15,16,19</sup> *Ab initio* data have been fitted with some analytic functions in order to provide a whole PES to be used in spectra simulations.<sup>15</sup> Although the accuracy of these calculations is not enough to reproduce high resolution microwave spectra on these systems, they can provide a way to check the analytic functional forms used to produce empirical PES. The commonly used form, based on a superposition of pairwise Lennard-Jones potentials<sup>11,12,17</sup> between the rare-gas atom and each of the atoms of benzene, is able to fit the *ab initio* points in the region of the well but fails to reproduce the configurations in which the rare-gas atom is in the plane of the aromatic ring. Moreover, it has been theoretically found that the dispersion energy for  $\pi$ -electrons of benzene cannot be described by simple atom-atom terms especially in planar configurations, but the error made using these forms is generally small at the equilibrium configuration.<sup>13</sup>

Along this line, empirical PES's have been proposed including three-body terms based on Lennard-Jones-type functions that accurately describe the microwave spectra of several complexes of rare-gas atoms with benzene.<sup>3</sup> When the potential of Brupbacher *et al.*<sup>3</sup> for the case of the Ne-benzene complex (in which  $R_C = 1.395 \text{ \AA}$ ,  $V_e = -151 \text{ cm}^{-1}$  and  $R_e = 3.2989 \text{ \AA}$ ) is fitted by a pure pairwise Lennard-Jones potential using Eqs. (18) and (19), we obtain  $\epsilon = 25.1667 \text{ cm}^{-1}$  and  $\sigma = 3.191 \text{ \AA}$ . For the  $C_{6v}$  configuration, the pure Lennard-Jones potential coincides with the Brupbacher potential and is in good agreement with high quality *ab initio* data that have recently appeared<sup>16</sup> [see Fig. 1(a)]. However, in the planar configuration (with  $\theta = \pi/2$  and  $\phi = \pi/6$ ), the pure Lennard-Jones potential overestimates the depth of the well and underestimates the equilibrium distance (unfortunately, for this last configuration there are not

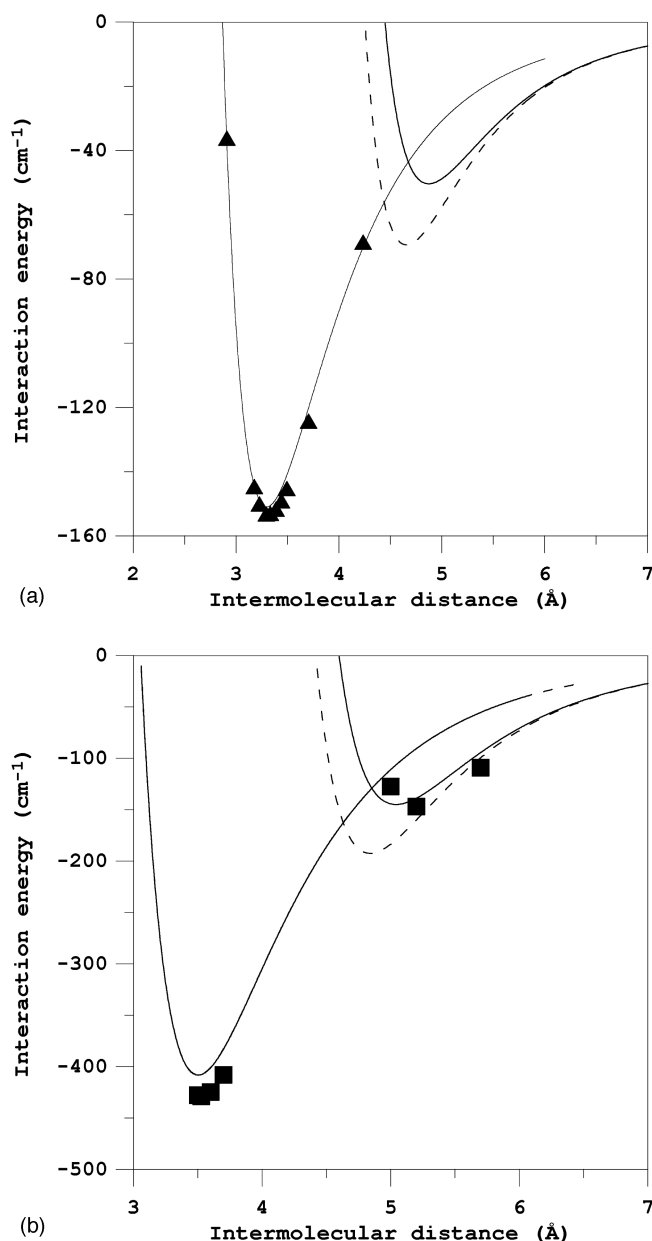


FIG. 1. Potential energy for Ne-benzene (a) and Ar-benzene (b) at two angular configurations,  $\theta=0$  the deepest one, and at  $\theta=\pi/2$ ,  $\phi=\pi/6$ . Solid lines correspond to Brupbacher *et al.* PES (Ref. 3), while dashed lines are the pure atom-atom Lennard-Jones potential. Points are *ab initio* calculations taken from Ref. 16 for Ne-benzene and from Ref. 15.

*ab initio* data of the same quality). In Fig. 1(b) similar plots are shown, but for Ar-benzene, and the *ab initio* points are taken from Ref. 15. We observe essentially the same behavior as in the Ne-benzene case, particularly the discrepancies between the three models at planar configurations. The situation for the complexes of Kr and Xe is also similar, indicating that a simple Lennard-Jones pairwise potential is unable to describe planar configurations for X-benzene complexes and three-body terms should be included.

Recent experiments on intermolecular spectroscopy of the Ar-benzene ground state<sup>6,10</sup> are in very good agreement with bound state calculations<sup>18,10</sup> using the empirical PES already mentioned.<sup>3</sup> The excellent agreement obtained up to

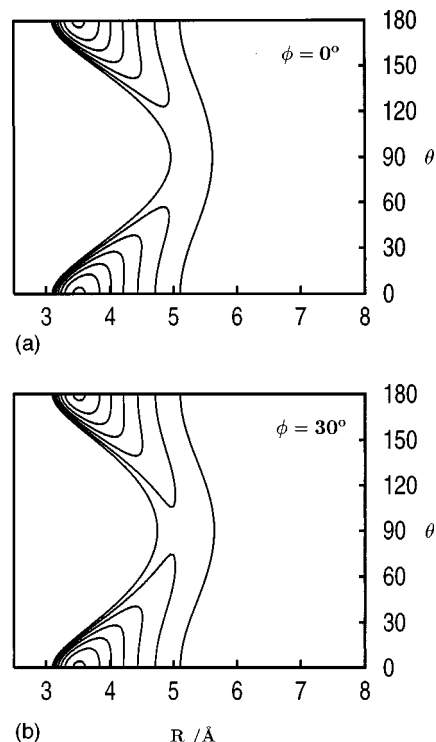


FIG. 2. Contour plots of the PES of Ar-benzene (Ref. 3), (a) for  $\phi=0$  and (b) for  $\phi=\pi/6$ . The contours start at  $-400$ , in intervals of  $50 \text{ cm}^{-1}$ .

a relatively high excitation of van der Waals modes ( $\approx$ one-third of the binding energy) clearly indicates that the high resolution microwave spectra not only provide detailed information on the structure of the complex but also on the shape of the PES near the equilibrium configuration. The success of this PES, provided that none of the states involved can reach configurations in which the rare-gas atom is in the carbon ring plane, supports the idea that functional forms based on Lennard-Jones-type functions, including three-body terms, are well adapted to describe the PES of rare-gas atoms-aromatic clusters.

For complexes of benzene we use the PES of Brupbacher *et al.*<sup>3</sup> that can be rewritten in the form

$$V(R, \theta, \phi) = \sum_i 4\epsilon \left( \frac{\sigma^{12}}{R_i^{12}} - \frac{\sigma^6}{R_i^6} \right) + \frac{1}{2} \sum_{i,j} \frac{\gamma}{R_i^6 R_j^6}, \quad (20)$$

where  $R_i$  is the distance between the  $i$ th carbon of the ring and the rare gas, and  $\epsilon$ ,  $\sigma$  and  $\gamma$  are effective potential parameters which are expressed in terms of the original ones.<sup>3</sup> The effect of the hydrogen atoms was included implicitly in the parameters corresponding to the carbon atoms. The first term in the right-hand side corresponds to pure atom-atom interactions while the second one corresponds to three-body corrections, involving the rare gas and two carbon atoms. The three-body contribution in Eq. (20) can also be expanded in Fourier series by using Eq. (16) with the sum restricted to  $k=6$ . In Fig. 2, contour plots of the PES for Ar-benzene are shown at two relevant configurations, that in the plane correspond to the rare-gas atom facing a carbon atom,  $\phi=0$ , and at equivalent distances from two carbon atoms,  $\phi=\pi/6$ . The equilibrium position is at  $C_{6v}$  configu-

TABLE IV. Lennard-Jones potential parameters for the *X*-cyclopropane complexes.

<i>X</i>	$\sigma_{CX}/\text{\AA}$	$\epsilon_{CX}/\text{cm}^{-1}$	$\sigma_{HX}/\text{\AA}$	$\epsilon_{HX}/\text{cm}^{-1}$
Ne	3.2075	31.6667	2.6282	30
Ar	3.2506	80	2.8776	50
Kr	3.3643	96.6667	2.9845	50

ration while planar configurations, both at  $\phi=0$  and at  $\phi=\pi/6$ , are at much higher energy and show saddle points with maxima as a function of  $\theta$  and minima as a function of *R*.

## B. Cyclopropane

The fact that in cyclopropane the hydrogen atoms are not in the carbon ring plane originates new features in the PES of its complexes with rare-gas atoms, leading to noticeable steric effects, absent in *X*-benzene complexes. In addition, since three-body corrections are mainly attributed to  $\pi$ -electrons and cyclopropane is weakly aromatic, its interaction with rare-gas atoms can be described with pure atom-atom Lennard-Jones potentials, and no three-body corrections have to be accounted for. Thus, the Lennard-Jones parameters have been fitted to reproduce the high resolution microwave spectra recently reported by Xu and Jäger,<sup>20</sup> and are listed in Table IV.

In Fig. 3 two contour plots of the PES for Ar-cyclopropane are shown. The main difference with respect to Ar-benzene is that in this case there are minima in the carbon ring plane, for  $\theta=\pi/2$  and  $\phi=\pi/3+2n\pi/3$ , with a depth comparable to those of the two minima at  $\theta=0$  and  $\pi$ , and

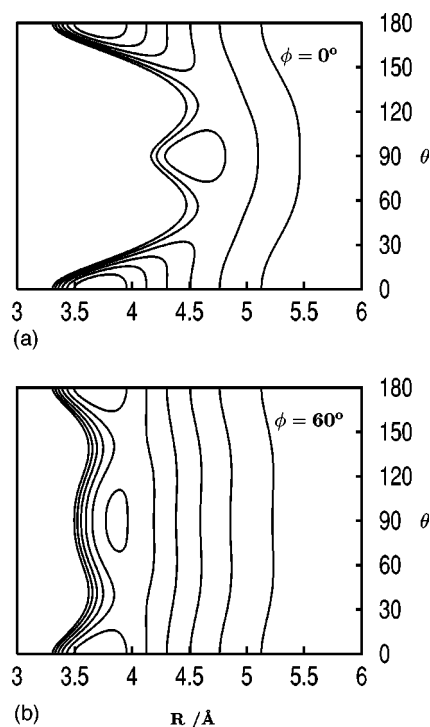


FIG. 3. Contour plots of the PES of Ar-cyclopropane, (a) for  $\phi=0$  and (b) for  $\phi=\pi/3$ . The contours start at  $-350$  in intervals of  $50 \text{ cm}^{-1}$ .

the barrier between all of them is relatively low. The same happens for complexes of Ne and Kr. This feature of the PES gives rise to a tunneling around the carbon ring, even for the ground van der Waals state of the complexes, which leads to a splitting of the microwave transitions as it has been recently reported for Ne-cyclopropane.<sup>20</sup> This effect is even more notorious for excited van der Waals states as it will be discussed below.

## IV. RESULTS AND DISCUSSION

### A. Microwave spectra and rotational constants

In order to simulate the microwave spectra, the dipole moment,  $\mathbf{d}$ , is assumed to be proportional to  $Y_{10}(\theta, \phi)$ . The transition operator in the electric dipole approach,  $\mathbf{d} \cdot \mathbf{e}$  (with  $\mathbf{e}$  being the light polarization vector), belongs to the  $A_{1u}$  and  $A_1'$  irreducible representations for benzene and cyclopropane, respectively. With this assumption, the typical selection rules involving  $\Delta K=0$  of symmetric tops are obtained. The microwave spectra for all the complexes under study are well described by the energy levels of a symmetric top, of energy  $E_{JK}$ . It should be noted that *K* is an approximate quantum number which in the exact calculation corresponds to the  $\Omega$  of higher probability and is only introduced to compare with the rigid rotor approach. The mixing among  $\Omega$  quantum numbers arises from Coriolis couplings in Eq. (7). For instance, the  $E'$ ,  $J=2$  state of <sup>20</sup>Ne-cyclopropane ( $v_{\text{tunn}}=0$ ), which corresponds to  $K=1$ , has a distribution of 0.05, 0.91 and 0.04 for  $\Omega=0, 1$  and  $2$ , respectively, and for Ar-benzene the  $E_{1g}$ ,  $J=2$ ,  $K=1$  eigenstate the decomposition is 0.01, 0.98 and 0.01 for  $\Omega=0, 1$  and  $2$ , respectively.

Simulated microwave transitions for Ar-benzene and complexes of cyclopropane are shown in Table V, compared with the experimental values.<sup>1,20</sup> The results for Ar-benzene show the reliability of the procedure of this work, since the potential of Brupbacher *et al.*<sup>3</sup> used was fit to the experimental microwave transitions.<sup>1</sup> As it can be seen, the discrepancies are of a few MHz and may be attributed to the different treatment made on the Coriolis coupling term. In the work of Brupbacher and co-workers,<sup>3</sup> the body-fixed frame was optimized to minimize the Coriolis term and, then, the residual coupling was neglected. On the contrary, in the present treatment the Coriolis term is fully accounted for. Nevertheless, the agreement between the calculated and experimental transitions is excellent, with about four reliable significant figures, and the general trend as a function of *J* and *K* coincides with that exhibited by the observed transitions.

The calculated transitions for complexes of cyclopropane are in even better agreement with the experimental data,<sup>20</sup> as can be seen in Table V. The experimental transitions for Ne-cyclopropane show a splitting that was attributed to a tunneling around the plane.<sup>20</sup> This splitting is well reproduced in the calculations presented in this work. The experimental and calculated splittings for the 1,0-0,0 transition are 0.3732 and 0.16 MHz, respectively, for the complex of <sup>20</sup>Ne (and decrease to 0.2934 and 0.13 MHz, respectively, for <sup>22</sup>Ne). Even when there is not a quantitative agreement, the calculated shift is of the order of the experimental one and shows the same behavior under isotope substitution.



TABLE V. Microwave spectra for complexes of benzene and cyclopropane for the  $J'K\Gamma' \leftarrow JK\Gamma$  transition,  $\Gamma$  being the irreducible representation of each state. For the case of  $^{20}\text{Ne}$ -cyclopropane, the two tunneling components,  $v_{\text{tun}}=0$  and 1, are given separately. The experimental frequencies are taken from Ref. 20 for X-cyclopropane complexes and from Ref. 1 for Ar-benzene.

$J'$	$\Gamma'$	$J$	$\Gamma$	$K$	$\nu_{\text{calc}}/\text{MHz}$	$\nu_{\text{exp}}/\text{MHz}$
$^{40}\text{Ar}$ -benzene						
4	$A_{1g}$	3	$A_{1u}$	0	9443.907	9449.243
5	$A_{1u}$	4	$A_{1g}$	0	11 804.298	11 810.965
6	$A_{1g}$	5	$A_{1u}$	0	14 164.298	14 172.301
7	$A_{1u}$	6	$A_{1g}$	0	16 523.831	16 533.166
4	$E_{1g}$	3	$E_{1u}$	1	9443.767	9449.100
5	$E_{1u}$	4	$E_{1g}$	1	11 804.123	11 810.789
6	$E_{1g}$	5	$E_{1u}$	1	14 164.087	14 172.087
4	$E_{2g}$	3	$E_{2u}$	2	9443.341	9448.671
5	$E_{2u}$	4	$E_{2g}$	2	11 803.617	11 810.253
6	$E_{2g}$	5	$E_{2u}$	2	14 163.436	14 171.444
4	$B_{1g}$	3	$B_{1u}$	3	9442.649	9447.959
5	$B_{1u}$	4	$B_{1g}$	3	11 802.722	11 809.365
6	$B_{1g}$	5	$B_{1u}$	3	14 162.406	14 170.376
7	$B_{1u}$	6	$B_{1g}$	3	16 521.618	16 530.917
$^{20}\text{Ne}$ -cyclopropane $v_{\text{tun}}=0$						
1	$A_1''$	0	$A_1'$	0	4861.261	4861.1235
2	$A_1'$	1	$A_1''$	0	9721.540	9720.4353
3	$A_1''$	2	$A_1'$	0	14 579.913	14 576.1044
4	$A_1'$	3	$A_1''$	0	19 435.408	19 426.2964
2	$E'$	1	$E''$	1	9719.416	9718.4342
$^{20}\text{Ne}$ -cyclopropane $v_{\text{tun}}=1$						
1	$A_2'$	0	$A_2''$	0	4861.099	4860.7503
2	$A_2''$	1	$A_2'$	0	9721.266	9719.6995
3	$A_2'$	2	$A_2''$	0	14 579.510	14 575.0356
4	$A_2''$	3	$A_2'$	0	19 434.882	19 424.9330
2	$E''$	1	$E'$	1	9719.312	9717.9062
$^{40}\text{Ar}$ -cyclopropane						
2	$A_1'$	1	$A_1''$	0	6289.498	6289.4183
3	$A_1''$	2	$A_1'$	0	9433.891	9433.5373
4	$A_1'$	3	$A_1''$	0	12 577.766	12 576.9507
5	$A_1''$	4	$A_1'$	0	15 721.003	15 719.4239
2	$E'$	1	$E''$	1	6289.260	6289.1700
$^{84}\text{Kr}$ -cyclopropane						
2	$A_1'$	1	$A_1''$	0	4467.343	4467.3303
3	$A_1''$	2	$A_1'$	0	6700.879	6700.7524
4	$A_1'$	3	$A_1''$	0	8934.180	8933.8881
5	$A_1''$	4	$A_1'$	0	11 167.409	11 166.6402
6	$A_1'$	5	$A_1''$	0	13 400.193	13 398.9192
2	$E'$	1	$E''$	1	4467.229	4467.2243

For Kr and Ar-cyclopropane, the calculated splittings are reduced by an order of magnitude, which can explain why they were not observed experimentally. For this reason, in Table V the splitted transitions are only shown for the case of Ne.

In order to illustrate the nature of the splitting it is interesting to analyze the nature of the bound states involved. The ground ( $A_1'$ ,  $J=0$  named  $v_{\text{tun}}=0$ ) and first excited ( $A_2''$ ,  $J=0$  named  $v_{\text{tun}}=1$ ) van der Waals states of complexes of cyclopropane (which correspond to symmetric and antisymmetric states, respectively, with respect to the reflection in the plane), are nearly degenerate, and the small splitting,  $\Delta$ , is a result of the tunneling around the carbon ring plane. This effect does not appear in the first van der Waals states of complexes of benzene. The splitting obtained for complexes of cyclopropane with  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$  and  $^{84}\text{Kr}$  are 2.67, 0.07 and 0.003 MHz, respectively. As the interaction becomes stron-

ger and the bond more localized, as happens for Ar and Kr, the tunneling probability decreases. The tunneling around the carbon ring is well illustrated in Figs. 4 for  $^{20}\text{Ne}$ -cyclopropane, where contour plots of the ground ( $A_1'$ ,  $v_{\text{tun}}=0$ ,  $J=0$ ) and first excited states ( $A_2''$ ,  $v_{\text{tun}}=1$ ,  $J=0$ ) are compared. The even  $A_1'$  wave function is nonzero in the plane only for  $\phi=\pi/3$  while for  $\phi=0$  is zero, which shows that the tunneling occurs between two carbon atom of the ring. The  $A_2''$  wave function, however, is always zero in the plane since it is odd under reflection in the  $x$ - $y$  plane. This small difference explains the energy shift between these two states.

As was already mentioned, the energy levels are well reproduced using a symmetric top model for these complexes. The corresponding  $B$ ,  $D_J$  and  $D_{JK}$  parameters are listed in Table VI and compared with those obtained from

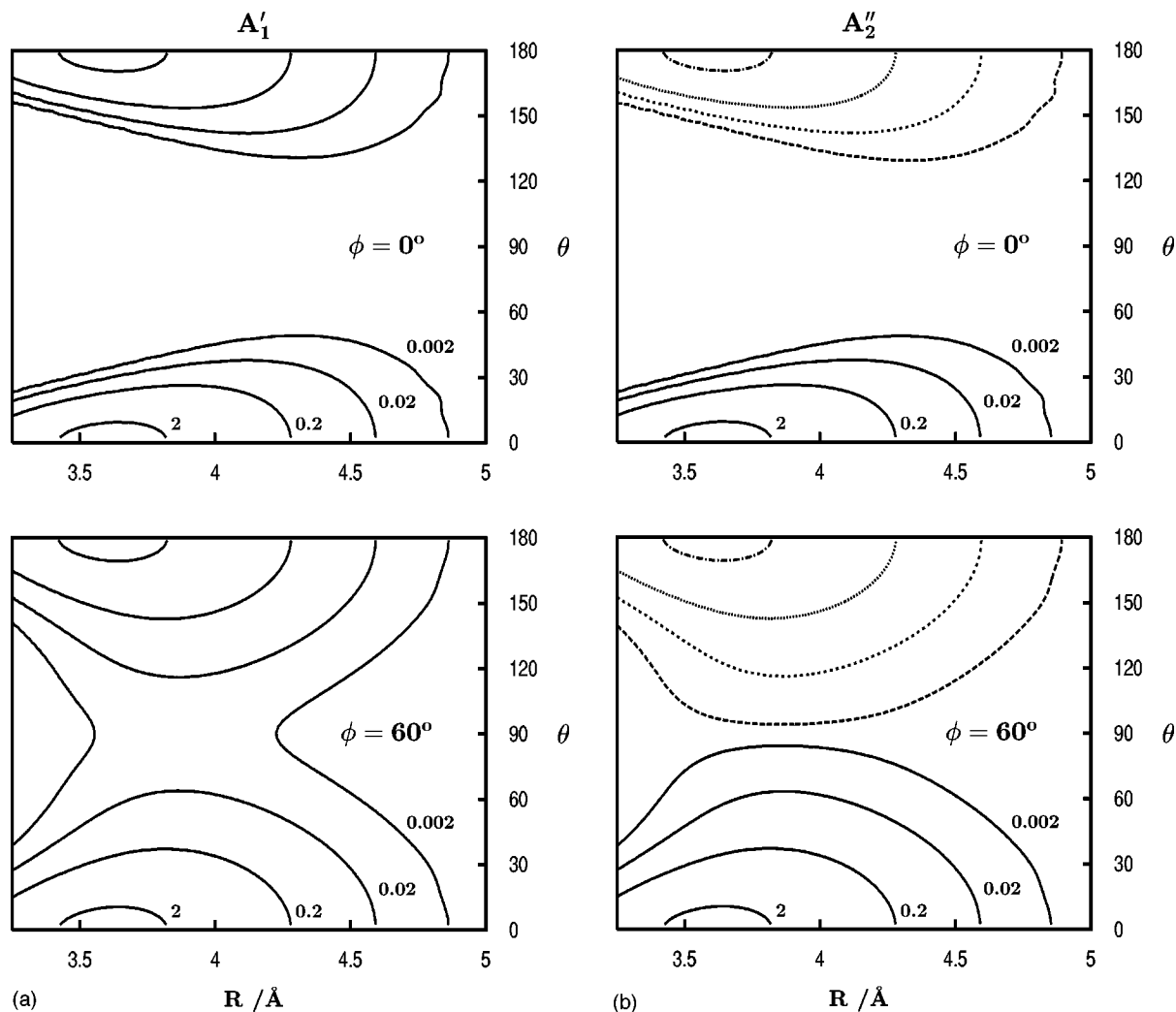


FIG. 4. Contour plots of the amplitude of the ground  $A'_1$  (a) and first excited  $A''_2$  (b) wave functions of  $^{20}\text{Ne}$ -cyclopropane for  $\phi=0$  and  $\pi/3$ .

the observed spectra. The theoretical constants are calculated from the lower transitions as

$$B = \frac{8(E_{10} - E_{00}) - (E_{20} - E_{10})}{12},$$

$$D_J = \frac{2(E_{10} - E_{00}) - (E_{20} - E_{10})}{24},$$

$$D_{JK} = \frac{(E_{20} - E_{10}) - (E_{21} - E_{11})}{4}.$$

For Ne-cyclopropane, the calculated  $D_J$  and  $D_{JK}$  spectroscopic constants present larger deviations with respect to the experimental data than for the rest of the complexes of cyclopropane. This is attributed to the larger tunneling splitting

TABLE VI. Rotational constants. The experimental values are taken from Ref. 3 for benzene and from Ref. 20 for cyclopropane.

System	Calculated			Experiment <sup>a</sup>		
	$B/\text{MHz}$	$D_J/\text{kHz}$	$D_{JK}/\text{kHz}$	$B/\text{MHz}$	$D_J/\text{kHz}$	$D_{JK}/\text{kHz}$
$^{20}\text{Ne}-\text{C}_6\text{H}_6$	1809.12	19.70	87.04	1810.25527	19.384	88.400
$^{40}\text{Ar}-\text{C}_6\text{H}_6$	1180.59	3.26	17.48	1181.25953	3.257	17.8011
$^{84}\text{Kr}-\text{C}_6\text{H}_6$	795.45	1.26	7.88	795.6821	1.315	7.895
$^{20}\text{Ne}-\text{C}_3\text{H}_6(v_{\text{tunn}}=0)$	2430.71	40.94	530.96	2430.7131	75.49	497.1
$^{20}\text{Ne}-\text{C}_3\text{H}_6(v_{\text{tunn}}=1)$	2430.63	38.84	488.37	2430.5260	75.08	445.5
$^{22}\text{Ne}-\text{C}_3\text{H}_6(v_{\text{tunn}}=0)$	2301.16	37.05	467.16	2302.2259	68.17	432.9
$^{22}\text{Ne}-\text{C}_3\text{H}_6(v_{\text{tunn}}=1)$	2301.09	35.01	378.09	2302.0778	67.80	393.6
$^{40}\text{Ar}-\text{C}_3\text{H}_6$	1572.432	7.23	59.40	1572.4338	9.89	60.2
$^{84}\text{Kr}-\text{C}_3\text{H}_6$	1116.861	3.11	28.53	1116.8642	4.0053	26.12

<sup>a</sup>References 3 and 20.

TABLE VII. Van der Waals vibrational frequencies for the first excited states of the complexes of benzene and  $J=0$ . The binding energies of the  $X$ -benzene complexes are 108.52, 349.10 and 452.73  $\text{cm}^{-1}$  for  $^{20}\text{Ne}$ , Ar and  $^{84}\text{Kr}$ , respectively.

$^{20}\text{Ne}$ -benzene		$^{40}\text{Ar}$ -benzene				$^{84}\text{Kr}$ -benzene		
$\Gamma(D_{6h})$	$\Delta E/\text{cm}^{-1}$	$\Gamma(D_{6h})$	$\Delta E/\text{cm}^{-1}$	Experiment <sup>a</sup>	Experiment <sup>b</sup>	$\Gamma(D_{6h})$	$\Delta E/\text{cm}^{-1}$	Experiment <sup>c</sup>
$E_{1u}, E_{1g}$	20.07	$E_{1u}, E_{1g}$	33.04	33.03	32.8	$E_{1u}, E_{1g}$	35.26	35.2
$A_{1g}, A_{2u}$	25.79	$A_{1g}, A_{2u}$	39.55	39.89	39.99	$A_{1g}, A_{2u}$	36.79	...
$E_{2g}, E_{2u}$	36.76	$E_{2g}, E_{2u}$	63.38	63.32	...	$E_{2g}, E_{2u}$	68.18	...
$E_{1u}, E_{1g}$	40.26	$A_{1g}, A_{2u}$	66.36	65.53	65.39	$E_{1u}, E_{1g}$	68.97	...
$A_{1g}, A_{2u}$	40.41	$E_{1u}, E_{1g}$	68.30	68.70	...	$A_{1g}, A_{2u}$	69.35	...
$A_{1g}, A_{2u}$	47.20	$A_{1g}, A_{2u}$	76.37	...	77.11	$A_{1g}, A_{2u}$	72.90	...
$B_{1g}, B_{2u}$	50.10	$B_{1g}, B_{2u}$	91.00	...	...	$B_{1g}, B_{2u}$	98.73	...
$B_{1u}, B_{2g}$	60.65	$B_{1u}, B_{2g}$	91.24	...	...	$B_{1u}, B_{2g}$	98.92	...

<sup>a</sup>Reference 6.<sup>b</sup>Reference 10.<sup>c</sup>Reference 4.

for this complex which produces the result that the wave functions are distributed over a larger region of the configuration space, with a nonzero probability of finding the Ne atom in the carbon plane of cyclopropane. As it was discussed above, the analytic form used to describe the PES might not be perfectly adapted to describe such configurations, which would explain the inaccuracy of the PES to reproduce the spectroscopic constants in the case of Ne-cyclopropane.

## B. Intermolecular spectroscopy

Microwave spectra provide information on the ground van der Waals level of the complexes, not only in the equilibrium configuration but also on the shape of the PES well, provided that the  $B$ ,  $D_J$  and  $D_{JK}$  constants are accurately reproduced. As an example, several frequencies for the intermolecular transitions of Ar-benzene have been measured recently using ionization-detected stimulated Raman spectroscopy<sup>6</sup> and ion dip spectroscopy<sup>10</sup> in very good agreement with calculations reported by Riedle and van der Avoird<sup>18</sup> and Neuhauser *et al.*<sup>10</sup> using the PES of Brupbacher *et al.*<sup>3</sup> The calculations performed in this work for Ar-benzene are in very good agreement with the previous ones<sup>18</sup> and are listed in Table VII, together with those of  $^{20}\text{Ne}$ -benzene and  $^{84}\text{Kr}$ -benzene, and compared with the available experimental data.<sup>4,6,10</sup> All the states present a regular ordering for the different systems and their nature was discussed previously.<sup>10,18</sup> The good agreement obtained between the experimental and theoretical values using the empirical PES of Brupbacher *et al.*<sup>3</sup> suggests that the high resolution microwave spectra can provide a good description of the well up to a relatively high energy, at least for  $\approx 100 \text{ cm}^{-1}$  for the case of Ar-benzene, that represents approximately a third of the binding energy.

The first van der Waals levels of the complexes of cyclopropane are listed in Table VIII. The first two states,  $A'_1$  and  $A''_2$ , are nearly degenerated and are even and odd states with respect to the reflection in the  $x$ - $y$  body-fixed plane, the carbon ring plane. The small separation between them arises from the tunneling around the plane, as it was discussed above, and it is a consequence of the low barrier for inversion appearing in complexes of cyclopropane. The planar

configuration is stabilized by the interaction of the rare-gas atoms with hydrogen atoms which produces a relatively deep well for the rare-gas atom in the plane and  $\phi = \pi/3 + n\pi/3$ , i.e., the middle of the C-C bond (as it is shown in Fig. 3).

The first excited van der Waals states are over the inversion barrier, and the ring-plane-tunneling pairs split, so that the energy difference between them ( $A'_1 - A''_2$ ,  $A''_2 - A'_1$  and  $E' - E''$ ) becomes of several  $\text{cm}^{-1}$ . These excited states are mainly located in the three symmetric wells appearing in the  $x$ - $y$  body-fixed plane, between two carbon atoms of the ring. This is the reason why a new quasidegeneracy appears between one  $A'_1$  and two  $E'$  states (or equivalently one  $A''_2$  and two  $E''$ ) which are symmetric under reflection in the  $x$ - $y$  plane (or antisymmetric). The first excited  $A'_1$  state of Ar-cyclopropane, in Fig. 5, clearly shows that the larger amplitude of the wave functions is located in the plane, between two carbon atoms, and the two  $E'$  states show an equivalent situation. These quasidegenerate triplets can be constructed as linear combinations of three zero-order states, each one located in one of the three potential wells in the plane. The small splitting between the nondegenerate  $A'_1$  state and the

TABLE VIII. Van der Waals vibrational frequencies for the first excited states of the complexes of cyclopropane and  $J=0$ . The binding energies of the  $X$ -cyclopropane complexes are 132.36, 311.00 and 365.24  $\text{cm}^{-1}$  for  $^{20}\text{Ne}$ , Ar and  $^{84}\text{Kr}$ , respectively. The  $A'_1$ ,  $A''_2$  and  $E'$  representation are symmetric under reflection in the  $x$ - $y$  plane, while the  $A''_1$ ,  $A''_2$  and  $E''$  are antisymmetric.

$^{20}\text{Ne}$ -cyclopropane		$^{40}\text{Ar}$ -cyclopropane		$^{84}\text{Kr}$ -cyclopropane	
$\Gamma(D_{3h})$	$\Delta E/\text{cm}^{-1}$	$\Gamma(D_{3h})$	$\Delta E/\text{cm}^{-1}$	$\Gamma(D_{3h})$	$\Delta E/\text{cm}^{-1}$
$A'_1$	0	$A'_1$	0	$A'_1$	0
$A''_2$	$1 \times 10^{-4}$	$A''_2$	$2 \times 10^{-6}$	$A''_2$	$2 \times 10^{-7}$
$E'$	16.01	$A'_1$	6.52	$A'_1$	14.18
$A'_1$	16.10	$E'$	6.55	$E'$	14.21
$E''$	20.34	$A''_2$	24.54	$A''_2$	31.15
$A''_2$	21.41	$E''$	24.57	$E''$	31.19
$E'$	23.67	$E'$	40.30	$A'_1$	40.25
$A'_1$	26.33	$A'_1$	40.33	$A''_2$	40.27
$E''$	26.40	$E'$	41.17	$E'$	45.06
$A''_2$	30.20	$A''_2$	43.43	$E''$	45.39
$E'$	33.00	$A'_1$	43.68	$A'_1$	46.62
$A'_1$	34.78	$E''$	43.99	$E'$	47.06

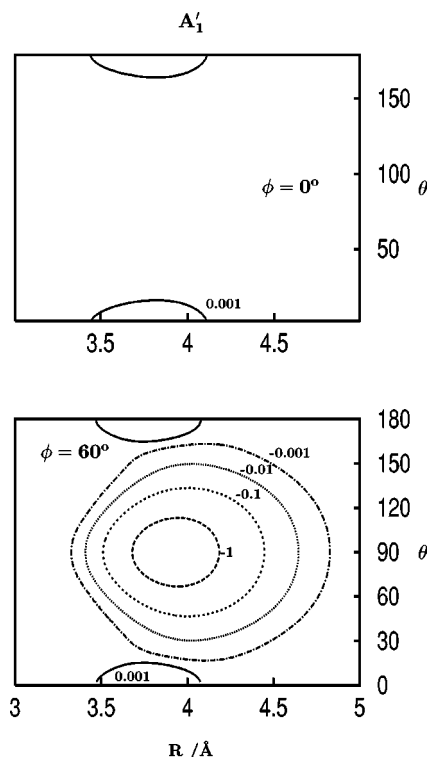


FIG. 5. Contour plots of the amplitude of the first excited  $A_1'$  wave function (of energy  $6.52 \text{ cm}^{-1}$  in Table VIII) of  $^{40}\text{Cyclopropane}$  for  $\phi=0$  and  $\pi/3$ .

two degenerate  $E'$  states arises from a probability of passing from one well to the next one, both of them in the plane, and it is a second kind of tunneling in the cyclopropane complexes.

The excited states of all these complexes spread over a wide region of the configuration space. Therefore, the experimental measurement of the intramolecular spectra of these complexes would provide important information of the PES's in a large region, and not only in the region of the potential well around the equilibrium configuration, as is the case of Ar-benzene. All the motions in the complexes of cyclopropane are strongly mixed, which makes it difficult to assign a characteristic frequency to each individual coordinate.

## V. CONCLUSIONS

In this work, empirical potential energy surfaces are presented for complexes of cyclopropane with several rare-gas atoms. The functional form of the PES's is based on pairwise Lennard-Jones-type functions which have been widely used to describe the van der Waals interaction between rare-gas atoms and aromatic molecules. Three-body terms are expected to have a rather small contribution because cyclopropane is only weakly aromatic, while for complexes of benzene they are important.<sup>3,13</sup> The parameters of the PES's presented in this work were obtained by fitting to high resolution microwave spectra recently reported by Xu and Jäger.<sup>20</sup> To this end, a numerical procedure was developed, based on the Lanczos algorithm and taking into account the full symmetry of these complexes. It has been checked in benzene complexes and allows the accurate calculation of the

bound states of the complexes at  $J>0$ , including Coriolis couplings, where standard diagonalization schemes become unfeasible. Moreover, the potential is expanded in a Fourier series analytically for the functional form chosen, which provides an improvement of the numerical accuracy.

The observed splitting in the microwave spectra of Ne-cyclopropane<sup>20</sup> was reasonably reproduced and is a consequence of the rotational tunneling around the carbon ring of cyclopropane, between two carbon atoms. The ground and first excited van der Waals levels, corresponding to symmetric and antisymmetric states with respect to the reflection in the carbon plane, are separated by only  $\approx 10^{-4} \text{ cm}^{-1}$ . Ar and Kr complexes also show tunneling splitting, but much smaller, which explains why this effect was not experimentally observed. On the contrary, complexes of benzene do not show such a tunneling process probably because the carbon ring is significantly larger and, mainly, because the presence of hydrogen atoms in parallel rings to the carbon one in the case of cyclopropane yields significant differences. This arrangement stabilizes configurations of the complexes in which the rare-gas atom lies in the carbon ring plane, mainly between two carbon atoms.

Similar rotational tunneling effects have been theoretically predicted in some endohedral fullerene  $C_{60}$  complexes<sup>36-39</sup> where the rotational ground state splits in a quasiband composed of 20 rotational states, because there are 20 hexagon wells in the PES used.

The excited van der Waals states for complexes of cyclopropane are above the rotational barrier and, therefore, their probability density is distributed in a wide region of the configuration space. In particular, there is an important probability of finding the rare-gas atom in the carbon ring plane, distributed in the three symmetric wells of the potential placed between two carbon atoms. For this reason, the excited van der Waals states are grouped in triplets, which correspond to three nearly degenerate states (either  $A_1', E'$  or  $A_2', E''$  which are symmetric or antisymmetric under reflection in the  $x$ - $y$  plane, respectively). The small shift in the triplets between the two degenerate states and the nondegenerate state is evidence of a second kind of rotational tunneling. It would be desirable to perform intramolecular spectroscopy studies<sup>5</sup> on these clusters to check the validity of the PES's obtained in this work from high resolution microwave spectra. The success of the empirical PES obtained from microwave spectra<sup>3</sup> may lie in the fact that all the complexes between rare-gas atoms and benzene are well located at the equilibrium configuration. Since the bound states of complexes of cyclopropane spread over a larger region of the configuration space, the adequacy of the empirical PES's determined in this work could be analyzed. Such studies would help to establish the role of three-body terms in the rare-gas atom-cyclopropane clusters and, by comparing with the available data on benzene complexes, in aromatic clusters in general.

## ACKNOWLEDGMENTS

This work has been supported by Consejería de Educación, Cultura y Deportes del Gobierno de Canarias under

Grant No. PI 2/95, DGYCIT(Spain) under Grant No. PB95-0071, and by the European TMR network Contract No. ERBFMRX-CT96-0088.

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