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Vibrational predissociation of $\text{He-I}_2^*(\nu)\text{-Ne}$: An approximate quantal study^{a)}

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The vibrational predissociation (VP) of the $\text{He-I}_2(B^3\Pi_{0_u^+}, \nu)\text{-Ne}$ complex is studied in the range of initial vibrational excitations $25 \leq \nu \leq 35$. The rare gas atoms are restricted to move on a perpendicular plane to the I_2 axis. A simple addition of pairwise Morse atom-atom interactions is used to describe the potential energy surface. The breaking up of the $\text{I}_2\text{-Ne}$ bond is found to be the dominant dissociation channel for $\nu \leq 29$. However, due to the anharmonicity of the I_2 stretch, the situation for $\nu > 29$ is just the opposite and the He atom escapes first.

I. INTRODUCTION

Energetics and dynamics of van der Waals (vdW) complexes is a field of current interest. In particular, the VP of these molecules provides a clear example of intramolecular energy redistribution on a single potential energy surface. Most of the experimental and theoretical studies on VP of vdW molecules have been devoted to rare gas atom-diatomic molecule systems^{1,2} but nowadays complexes with one vdW bond and several chemical bonds are receiving an increasing attention.^{3,4} Besides the study of this class of molecules it is also relevant to deal with those systems presenting one chemical bond and two or more weak bonds in order to elucidate the competition in the flowing of energy from the excited stable subunit to each weak bond, i.e., the branching ratios among the different dissociative channels, together with its dependence on the initial excitation in the chemical bond. In this context, some experimental⁵ and theoretical^{6(a)-8} studies have been done on the dissociation dynamics of vibrational excited complexes of I_2 with two or more rare gas atoms.

In this paper we present an approximate quantal treatment on VP of the $\text{He-I}_2^*(\nu)\text{-Ne}$ complex, where the I_2 is vibrationally excited in the $B^3\Pi_{0_u^+}$ electronic state. As it is widely realized, a full quantal treatment of the four-body system becomes prohibitively difficult^{6(a)} and, hence, it may be useful to explore new methods^{6b} or to reduce the dimensionality of the problem still describing the main physical features of the process. Thus, we have recently performed quasiclassical trajectory calculations^{7,8} as well as approximate quantal ones⁸ on the $\text{He-I}_2^*\text{-Ne}$ complex assuming a coplanar configuration.⁸ However, we can consider a more realistic situation. Since the perpendicular configuration is the most probable for each triatomic X-I_2^* molecule, $\text{X} = \text{He},^9 \text{Ne},^{10}$ and the rotational constants associated to I_2^* ($B_e \sim 0.04 \text{ cm}^{-1}$), Ne-I_2^* ($\sim 0.05 \text{ cm}^{-1}$), and He-I_2^* ($\sim 0.3 \text{ cm}^{-1}$) are really low, we assume a particular configuration in which the He and Ne atoms are restricted to move on a perpendicular plane to the axis of the (nonrotating) I_2 molecule. In this way, four motions are accounted for within the complex: the stretching of I_2 , the vibrations of He and Ne

with respect to the center of mass of I_2 and also the oscillation (bending) of the angle formed by both weak bonds, γ . Taking advantage of the large vibrational spacing of the I_2 molecule, at least for low and medium excitations $\nu \leq 40$, we apply then a diabatic distorted-wave approximation to describe diatomic vibrations in such a way that the original problem is reduced to an effective three-body one. It may be considered like constituted by two light atoms, He and Ne plus a heavy "atom," I_2 , for which an adiabatic angular treatment¹¹ becomes particularly adequate. Then, following closely the spirit of an "infinite order sudden" approximation successfully employed to study VP of He-I_2^* ,¹² we estimate via Fermi's golden rule VP rates for breaking one vdW bond as functions of the initial excitation of I_2 and γ . Finally, these rates are properly averaged by means of the angular functions associated to the bending motion in γ .

The paper is organized as follows. Section II is devoted to show the theoretical treatment for VP of a tetraatomic X-BC-Y complex in the particular configuration already mentioned. In Sec. III, together with the description of the potential energy surface used, we show the details of the calculations carried out and the results obtained. In a separate Appendix, a full solution of the effective triatomic discrete problem within the adiabatic angular approximation is presented.

II. THEORETICAL TREATMENT

After separation of the center of mass motion of the whole system the Hamiltonian function for the X-BC-Y complex, where the rare gas atoms X and Y are restricted to move on a perpendicular plane to the nonrotating BC molecule, may be written¹³

$$H = \frac{P_r^2}{2m} + \frac{\mathbf{P}_1^2}{2\mu_1} + \frac{\mathbf{P}_2^2}{2\mu_2} + \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{\mathcal{M}} + V(r, R_1, R_2, \gamma), \quad (1)$$

where r is the BC bondlength with conjugate momentum P_r , $\mathbf{R}_1$ and $\mathbf{R}_2$ are vectors going from the BC center of mass to the X and Y atoms, respectively, with conjugate momenta $\mathbf{P}_1$ and $\mathbf{P}_2$. In Eq. (1), $\mathcal{M} = m_B + m_C$ is the total BC mass while $m = m_B m_C / \mathcal{M}$, $\mu_1 = m_X \cdot \mathcal{M} / (m_X + \mathcal{M})$ and $\mu_2 = m_Y \cdot \mathcal{M} / (m_Y + \mathcal{M})$ are reduced masses. Finally, V de-

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scribes the potential energy function depending on the distances r , R_1 , R_2 and also on the angle γ formed by $\mathbf{R}_1$ and $\mathbf{R}_2$. Due to the weakness of the van der Waals interactions, V is represented by the sum of the potential for the isolated BC molecule, the potentials for T-shaped X-BC and Y-BC triatomic molecules plus the X-Y interaction,

$$V = V_{\text{BC}}(r) + V_{\text{X-BC}}(r, R_1) + V_{\text{Y-BC}}(r, R_2) + V_{\text{X-Y}}(R_1, R_2, \gamma). \quad (2)$$

By expressing the momentum operators in terms of the corresponding gradients, the Hamiltonian (1) can be rewritten (in atomic units) as

$$H = -\frac{1}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{1}{2\mu_1} \left(\frac{\partial^2}{\partial R_1^2} + \frac{2}{R_1} \frac{\partial}{\partial R_1} \right) - \frac{1}{2\mu_2} \left(\frac{\partial^2}{\partial R_2^2} + \frac{2}{R_2} \frac{\partial}{\partial R_2} \right) + \frac{j_1^2}{2\mu_1 R_1^2} + \frac{j_2^2}{2\mu_2 R_2^2} + \frac{1}{\mathcal{M}} \left(-\frac{\partial^2}{\partial R_1 \partial R_2} \hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2 - \frac{1}{R_1 R_2} \nabla_{\theta_1 \varphi_1} \cdot \nabla_{\theta_2 \varphi_2} - \frac{1}{R_1} \hat{\mathbf{R}}_2 \cdot \nabla_{\theta_1 \varphi_1} \frac{\partial}{\partial R_2} - \frac{1}{R_2} \hat{\mathbf{R}}_1 \cdot \nabla_{\theta_2 \varphi_2} \frac{\partial}{\partial R_1} \right) + V, \quad (3)$$

where $\hat{\mathbf{R}}_k = \mathbf{R}_k/R_k$ is the unit vector in the $\mathbf{R}_k$ direction, $\nabla_{\theta_k \varphi_k}/R_k$ is the tangential component of the gradient, while $\mathbf{j}_k = -i\hat{\mathbf{R}}_k \times \nabla_{\theta_k \varphi_k}$ is the angular momentum operator associated to $\mathbf{R}_k$, $k = 1, 2$. The kinetic part of this Hamiltonian contains pure vibrational and rotational terms in the different bonds as well as several coupling terms with the inverse of the total BC mass, $1/\mathcal{M}$, as a common factor. Obviously, for heavy diatomic molecules, these kinetic couplings may be neglected, but we will retain them for possible future applications.

In order to solve the Schrödinger equation

$$H\psi(r, \mathbf{R}_1, \mathbf{R}_2) = E\psi(r, \mathbf{R}_1, \mathbf{R}_2)$$

we take advantage of the usual large vibrational spacing of BC to write the total wave function in the diabatic vibrational approximation,

$$\psi(r, \mathbf{R}_1, \mathbf{R}_2) \simeq \psi_v(r, \mathbf{R}_1, \mathbf{R}_2) = \frac{1}{r} \chi_v(r) \phi^{(v)}(\mathbf{R}_1, \mathbf{R}_2), \quad (4)$$

where χ_v is an eigenfunction of the isolated BC vibrator with associated eigenvalue E_{BC}^v ,

$$\left[-\frac{1}{2m} \frac{\partial^2}{\partial r^2} + V_{\text{BC}}(r) \right] \chi_v(r) = E_{\text{BC}}^v \chi_v(r) \quad (5)$$

and $\phi^{(v)}(\mathbf{R}_1, \mathbf{R}_2)$ satisfies the equation

$$\left[-\frac{1}{2\mu_1} \left(\frac{\partial^2}{\partial R_1^2} + \frac{2}{R_1} \frac{\partial}{\partial R_1} \right) - \frac{1}{2\mu_2} \left(\frac{\partial^2}{\partial R_2^2} + \frac{2}{R_2} \frac{\partial}{\partial R_2} \right) + \frac{j_1^2}{2\mu_1 R_1^2} + \frac{j_2^2}{2\mu_2 R_2^2} + \frac{1}{\mathcal{M}} \left(-\frac{\partial^2}{\partial R_1 \partial R_2} \cos \gamma - \frac{1}{R_1 R_2} \nabla_1 \cdot \nabla_2 - \frac{1}{R_1} \hat{\mathbf{R}}_2 \cdot \nabla_1 \frac{\partial}{\partial R_2} - \frac{1}{R_2} \hat{\mathbf{R}}_1 \cdot \nabla_2 \frac{\partial}{\partial R_1} \right) + V_{vv}(R_1, R_2, \gamma) \right] \phi^{(v)}(\mathbf{R}_1, \mathbf{R}_2) = (E - E_{\text{BC}}^v) \phi^{(v)}(\mathbf{R}_1, \mathbf{R}_2), \quad (6)$$

where we have replaced the subscripts θ_k, φ_k in the tangential gradient components by $k, k = 1, 2$, and where $V_{vv} = \langle \chi_v(r) | V(r, R_1, R_2, \gamma) | \chi_v(r) \rangle$ is the averaged potential

$$V_{vv} = V_{\text{X-BC}}^{(v,v)}(R_1) + V_{\text{Y-BC}}^{(v,v)}(R_2) + V_{\text{X-Y}}. \quad (7)$$

It is important to underline at this point that by considering the particular configuration of the complex, already mentioned at the beginning of this section, and by further applying the diabatic vibrational approximation, Eq. (4), the original four-body problem has been reduced to an effective three-body one, Eq. (6). The approach is reasonable for a system like He-I₂-Ne in which the most probable configuration of each triatomic subsystem is the perpendicular one^{9,10} with very low rotational constants associated to I₂, $\sim 0.04 \text{ cm}^{-1}$, Ne-I₂, $\sim 0.05 \text{ cm}^{-1}$, and He-I₂, $\sim 0.3 \text{ cm}^{-1}$, and a high enough stretching frequency of the diatomic subunit I₂, $\sim 125 \text{ cm}^{-1}$. Moreover, due to the difference existing between the stretching frequencies associated to Ne-I₂ and He-I₂, ~ 25 and 16 cm^{-1} , respectively, and to He-Ne,

$\sim 5 \text{ cm}^{-1}$, that is directly related to the oscillation in the angle γ , we write the function $\phi^{(v)}$ in the adiabatic angular approximation¹⁵

$$\phi^{(v)}(\mathbf{R}_1, \mathbf{R}_2) = \frac{1}{R_1 R_2} \varphi_v(R_1, R_2, \gamma) F^{(v)}(\mathbf{R}_1, \mathbf{R}_2), \quad (8)$$

where $F^{(v)}$ is a pure rotational function while φ_v is a radial function that depends parametrically on γ and is assumed to be transparent to the action of the angular operators. It is a solution of

$$\left[-\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} - \frac{\cos \gamma}{\mathcal{M}} \frac{\partial^2}{\partial R_1 \partial R_2} + V_{vv}(R_1, R_2, \gamma) \right] \varphi_v(R_1, R_2, \gamma) = \epsilon \varphi_v(R_1, R_2, \gamma). \quad (9)$$

This equation has discrete as well as continuum solutions. In the first case, the function φ depends on an additional quantum number k necessary to specify the two-dimensional stretching problem, while the associated eigenvalue ϵ becomes an angular dependent function $W_k^{(v)}(\gamma)$. This kind of solution can be efficiently obtained by expanding the function φ in terms of products of triatomic stretching functions,⁸ i.e.,

$$\varphi_{vk}^{\text{dis}}(R_1, R_2; \gamma) = \sum_{mn} a_{mn}^{(v,k)}(\gamma) \xi_m^{(v)}(R_1) \eta_n^{(v)}(R_2), \quad (10)$$

where ξ and η are discrete solutions of

$$H_{mn; m'n'}^{(v)}(\gamma) = [E_{X-BC}^{(v,m)} + E_{Y-BC}^{(v,n)}] \delta_{mm'} \delta_{nn'} - \frac{\cos \gamma}{\mathcal{M}} \left[\frac{\langle \xi_m^{(v)} | dV_{X-BC}^{(v,v)}(R_1)/dR_1 | \xi_{m'}^{(v)} \rangle}{E_{X-BC}^{(v,m)} - E_{X-BC}^{(v,m')}} (1 - \delta_{mm'}) \right. \\ \left. \times \frac{\langle \eta_n^{(v)} | dV_{Y-BC}^{(v,v)}(R_2)/dR_2 | \eta_{n'}^{(v)} \rangle}{E_{Y-BC}^{(v,n)} - E_{Y-BC}^{(v,n')}} (1 - \delta_{nn'}) \right] + \langle \xi_m^{(v)} \eta_n^{(v)} | V_{X-Y} | \xi_{m'}^{(v)} \eta_{n'}^{(v)} \rangle. \quad (13)$$

We now consider for each value of the γ angle the continuum states which describe the rare gas atom X plus a triatomic fragment Y-BC in a given stretching n'' state, where the diatomic subunit is in a lower $v' < v$ vibrational level, as a product

$$\varphi_{v'\epsilon_1 n''}^{\text{cont}, X}(R_1, R_2; \gamma) = \xi_{\epsilon_1}^{(v', n'')}(R_1; \gamma) \eta_{n''}^{(v')}(R_2), \quad (14)$$

where η is defined by Eq. (12) and ξ fulfills the equation

$$\left[-\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} + V_{X-BC}^{(v', v')}(R_1) + \langle \eta_{n''}^{(v')}(R_2) | V_{X-Y}(R_1, R_2, \gamma) | \eta_{n''}^{(v')}(R_2) \rangle - \epsilon_1 \right] \\ \times \xi_{\epsilon_1}^{(v', n'')}(R_1; \gamma) = 0 \quad (15)$$

in which ϵ_1 is the kinetic energy between the fragments. In a similar way, we may describe continuum states at each γ angle corresponding to Y plus X-BC as

$$\varphi_{v'\epsilon_2 m''}^{\text{cont}, Y}(R_1, R_2; \gamma) = \xi_{m''}^{(v')}(R_1) \eta_{\epsilon_2}^{(v', m'')}(R_2; \gamma), \quad (16)$$

where ξ is defined by Eq. (11) and η is a solution of

$$\left[-\frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} + V_{Y-BC}^{(v', v')}(R_2) + \langle \xi_{m''}^{(v')}(R_1) | V_{X-Y}(R_1, R_2, \gamma) | \xi_{m''}^{(v')}(R_1) \rangle - \epsilon_2 \right] \\ \times \eta_{\epsilon_2}^{(v', m'')}(R_2; \gamma) = 0. \quad (17)$$

By using Fermi's golden rule, two different γ -dependent half-widths for vibrational predissociation of X-BC(v)-Y in a given k state may be calculated. For breaking up the X-BC bond we have

$$\Gamma_{vk}^X(\gamma) = \pi \sum_{v' < v} \sum_{n''} |\langle \varphi_{vk}^{\text{dis}} | \langle \chi_v | V | \chi_{v'} \rangle | \varphi_{v'\epsilon_1 n''}^{\text{cont}, X} \rangle|^2 \\ = \pi \sum_{v' < v} \sum_{n''} \left| \sum_{m, n} a_{mn}^{(v,k)}(\gamma) \right. \\ \times [\langle \eta_n^{(v)} | \eta_{n''}^{(v')} \rangle \langle \xi_m^{(v)} | V_{X-BC}^{(v, v')} | \xi_{\epsilon_1}^{(v', n'')} \rangle \\ \left. + \langle \xi_m^{(v)} | \xi_{\epsilon_1}^{(v', n'')} \rangle \langle \eta_n^{(v)} | V_{Y-BC}^{(v, v')} | \eta_{n''}^{(v')} \rangle \right]|^2, \quad (18)$$

$$\left[-\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} + V_{X-BC}^{(v, v)}(R_1) \right] \xi_m^{(v)}(R_1) \\ = E_{X-BC}^{(v, m)} \xi_m^{(v)}(R_1) \quad (11)$$

and

$$\left[-\frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} + V_{Y-BC}^{(v, v)}(R_2) \right] \eta_n^{(v)}(R_2) \\ = E_{Y-BC}^{(v, n)} \eta_n^{(v)}(R_2), \quad (12)$$

respectively. The desired eigenvalues $W_k^{(v)}(\gamma)$ together with the coefficients $a_{mn}^{(v,k)}(\gamma)$ of Eq. (10) arise thus from a simple diagonalization of the following matrix:

where the continuum wave functions $\xi_{\epsilon_1}^{(v', n'')}(R_1; \gamma)$ are calculated on the energy shell, i.e.,

$$\epsilon_1 = (E_{BC}^v - E_{BC}^{v'}) + W_k^{(v)}(\gamma) - E_{Y-BC}^{(v', n'')}.$$

Similarly, for breaking up the Y-BC bond we have

$$\Gamma_{vk}^Y(\gamma) = \pi \sum_{v' < v} \sum_{m''} |\langle \varphi_{vk}^{\text{dis}} | \langle \chi_v | V | \chi_{v'} \rangle | \varphi_{v'\epsilon_2 m''}^{\text{cont}, Y} \rangle|^2 \\ = \pi \sum_{v' < v} \sum_{m''} \left| \sum_{m, n} a_{mn}^{(v,k)}(\gamma) \right. \\ \times [\langle \xi_m^{(v)} | \xi_{m''}^{(v')} \rangle \langle \eta_n^{(v)} | V_{Y-BC}^{(v, v')} | \eta_{\epsilon_2}^{(v', m'')} \rangle \\ \left. + \langle \eta_n^{(v)} | \eta_{\epsilon_2}^{(v', m'')} \rangle \langle \xi_m^{(v)} | V_{X-BC}^{(v, v')} | \xi_{m''}^{(v')} \rangle \right]|^2, \quad (19)$$

with $\epsilon_2 = (E_{BC}^v - E_{BC}^{v'}) + W_k^{(v)}(\gamma) - E_{X-BC}^{(v', m'')}.$

Therefore in the frame of the angular adiabatic approximation applied here we obtain half-widths for VP of X-BC-Y as functions of the angle γ . Following closely the treatment already used to study the VP of the He I₂ van der Waals molecule,¹² we need to solve fully the discrete problem calculating the rotational functions $F^{(v)}(\hat{R}_1, \hat{R}_2)$ of Eq. (8) that are now labeled by the quantum numbers v and k , associated to the stretching motions, and a third quantum number l associated to the bending motion in γ . This is presented in the Appendix. For a tetraatomic level specified by (v, k, l) we may estimate the associated VP rates as the following averages:

$$\Gamma_{vkl}^X = \langle F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2) | \Gamma_{vk}^X(\gamma) | F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2) \rangle, \quad (20)$$

$$\Gamma_{vkl}^Y = \langle F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2) | \Gamma_{vk}^Y(\gamma) | F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2) \rangle, \quad (21)$$

and the total rate for VP of the complex becomes

$$\Gamma_{vkl} = \Gamma_{vkl}^X + \Gamma_{vkl}^Y. \quad (22)$$

It is interesting to point out that, in fact, this treatment considers that the breaking of the complex is sequential,⁸ i.e., either X escapes first or Y does, but the possibility of escaping both at the same time is not accounted for. The approach may be accurate when there is a large difference between the rates Γ^X and Γ^Y . However, because these quantities strongly

depend on the initial vibrational excitation of BC, it is possible that they become very close and then it would be important to take into account the interference between both reaction channels.

III. POTENTIAL ENERGY SURFACE: CALCULATIONS AND RESULTS

A. Potential surface

As it was already pointed out, the potential energy surface used here corresponding to the He-I₂(*B*)-Ne system is represented by the addition of a diatomic potential describing an isolated I₂(*B*) molecule, two triatomic vdW potentials for the T-shaped He-I₂(*B*) and Ne-I₂(*B*) molecules, and the weak He-Ne interaction, see Eq. (2),

$$V(r, R_1, R_2, \gamma) = V_{I_2}(r) + V_{He-I_2}(r, R_1) + V_{Ne-I_2}(r, R_2) + V_{He-Ne}(d), \quad (23)$$

where $d = (R_1^2 + R_2^2 - 2R_1R_2 \cos \gamma)^{1/2}$ is the He-Ne distance. Furthermore, the triatomic vdW potentials are written down in the dumbbell approximation,⁹

$$\begin{aligned} V_{He-I_2}(r, R_1) &= 2V_{He-I}(\rho_1), \\ V_{Ne-I_2}(r, R_2) &= 2V_{Ne-I}(\rho_2) \end{aligned} \quad (24)$$

with $\rho_i = (R_i^2 + r^2/4)^{1/2}$ being the distances of He(*i* = 1) and Ne(*i* = 2) to each I atom, respectively. Hence, the potential (2) consists of the simple sum of atom-atom pairwise potentials,

$$V = V_{I_2}(r) + 2V_{He-I}(\rho_1) + 2V_{Ne-I}(\rho_2) + V_{He-Ne}(d). \quad (25)$$

We represent each iteration in Eq. (25) by a Morse function

$$V(q) = D[1 - \exp[\alpha(q_{eq} - q)]]^2 - D, \quad (26)$$

where $q = (r, \rho_1, \rho_2, d)$ is the interatomic distance with equilibrium value q_{eq} , D is the well depth, and α the characteristic inverse length. The values of these parameters are the same previously used (see Table I in Ref. 8). In order to calculate the necessary integrals involving diatomic vibrational wave functions, we have performed Taylor expansions of V_{He-I} , V_{Ne-I} around r_{eq} up to the fourth order,

$$V_{He-I} \simeq \sum_{s=0}^4 \frac{(r - r_{eq})^s}{s!} \left(\frac{\partial^s V_{He-I}}{\partial r^s} \right)_{r=r_{eq}}, \quad (27)$$

and a similar expression for V_{Ne-I} .

B. Details of the calculations

Twenty-one values of the angle γ equally spaced in the range $[0, \pi]$ have been taken into account. With the exception of those integrals involving angular functions, that were analytically evaluated, all the integrations needed in this work were performed using a $h/3$ Simpson rule, with h being the integration step. Considering a regular grid of 2000 points in the range $[1, 10]$ Å, vibrational diatomic energies and wave functions, Eq. (5), were obtained by means of an efficient mixed Truhlar-Numerov numerical procedure.²⁰ It has also been applied to solve the discrete triatomic problems, Eqs. (11) and (12). To this end, 1041 points in the range $[2.5, 15]$ Å were considered for R_1 , while 1400 points

in the range $[2.6, 20]$ Å were used for R_2 . As regards the double integrals appearing in Eq. (13), we have considered the He-Ne interaction as negligible for interatomic distances larger than 15 Å. Thus, for each R_1 value within its range, we carried out the integration in R_2 according to that constraint, that allowed us in general to consider a narrower range than 17.4 Å yielding an enhancement of efficiency in the calculation.

Concerning the continuum functions, Eqs. (15) and (17), they were also numerically obtained through a Fox-Numerov propagating method of the solution and matching of it to a sinus behavior at long distances.²¹

Expansion of γ -dependent functions in terms of Legendre polynomials were done by a collocation procedure, and a standard Jacobi method was applied to carry out the necessary diagonalizations.

C. Results

In the range of initial vibrational excitations of I₂ $25 \leq v \leq 35$, the T-shaped molecules, He-I₂ and Ne-I₂, show two and five discrete levels, respectively. Due to the presence of the effective averaged potentials $V_{He-I_2}^{(v,v)}$ and $V_{Ne-I_2}^{(v,v)}$ in Eqs. (11) and (12), a slight variation of the corresponding energies as functions of v was found. In Table I we list these energy levels for $v = 25$. When we compare the values of the respective ground energies with those of Table II in Ref. 8, a discrepancy of $\sim 1\%$ – 2% can be observed. This difference arises since only the first term of expansion (27) was considered in that work, i.e., $V_{He-I_2}^{(v,v)} \simeq 2V_{He-I}(r_{eq}, R_1)$.

For the same diatomic vibrational level, $v = 25$, the effective angular potentials $W_k^{(v=25)}(\gamma)$, $k = 0, 1$, obtained after diagonalization of matrix (13), are plotted in Fig. 1 vs γ . As expected, due to the large value of mass $\mathcal{M}$ ($= 254$ amu), the matrix elements described in Eq. (13), are almost reduced to the first and last terms, i.e., to the (diagonal) addition of triatomic energies plus the coupling through the He-Ne interaction. Hence, for the lowest eigenvalue $k = 0$, the function $W_0^{(25)}(\gamma)$ becomes

$$W_0^{(25)}(\gamma) \simeq E_{He-I_2}^{(25,0)} + E_{Ne-I_2}^{(25,0)} + V_{He-Ne}(\bar{R}_1, \bar{R}_2, \gamma)$$

showing a minimum at $\gamma = \pi/4$ with a value (in cm^{-1}),

$$\begin{aligned} W_0^{(25)}(\pi/4) &= -98.89 \simeq -18.37 - 71.24 - D_{He-Ne} (= 9.94) \\ &= 99.55 \end{aligned}$$

corresponding to the equilibrium in the He-Ne potential. For $k = 1$, the behavior is similar and we may recognize that

TABLE I. Energy levels (cm^{-1}) of the T-shaped triatomic molecules He-I₂ and Ne-I₂. They correspond to an initial vibrational excitation $v = 25$ of I₂.

He-I ₂	<i>m</i>	Ne-I ₂	<i>n</i>
-18.37	0	-71.24	0
-1.97	1	-45.81	1
...	...	-25.88	2
...	...	-11.52	3
...	...	-2.84	4

FIG. 1. Effective angular potentials $W_k^{v=25}(\gamma)$ for the ground ($k=0$) and first excited ($k=1$) stretching states in the full range $0 < \gamma < 2\pi$ and tetraatomic bending energies, labeled here by (k,l) , obtained after diagonalization of Eq. (28) for a total angular momentum $J=0$. The angular dependent rates $\Gamma^{\text{He}}, \Gamma^{\text{Ne}}$ are also included for $k=0$ in the range $0 < \gamma < \pi$.

it corresponds to a stretching excitation in the He-I₂ bond,

$$W_1^{(25)}(\gamma) \approx E_{\text{He-I}_2}^{(25,1)} + E_{\text{Ne-I}_2}^{(25,0)} + \langle \xi_1^{(25)}(R_1) \eta_0^{(25)}(R_2) | V_{\text{He-Ne}}(R_1, R_2, \gamma) | \times \xi_1^{(25)}(R_1) \eta_0^{(25)}(R_2) \rangle$$

in such a way that, in the neighborhood of $\gamma = \pi$ for which the He-Ne potential becomes negligible, we have

$$W_1^{(25)}(\pi) = -73.52 \approx -1.97 - 71.24 = -73.21 \text{ cm}^{-1}.$$

Also in Fig. 1 we have included the van der Waals energy levels $E_{v=25,k,l}$ obtained after diagonalization of Eq. (28) for a total angular momentum $J=0$. To this end, a basis set of 25 rotational functions was used. The ground tetraatomic level, measured from the diatomic vibrational energy $E_{I_2}(25)$, is $E_{25,0,0} = -94.28 \text{ cm}^{-1}$ that roughly corresponds to the simple sum of the ground triatomic energies plus the unique level supported by the He-Ne potential. As can be seen, the ground bending level, $l=0$, corresponding to the first stretching excitation $k=1$, $E_{25,1,0} = -73.83 \text{ cm}^{-1}$, is found over the sixth bending excitation ($l=5$) in the ground level $k=0$, $E_{25,0,5} = -76.97 \text{ cm}^{-1}$, providing us an internal justification to the adiabatic angular approximation used here. In addition, the stretching excitation

$$E_{25,1,0} - E_{25,0,0} = 20.76 \text{ cm}^{-1}$$

is very close to the difference between the position in the fluorescence excitation spectrum reported by Kenny *et al.*,⁵ see Table I in that work for $v'=25$,

$$(I_2 \text{ NeHe}, \omega' = 1) - (I_2 \text{ NeHe})$$

$$= 30.86 - 10.77 = 20.09 \text{ cm}^{-1}$$

suggesting that the second observed peak, denoted there by $\omega' = 1$, mainly corresponds to a stretching excitation in the He-I₂ bond. On the other hand, the ground energy levels $E_{v,0,0}$ range from -94.28 cm^{-1} ($v=25$) up to -93.10 cm^{-1} ($v=35$) showing an increase blue shift in the direction of higher diatomic excitations that is in qualitative, and even quantitative, agreement with the experimental findings (for example, the difference in positions for the first level between $v'=26$ and $v'=16$ in Table I of Ref. 5 is $10.82 - 9.95 = 0.87 \text{ cm}^{-1}$, that may be compared with our result of $9.428 - 93.10 = 1.18 \text{ cm}^{-1}$ in the different range 25-35).

As regards the dynamical calculations, we have estimated VP rates for breaking the He-I₂ bond or the Ne-I₂ one for the ground tetraatomic stretching state $k=0$ and for the different diatomic excitations $v=25, 26, \dots, 35$. Corresponding to $v=25$, we have plotted also in Fig. 1 the functions $\Gamma_{25,0}^{\text{He}}(\gamma)$ and $\Gamma_{25,0}^{\text{Ne}}(\gamma)$ in the range $\gamma \in [0, \pi]$ (the corresponding values for $\gamma \in [\pi/2, \pi]$ are obviously symmetric). They were evaluated by means of Eqs. (18) and (19) including the exiting channels $v'=v-1$ and $v-2$. In fact, the importance of the $v-2$ channel in the rates was lower than 1% in all the cases, according to previous results⁶⁻⁸ and experimental data.⁵

On the other hand, Eqs. (18) and (19) involve all the allowed states of the exiting triatomic fragments. However, for the ground tetraatomic stretching level $k=0$, the dominant contribution arises from the triatomic ground states, i.e., the coefficients $a_{mn}^{(v,0)}$ in Eq. (10) for $m \neq 0$ or $n \neq 0$ are negligible ($a_{00}^{(v,0)} > 0.99$ at every angle). As an example, at $v=25$ and $\gamma = \pi/5$, the contribution of the excited states of Ne-I₂ ($v=24$) to Γ^{He} , and those of He-I₂ ($v=24$) to Γ^{Ne} is of $\sim 0.2\%$. Therefore, the breaking up of one vdW bond mainly yields a triatomic fragment in its ground level with the I₂ partner deexcited by one vibrational quantum.

Despite these angular dependent rates are physically meaningless, we can observe that the Ne rate is always higher than the He one. In particular, this fact holds in the region of the well where the corresponding values are mainly contributing to the (meaningful) averages of Eqs. (20) and (21). The same happens for $v=26, 27$, and 28 at every angle. However, for $v=29$, due to the anharmonicity of the I₂ potential, the $v-1$ channel for escaping Ne becomes energetically closed at $\gamma = \pi/4$ and the corresponding rate $\Gamma_{29,0}^{\text{Ne}}(\pi/4) = 0.86 \times 10^{-3} \text{ cm}^{-1}$ results smaller than $\Gamma_{29,0}^{\text{He}}(\pi/4) = 0.27 \text{ cm}^{-1}$. As v increases, the angular region for which only the $v-2$ channel contributes to Γ^{Ne} is wider and, finally, for $v \geq 34$ at all the angles $\gamma \geq \pi/4$, the Ne-I₂ bond needs two vibrational quanta to be broken. This behavior is reflected in the variation of the averaged rates in the ground state $k=l=0$, Eqs. (20) and (21), vs the initial diatomic excitation v , that are shown in Fig. 2. In the range $25 \leq v < 28$, $\Gamma_{v,0}^{\text{Ne}}$ is roughly two times $\Gamma_{v,0}^{\text{He}}$ and both show a superlinear increasing as v increases. Hence, the total rate $\Gamma_{v,0} = \Gamma_{v,0}^{\text{He}} + \Gamma_{v,0}^{\text{Ne}}$, that could be compared with possible experiments follows also a superlinear increasing with

FIG. 2. Averaged rates for escaping either the He atom or the Ne one by vibrational predissociation of the He-I₂(v)-Ne complex, together with the total rate, as functions of the initial vibrational excitation of the I₂ subunit.

$v \cdot \Gamma_{00}^{\text{He}}$ continues its tendency in the full range studied here, but Γ_{00}^{Ne} decreases sharply for $v > 28$ and, consequently, the total rate does. At $v = 29$, $\Gamma_{29,0,0}^{\text{Ne}} = 0.32 \text{ cm}^{-1}$ is still higher but very close to $\Gamma_{29,0,0}^{\text{He}} = 0.26 \text{ cm}^{-1}$, but at $v = 30$ the situation already changes and $\Gamma_{30,0,0}^{\text{Ne}} = 0.20 \text{ cm}^{-1}$ is smaller than $\Gamma_{30,0,0}^{\text{He}} = 0.29 \text{ cm}^{-1}$. Here on, the He atom clearly escapes first. For $v \geq 34$, the very small contribution of the two quanta channel to Γ^{Ne} yields a total rate that practically coincides with Γ^{He} .

IV. CONCLUDING REMARKS

We have presented an approximate quantal study of the vibrational predissociation of He-I₂(B,v)-Ne. The model applied rests on the assumption of a near-equilibrium possible geometry in which the rare gas atoms move on a perpendicular plane to the I₂ axis. At each relative orientation γ of the He-I₂ and Ne-I₂ bonds, we have calculated energy levels and rates for escaping He or Ne. Those become effective potentials for the bending motion in γ . Tetraatomic energy levels were then calculated, and the corresponding angular wave functions used to obtain averaged predissociation rates. For low diatomic initial excitations, $v \leq 28$, the breaking of the Ne-I₂ bond is more probable than the He-I₂, but this situation changes for $v \geq 31$ where Γ^{He} is higher than Γ^{Ne} . For $v = 29$ and 30, both rates are very close and, thus, the model used, that neglects the interference between both exiting channels, may yield wrong results. The consideration of such effect falls into a reactive problem that is, in fact, out of the scope of this work.

APPENDIX

We turn now to the determination of the rotational functions $F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2)$. Substituting φ in Eq. (8) by $\varphi_{vk}^{\text{dis}}$, Eq. (10), carrying the resulting expression for $\phi^{(v)}$ to Eq. (6), and taking into account the "transparency" of $\varphi_{vk}^{\text{dis}}$ to the action of the angular operators, we reach after multiplying by $R_1 R_2 \varphi_{vk}^{\text{dis}}$ and integrating over the radial variables¹¹ the following equation:

$$\left[\frac{1}{2\mu_1} \frac{1}{2} \{f_1^2, f_1^{(v,k)}(\gamma)\} + \frac{1}{2\mu_2} \frac{1}{2} \{f_2^2, f_2^{(v,k)}(\gamma)\} - \frac{1}{\mathcal{M}} \frac{1}{2} \{Q, f_{12}^{(v,k)}(\gamma)\} + W_k^{(v)}(\gamma) \right] F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2) = E_{vkl} F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2), \quad (\text{A1})$$

where

$$f_1^{(v,k)}(\gamma) = \sum_{m,m',n} a_{mn}^{(v,k)}(\gamma) a_{m'n}^{(v,k)}(\gamma) \langle \xi_m^{(v)} | R_1^{-2} | \xi_{m'}^{(v)} \rangle,$$

$$f_2^{(v,k)} = \sum_{m,n,n'} a_{mn}^{(v,k)}(\gamma) a_{mn'}^{(v,k)}(\gamma) \langle \eta_n^{(v)} | R_2^{-2} | \eta_{n'}^{(v)} \rangle,$$

$$f_{12}^{(v,k)}(\gamma) = \sum_{m,m',n,n'} a_{mn}^{(v,k)}(\gamma) a_{m'n'}^{(v,k)}(\gamma) \times \langle \xi_m^{(v)} | R_1^{-1} | \xi_{m'}^{(v)} \rangle \langle \eta_n^{(v)} | R_2^{-1} | \eta_{n'}^{(v)} \rangle,$$

$$Q = (\nabla_1 - \hat{R}_1) \cdot (\nabla_2 - \hat{R}_2) = \mathbf{q}_1 \cdot \mathbf{q}_2, \quad (\text{A2})$$

and $\{A, B\} = AB + BA$ stands for the usual anticommutator. Note that a trivial symmetrization has been included in order to overcome the noncommutativity among angular operators and γ -dependent functions.¹⁵⁻¹⁷ In this approach, the energy of a tetraatomic level specified by the quantum numbers v, k, l becomes

$$E(v, k, l) = E_{\text{BC}}^v + E_{vkl},$$

where E_{vkl} is the eigenvalue associated to $F_{kl}^{(v)}$.

For given values of the quantum numbers J and M , associated to the total angular momentum $\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$ and its third component in a space-fixed (SF) reference system, respectively, we expand the F function in terms of the basis set of Arthurs and Dalgarno¹⁴

$$F_{kl}^{(v)}(\hat{R}_1, \hat{R}_2) = \sum_{j_1, j_2} C_{j_1, j_2}^{(vkl)} \langle \hat{R}_1, \hat{R}_2 | JM j_1 j_2 \rangle, \quad (\text{A3})$$

where

$$\langle \hat{R}_1, \hat{R}_2 | JM j_1 j_2 \rangle = \sum_{m_1} (j_1, m_1, j_2, M - m_1 | j_1, j_2, J, M) \times Y_{j_1, m_1}(\theta_1, \varphi_1) Y_{j_2, M - m_1}(\theta_2, \varphi_2) \quad (\text{A4})$$

with $(j_1, m_1, j_2, M - m_1 | j_1, j_2, J, M)$ being Clebsch-Gordan coefficients and Y 's spherical harmonics in the notation of Edmonds.¹⁸ The basis functions $\langle \hat{R}_1, \hat{R}_2 | JM j_1 j_2 \rangle$ are eigenfunctions of J^2 , J_z , j_1^2 , and j_2^2 with corresponding eigenvalues (atomic units) $J(J+1)$, M , $j_1(j_1+1)$, and $j_2(j_2+1)$, respectively. The eigenvalues E_{vkl} together with the coefficients $C_{j_1, j_2}^{(vkl)}$, Eq. (A3), are simultaneously obtained by simple diagonalization of the Hamiltonian function appearing in Eq. (A1) once has been represented in the basis (31). To this end, we need to evaluate the matrix elements of the Q operator, Eq. (A2), as well as those of γ -dependent functions. For these last ones, let us call $G(\gamma)$ to one of them and consider the usual expansion in terms of Legendre polynomials:

$$G(\gamma) = \sum_{\lambda} g_{\lambda} P_{\lambda}(\cos \gamma)$$

then, we have¹⁹

$$\langle JMj_1j_2|G(\gamma)|JMj'_1j'_2\rangle = (-1)^{j_1+j'_1-J} [(2j_1+1)(2j'_1+1)(2j_2+1)(2j'_2+1)]^{1/2} \\ \times \sum_{\lambda} g_{\lambda} \begin{pmatrix} j'_1 & \lambda & j_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j'_2 & \lambda & j_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & j_2 & j_1 \\ \lambda & j'_1 & j'_2 \end{Bmatrix}, \quad (\text{A5})$$

where $\begin{pmatrix} \dots \end{pmatrix}$ and $\begin{Bmatrix} \dots \end{Bmatrix}$ are 3- j and 6- j symbols, respectively.¹⁸

As regards the Q operator, it is useful to introduce the spherical components of $\mathbf{q}_1$ and $\mathbf{q}_2$,

$$q_{k,\pm 1} = \mp \frac{1}{\sqrt{2}} (q_{k,x} \pm iq_{k,y}), \quad q_{k,0} = q_{k,z} \quad (k=1,2),$$

i.e., explicitly

$$q_{k,\mu} = \nabla_{k,\mu} - \left(\frac{4\pi}{3}\right)^{1/2} Y_{1\mu}(\theta_k, \varphi_k), \quad k=1,2, \quad \mu=0, \pm 1.$$

In this way we have

$$\langle JMj_1j_2|Q|JMj'_1j'_2\rangle = \sum_{m_1, m'_1} (j_1, m_1, j_2, M-m_1 | j_1, j_2, J, M) (j'_1, m'_1, j'_2, M-m'_1 | j'_1, j'_2, J, M) \\ \times \sum_{\mu=-1}^{+1} [(-1)^{\mu} \langle Y_{j_1 m_1} | q_{1, \mu} | Y_{j'_1 m'_1} \rangle \langle Y_{j_2 M-m_1} | q_{2, -\mu} | Y_{j'_2 M-m'_1} \rangle].$$

Now, following to Edmonds¹⁸

$$\langle Y_{j_k m_k} | q_{k, \mu} | Y_{j'_k m'_k} \rangle = (-1)^{m_k} \begin{pmatrix} j_k & 1 & j'_k \\ -m_k & \mu & m'_k \end{pmatrix} \begin{pmatrix} j_k & 1 & j'_k \\ 0 & 0 & 0 \end{pmatrix} \langle Y_{j_k 0} | \nabla_{k,0} | Y_{j'_k 0} \rangle - \left(\frac{4\pi}{3}\right)^{1/2} \langle Y_{j_k m_k} | Y_{1\mu} | Y_{j'_k m'_k} \rangle,$$

where the contribution of the tangential part of the gradient is

$$\langle Y_{j_k 0} | \nabla_{k,0} | Y_{j'_k 0} \rangle = -\delta_{j_k j'_k + 1} \frac{j'_k (j'_k + 1)}{[(2j'_k + 1)(2j'_k + 3)]^{1/2}} + \delta_{j_k j'_k - 1} \frac{j'_k (j'_k + 1)}{[(2j'_k - 1)(2j'_k + 1)]^{1/2}}$$

and

$$\langle Y_{j_k m_k} | Y_{1\mu} | Y_{j'_k m'_k} \rangle = \left[\frac{(2j_k + 1) \cdot 3}{4\pi(2j'_k + 1)} \right]^{1/2} (j_k, m_k, 1, \mu | j_k, 1, j'_k, m'_k) (j_k, 0, 1, 0 | j_k, 1, j'_k, 0).$$

Thus, we obtain

$$\langle JMj_1j_2|Q|JMj'_1j'_2\rangle \\ = \sum_{m_1, m'_1} (j_1, m_1, j_2, M-m_1 | j_1, j_2, J, M) (j'_1, m'_1, j'_2, M-m'_1 | j'_1, j'_2, J, M) \\ \times \sum_{\mu=-1}^{+1} (-1)^{\mu} \left\{ (-1)^{m_1} \begin{pmatrix} j_1 & 1 & j'_1 \\ -m_1 & \mu & m'_1 \end{pmatrix} \begin{pmatrix} j_1 & 1 & j'_1 \\ 0 & 0 & 0 \end{pmatrix} \right. \\ \times \left[\frac{\delta_{j_1 j'_1 - 1}}{(2j'_1 - 1)^{1/2}} - \frac{\delta_{j_1 j'_1 + 1}}{(2j'_1 + 3)^{1/2}} \right] \frac{j'_1 (j'_1 + 1)}{(2j'_1 + 1)^{1/2}} - \left(\frac{2j_1 + 1}{2j'_1 + 1} \right)^{1/2} (j_1, m_1, 1, \mu | j_1, 1, j'_1, m'_1) (j_1, 0, 1, 0 | j_1, 1, j'_1, 0) \Big\} \\ \times \left\{ (-1)^{M-m_1} \begin{pmatrix} j_2 & 1 & j'_2 \\ m_1 - M & -\mu & M - m'_1 \end{pmatrix} \begin{pmatrix} j_2 & 1 & j'_2 \\ 0 & 0 & 0 \end{pmatrix} \left[\frac{\delta_{j_2 j'_2 - 1}}{(2j'_2 - 1)^{1/2}} - \frac{\delta_{j_2 j'_2 + 1}}{(2j'_2 + 3)^{1/2}} \right] \right. \\ \times \left. \frac{j'_2 (j'_2 + 1)}{(2j'_2 + 1)^{1/2}} - \left(\frac{2j_2 + 1}{2j'_2 + 1} \right)^{1/2} (j_2, M - m_1, 1, -\mu | j_2, 1, j'_2, M - m'_1) (j_2, 0, 1, 0 | j_2, 1, j'_2, 0) \right\}. \quad (\text{A6})$$

Finally, the completeness of the SF basis set is used to represent the different anticommutators in Eq. (28), i.e.,

$$\langle JMj_1j_2|\{A, B\}|JMj'_1j'_2\rangle \\ = \sum_{l, l'} [\langle JMj_1j_2|A|JMLl'\rangle \langle JMLl'|B|JMj'_1j'_2\rangle \\ + \langle JMj_1j_2|B|JMLl'\rangle \langle JMLl'|A|JMj'_1j'_2\rangle]. \quad (\text{A7})$$

Equations (A5), (A6), and (A7), in the particular case $J=M=0$, constitute the final expressions used here to solve the bending problem, Eq. (A1). Also, averaged rates,

Eqs. (20) and (21), are evaluated by means of expressions (A3) and (A5).

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