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Stability of van der Waals–London bonds outside metal surfaces

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Abstract. We analyse the weakening and stability of a van der Waals–London chemical bond parallel to and at a height z above a perfect metal surface. The bond is considered in both the retarded (large- z) and non-retarded (small- z) regions. By considering the energy difference between the dissociated and undissociated species, we discuss the criteria in which bond breakup may occur, relevant to dissociative physisorption. Our results are of interest to surface chemistry and catalysis.

1. Introduction

The subject of the behaviour of chemical† bonds outside metal surfaces has been of interest for several years, particularly in MBE and MOCVD technology. In 1976 Mahanty and March [1] developed a theory which showed that the non-retarded long-range dispersion interaction between a molecular pair is weakened near a metal surface (a simple picture to explain this is that of the second-order weakening of polarization effects due to a molecule via its electrical image). Although not discussed in that earlier work, this model lends itself to an analysis of the stability of the bond, and can be used with appropriate parameters to predict the possibility of breakup. This result is of considerable interest in physisorption processes, for example Xe on Al.

In the retarded region (distances of 100 Å or more from the surface), the weakening of the bond is naturally quite small, but for two extremely large molecules (like fullerenes or hyperfullerenes with anomalously large polarizabilities [2]) interacting via a dispersion force, the effect may be significant enough to be taken into account when considering the stability of such bonds between a pair of these types of molecules in this region. In such a context, the model outlined below is a considerably simplified picture that treats the dispersion interaction of fullerenes or hyperfullerenes as the interaction of two large spherical shells. Of course, any consideration of such a bond in this region would involve the recalculation of the weakening function $F(s)$ ‡ taking retardation into account, as we shall see below.

In section 2 we review the earlier theory and the results obtained from it. In section 3 we extend the earlier work by calculating the weakening function in the retarded region. In section 4 we derive a criteria for each region, which predicts whether bond breakup

† In keeping with the nomenclature of Mahanty and March [1], in this work we use the word ‘chemical’ to describe the van der Waals bond, despite being aware that some interpretations of the chemical bond exclude the van der Waals interaction on the grounds that it involves photon exchange as opposed to electron exchange.

‡ This is equation (5) of [1].

can occur. The criteria we derive neglects the actual processes involved in overcoming the energy barrier in the dissociative process (if favoured). We shall complete our analysis by discussing the role of dynamics in dispersion bond breakup.

2. Review of earlier theory

In the theory of Mahanty and March [1] the weakening of the dispersion interaction ($-A_{\text{London}}/\rho^6$ in free space, where ρ is the intermolecular distance and the bond is parallel to the surface) is given by the form

$$\frac{-A'(s)}{\rho^6} = \frac{-A_{\text{London}}F(s)}{\rho^6} \quad (1)$$

where $s = 2z/\rho$, and z is the distance of the molecular pair from the surface. The function $F(s)$ is calculated to be

$$F(s) = 1 + \frac{1}{(1+s^2)^3} - \frac{4(1+s^2/4)}{3(1+s^2)^{5/2}}. \quad (2)$$

We note that $F(s) \sim \frac{2}{3} + s^4$ for $s \rightarrow 0$ while $F(s) \sim 1 - 1/3s^3$ for $s \rightarrow \infty$ (we shall see later that this latter power law for the infinity limit is incorrect, and has to be modified by taking retardation into account).

The effective dispersion interaction for the molecular pair, to leading order in the polarizabilities, is given by

$$E = E_1 + E_2 + E_{12} \quad (3)$$

where E_1 and E_2 reflect the interaction of the individual molecules of the pair with their respective images, and E_{12} contains the direct dispersion interaction between one molecule and the other and an indirect interaction via the other's image. The energies are given by [1]†

$$E_1 = -\frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\xi \alpha_1(i\xi) \text{Tr} G_1(\mathbf{1}, \mathbf{1}) \quad (4)$$

$$E_2 = -\frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\xi \alpha_2(i\xi) \text{Tr} G_1(\mathbf{2}, \mathbf{2}) \quad (5)$$

and

$$E_{12} = -\frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\xi \alpha_1(i\xi) \alpha_2(i\xi) \text{Tr}[G(\mathbf{2}\mathbf{1})G(\mathbf{1}\mathbf{2})] \quad (6)$$

where $\alpha_j(i\xi)$ is the dynamic polarizability of the j th molecule and the G are the appropriate Green functions defined below. This result is achieved through the dyadic Green function

† The argument in the Green functions in the subsequent equations is as follows: (11) implies that molecule 1 is at position \mathbf{r} and the image of molecule 1 is at \mathbf{r}'_{im} etc.

G , which connects the electric field at r to a dipole source $\mu(\omega)$ at r' with a frequency ω , i.e.

$$E(r) = G(r, r'; \omega)\mu(\omega). \quad (7)$$

In the presence of a dielectric surface (taken to be in the (x, y) plane with both r and r' outside the dielectric) $G(r, r'; \omega)$ has the form

$$G(r, r'; \omega) = G_D(r - r') - \Delta(\omega)G_1(r, r') \quad (8)$$

where $G_D(r - r')$ is due to a free-space dipole source at r' , having the form

$$G_D(r - r') = -(\nabla\nabla') \frac{1}{|r - r'|} \quad (9)$$

and $G_1(r, r')$ is due to the semi-infinite dielectric medium. Image theory gives

$$G_1(r, r') = -(\nabla\nabla') \frac{1}{|r - r'_{im}|} \quad (10)$$

where r'_{im} is the image of the point r' and $\Delta(\omega) = [\epsilon(\omega) - 1]/[\epsilon(\omega) + 1]$ [3] with $\epsilon(\omega)$ being the frequency-dependent dielectric function. The results of [1] are reproduced here for the parallel case and with the correction of a small misprint:

$$\text{Tr } G_1(\mathbf{11}) = -\frac{1}{2z^3} \quad (11)$$

$$\text{Tr } G_1(\mathbf{22}) = -\frac{1}{2z^3} \quad (12)$$

$$\text{Tr}[G(\mathbf{21})G(\mathbf{12})] = \frac{6}{\rho^6} + \frac{6}{(\rho^2 + 4z^2)^3} - \frac{8\Delta(\omega)(\rho^2 + z^2)}{\rho^3(\rho^2 + 4z^2)(5/2)} \quad (13)$$

where $\rho^2 = x^2 + y^2$. By assuming the dielectric to be a perfect conductor the function $\Delta(\omega) \rightarrow 1$, and we obtain the weakening function $F(s)$ through (6) taking $A = (3\hbar/2\pi) \int_{-\infty}^{\infty} \alpha_1(i\xi)\alpha_2(i\xi)d\xi$ [4].

3. Retardation

The essential addition to the above theory lies in including retardation effects for large z . In the Mahanty and March paper [1] it was correctly surmised that retardation effects are unimportant for large ρ and small z . However for small ρ and large z , the distance of the molecules from their images may be large enough for retardation effects to be included. This is important in considering very large neutral molecule–molecule dispersion interactions, for example C_{60} and larger. The correction for the large- z behaviour merely involves modifying the image dyadic Green function to the form

$$G_1(r - r'_{im}, \omega) = -(\nabla\nabla' + k^2\hat{I}) \frac{e^{ik|r - r'_{im}|}}{|r - r'_{im}|} \quad (14)$$

where \hat{I} is the unit dyadic, $k = \omega/c$, ω is the frequency of the molecular dipole (of order 10^{15} – 10^{16} s) and c is the speed of light. The calculation can then proceed as before, after noting that the evaluation of equations (4)–(6) is slightly more complicated because the dyadics are now frequency dependent. Their respective traces are evaluated to be

$$\text{Tr } G_1(\mathbf{11}) = e^{-2ikz} \left(\frac{-k^2}{z} + \frac{ik}{z^2} - \frac{1}{2z^3} \right) \quad (15)$$

$$\text{Tr } G_1(\mathbf{22}) = e^{-2ikz} \left(\frac{-k^2}{z} + \frac{ik}{z^2} - \frac{1}{2z^3} \right) \quad (16)$$

$$\begin{aligned} \text{Tr}[G(\mathbf{21})G(\mathbf{12})] &= \frac{6}{\rho^6} + \frac{e^{2ik\rho\phi}}{\rho^6\phi^5} [3\phi^2(-ik\rho\phi^{1/2} + 1)^2 + 2k^2\rho^2\phi^3(-ik\rho\phi^{1/2} + 1) \\ &\quad - 2\phi^2(-ik\rho\phi^{1/2} + 1)(-k^2\rho^2\phi - 3ik\rho\phi^{1/2} + 3) + 3k^4\rho^4\phi^4 \\ &\quad + \phi^2(-k^2\rho^2\phi - 3ik\rho\phi^{1/2} + 3)^2 - 2k^2\rho^2\phi^2(2 - \phi)(-k^2\rho^2\phi - 3ik\rho\phi^{1/2} + 3)] \\ &\quad - \frac{2e^{ik\rho\phi^{1/2}}}{\rho^6\phi^{5/2}} [-2\phi(-ik\rho\phi^{1/2} + 1) + (1 + \phi)(-k^2\rho^2\phi - 3ik\rho\phi^{1/2} + 3)] \quad (17) \end{aligned}$$

where $\phi = (1 + 4z^2/\rho^2)$. To evaluate E_{12} (equation (6)) we use the approximation that $\alpha(i\xi) = \alpha(0)$, the static polarizability. This approximation is valid because for large z only values of ξ which are small will contribute to the integral, so to zeroth order $\alpha(i\xi)$ can be replaced with $\alpha(0)$ [5]. With this approximation all terms in the integral become gamma functions, which can be evaluated easily. Casimir and Polder [6] showed that two atoms interacting through a retarded dispersion force produce an energy contribution that behaves as $1/r^7$, where r is the interatomic distance. This is precisely what we observe in this context between one molecule and the retarded interaction with the other's image. The interaction energy between the molecules in the presence of the perfectly conducting surface now has a $1/\rho^6$ dependence and a $1/\rho^7$ dependence due to the retarded image interaction. Evaluating (6) and using the London formula† $A = \frac{3}{4}\hbar\alpha_1(0)\alpha_2(0)\omega_0$ we evaluate E_{12} to be

$$E_{12} = - \left[\frac{A}{\rho^6} + \frac{2Ac}{3\pi\omega_0\rho^7} \left(\frac{13}{2(1+s^2)^{7/2}} + \frac{21}{2(1+s^2)^{9/2}} - \frac{8}{(1+s^2)^2} - \frac{16}{(1+s^2)^3} \right) \right]. \quad (18)$$

We can see that a dimensionless weakening function $F(s)$ cannot be factored out of the above expression, but we can form

$$F_{\text{ret}}(s, \rho) = 1 + \frac{2c}{3\pi\omega_0\rho} \left(\frac{13}{2(1+s^2)^{7/2}} + \frac{21}{2(1+s^2)^{9/2}} - \frac{8}{(1+s^2)^2} - \frac{16}{(1+s^2)^3} \right). \quad (19)$$

In terms of a van der Waals–London interaction we have

$$\frac{A'}{\rho^6} = \frac{AF_{\text{ret}}(s, \rho)}{\rho^6} \quad (20)$$

and note that as $s \rightarrow \infty$, $F(s, \rho) \sim 1 - (2c/3\pi\omega_0\rho)(8/s^4)$ compared with the incorrect $F(s) \sim 1 - 1/3s^3$ for the non-retarded expression. If we evaluate E_1 and E_2 we get

$$E_j = - \frac{\hbar c \alpha_j(0)}{4\pi z^4} \quad -j = 1, 2 \quad (21)$$

which exhibits the Casimir–Polder form of an atom interacting with a perfect conducting surface.

† The constant ω_0 in the following equations is the first allowed dipole transition frequency, see [4].

4. Stability of the chemical bond

A complete analysis of the stability of the van der Waals–London chemical bond in the presence of a perfect metal surface requires a full quantum mechanical treatment [7], i.e. *ab initio* the Schrödinger equation. This may suggest that, in addition to A'_{London} , the other parameters involved in the total interaction of the molecular pair with the surface may also be dependent upon distance, and at best a Lennard-Jones potential is a simplified approximation. It is clear as we shall see later (see the proof of theorem 1 in the next subsection) that the Lennard-Jones potential on its own cannot lead to dissociation. This is because there never exists a solution $\rho_{\min} = \infty, z_{\min} \neq 0$ (the dissociative solution) which minimizes the static energy. In order to bypass the difficulties mentioned above, and since solving the *ab initio* problem is much more complicated, we adopt the following strategy, which is valid for the purpose of deriving a dissociation criteria. This approach consists of comparing the minimum total (static) energy of the two states (dissociated or bonded) near the surface using different Lennard-Jones models appropriate to the two cases. The price to be paid, however, is that we will not be able to assess the energy barriers and dynamics with this scheme. The simplification which results is nevertheless worthwhile. Our model reflects the main attributes of the physics of the system in the static condition. The criterion is derived by minimizing the total static energy of a molecular pair approaching the surface and comparing this minimum energy with the minimum static energy of a dissociated pair approaching the surface. Later, we shall discuss the role that dynamics plays in helping the individual molecules overcome the barrier to dissociative physisorption.

For the following analysis we assume a Lennard-Jones potential for the intermolecular interaction, modified by the appropriate weakening function for the van der Waals–London part, while for the surface the hard-core repulsion due to the effect of the surface is taken to be β_{sep}/z^9 [8].

4.1. The non-retarded region

For the non-retarded region, we have

$$H_{\text{bond}}(\rho, z) = \frac{B}{\rho^{12}} + E_1 + E_2 + E_{12} + \frac{2\beta_{\text{sep}}}{z^9} \quad (22)$$

or more precisely

$$H_{\text{bond}}(\rho, z) = \frac{B}{\rho^{12}} - \frac{2\gamma_{\text{sep}}}{z^3} - \frac{AF(2z/\rho)}{\rho^6} + \frac{2\beta_{\text{sep}}}{z^9} \quad (23)$$

where $\gamma_{\text{sep}} = \hbar\omega_0\alpha(0)/8$. Here we have made the approximation that the surface sees not the interacting molecular pair, but two separate non-interacting molecules with respect to the γ_{sep} and β_{sep} terms. The minimum energy is found by minimizing with respect to both ρ and z . It would seem possible that the weakening function makes it energetically favourable for bond breakup to occur by making the minimum energy of H_{bond} more than the minimum energy of the separated molecules reflected by the Hamiltonian H_{sep} , given by

$$H_{\text{sep}}(z) = \frac{2\beta_{\text{sep}}}{z^9} - \frac{2\gamma_{\text{sep}}}{z^3} \quad (24)$$

which represents the energy of two separated molecules interacting only with the surface. However, this is not the case and we construct a heuristic proof of the following theorem.

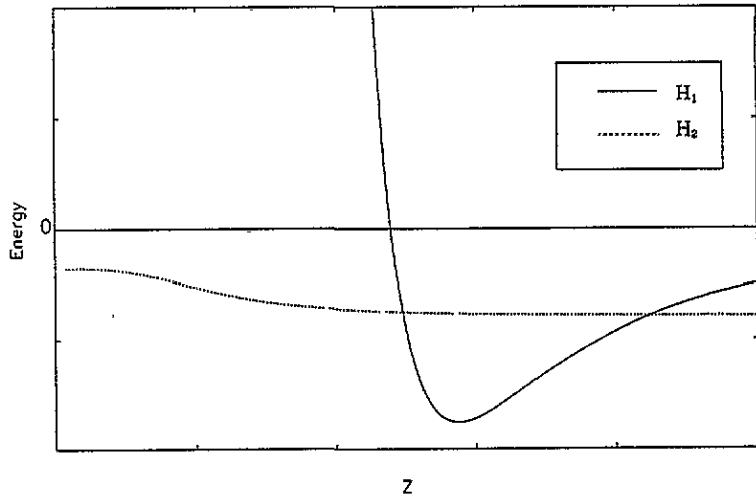


Figure 1. Schematic diagram of the behaviour of H_1 and H_2 as a function of z .

Theorem 1.

$$H_{\text{bond}}(\text{min}) \leq H_{\text{sep}}(\text{min}) \quad (25)$$

for any set of arbitrary parameters γ_{sep} , β_{sep} , A and B .

Proof. Let

$$H_1 = \frac{2\beta_{\text{sep}}}{z^9} - \frac{2\gamma_{\text{sep}}}{z^3} \quad H_2 = \frac{B}{\rho^{12}} - \frac{AF(2z/\rho)}{\rho^6}. \quad (26)$$

Now

$$H_1(\text{min}) = -\frac{4\gamma_{\text{sep}}^{3/2}}{3(3\beta_{\text{sep}})^{1/2}} \quad H_2(\text{min}) \approx \frac{-A^2 f^2}{4B} \quad (27)$$

where f is a parameter which varies between $2/3$ and $1\dagger$. Note also that $H_1 \equiv H_{\text{sep}}$. Now H_1 is a function of z only while H_2 is a function of both ρ and z . We can minimize H_2 with respect to ρ for each value of z and denote this by $\hat{H}_2(z)$ and the value of ρ that minimizes $\hat{H}_2(z)$ by $\hat{\rho}(z)$. The function $\hat{H}_2(z)$ is negative, as can be seen from (27), and the behaviour of H_1 and $\hat{H}_2(z)$ is shown schematically in figure 1. At z_{min} , for which H_1 is a minimum, we have

$$H_{\text{bond}}(\hat{\rho}(z_{\text{min}}), z_{\text{min}}) \equiv H_1(z_{\text{min}}) + \hat{H}_2(z_{\text{min}}) < H_1(z_{\text{min}}). \quad (28)$$

This implies that

$$H_{\text{bond}}(\text{min}) \leq H_{\text{bond}}(\hat{\rho}(z_{\text{min}}), z_{\text{min}}) < H_1(\text{min}) \quad (29)$$

or therefore

$$H_{\text{bond}}(\text{min}) < H_{\text{sep}}(\text{min}). \quad (30)$$

This concludes the proof.

\dagger As $F(s)$ in the non-retarded region varies between $2/3$ and 1 .

However, a more realistic Hamiltonian than H_{bond} is

$$H_{\text{bond}}^{\text{real}}(\rho, z) = \frac{B}{\rho^{12}} - \frac{AF(2z/\rho)}{\rho^6} + \frac{2\beta_{\text{sep}}}{z^9} - \frac{\gamma_{\text{bond}}}{z^3} \quad (31)$$

which reflects the fact that, while there is an intermolecular bond, the surface attracts an interacting molecule–molecule system, not two non-interacting ones. Here $\gamma_{\text{bond}} = \hbar\alpha_{\text{bond}}(0)\omega_0/8$. The parameter $\alpha_{\text{bond}}(0)$ is the static polarizability of the molecular pair. In general, a molecular pair will not have a polarizability that is just twice the individual molecule polarizabilities; usually $\gamma_{\text{bond}} < 2\gamma_{\text{sep}}$. With this Hamiltonian, bond breakup is possible, and in fact one can derive a criteria to predict its breakup.

To get an exact analytical expression for the bond lengths and minimum energy of $H_{\text{bond}}^{\text{real}}$, one is required to find the solution to two highly coupled polynomials, which is analytically intractable. However, another approach outlined below is more fruitful. A molecular pair interacting through a dispersion force in free space (not near a surface) has a bond length ρ_{mp} , where the subscript ‘mp’ means molecular pair. Numerical calculations show that near a surface this bond length is increased by a small amount to a new bond length $\rho_{\text{mp}+\text{sur}}$ such that $(\rho_{\text{mp}+\text{sur}} - \rho_{\text{mp}})/\rho_{\text{mp}} \ll 1$. Similarly, one molecule interacting with a surface has a surface bond length z_{sur} which is perturbed a small amount by the presence of another molecule, so that the new surface bond length is $z_{\text{sur}+\text{mp}}$ such that $(z_{\text{sur}+\text{mp}} - z_{\text{sur}})/z_{\text{sur}} \ll 1$. Therefore, we can get an approximate analytical expression (in terms of parameters only) for the bond lengths and the minimum energy of $H_{\text{bond}}^{\text{real}}$ by expanding this Hamiltonian to second order around ρ_{mp} and z_{sur} . If we let

$$\begin{aligned} a &= \left. \frac{\partial H_{\text{bond}}^{\text{real}}}{\partial \rho} \right|_{\rho_{\text{mp}}z_{\text{sur}}} & b &= \left. \frac{\partial H_{\text{bond}}^{\text{real}}}{\partial z} \right|_{\rho_{\text{mp}}z_{\text{sur}}} & c &= \left. \frac{\partial^2 H_{\text{bond}}^{\text{real}}}{\partial \rho^2} \right|_{\rho_{\text{mp}}z_{\text{sur}}} \\ d &= \left. \frac{\partial^2 H_{\text{bond}}^{\text{real}}}{\partial \rho \partial z} \right|_{\rho_{\text{mp}}z_{\text{sur}}} & e &= \left. \frac{\partial^2 H_{\text{bond}}^{\text{real}}}{\partial z^2} \right|_{\rho_{\text{mp}}z_{\text{sur}}} \end{aligned} \quad (32)$$

and using

$$\rho_{\text{mp}} = (2B/A)^{1/6} \quad z_{\text{sur}} = (3\beta_{\text{sep}}/\gamma_{\text{sep}})^{1/6} \quad (33)$$

then the solution that minimizes the second-order $H_{\text{bond}}^{\text{real}}$ is

$$\rho_{\text{mp}+\text{sur}} = \frac{e\sigma - d\eta}{2(ec - d^2)} \quad z_{\text{mp}+\text{sur}} = \frac{c\eta - d\sigma}{2(ec - d^2)} \quad (34)$$

where $\sigma = 2dz_{\text{sur}} + 2c\rho_{\text{mp}} - a$ and $\eta = 2ez_{\text{sur}} + 2d\rho_{\text{mp}} - b$. Substitution of these solutions into the second-order expansion of $H_{\text{bond}}^{\text{real}}$ then yields the minimum energy of the full surface molecular-pair interaction (to second order). Comparing this result to the minimum energy of H_{sep} yields the criterion (which is only dependent on the parameters A , B , γ_{bond} , β_{sep} and γ_{sep}) for bond breakup. Symbolically, the criterion for dissociation† is

$$H_{\text{sep}}(z_{\text{sur}}) < H_{\text{bond}}^{\text{real}} \left(\frac{e\sigma - d\eta}{2(ec - d^2)}, \frac{c\eta - d\sigma}{2(ec - d^2)} \right). \quad (35)$$

Algebraically, this criterion is very complicated, but the above scheme can be handled easily by a symbolic manipulation package.

† For molecular species on the borderline of dissociation, expansion to third order in $H_{\text{bond}}^{\text{real}}$ may be required.

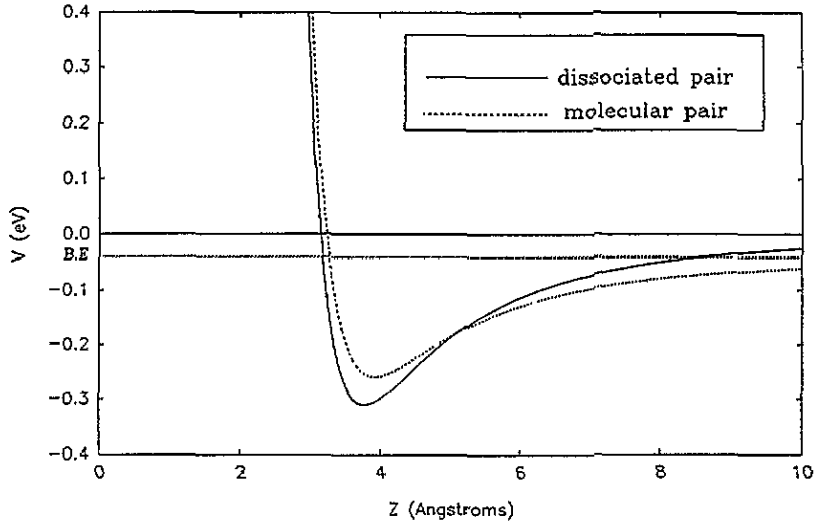


Figure 2. Potential energy curves for a molecular pair and a dissociated pair approaching the surface. The parameters are given by $A = 400 \text{ eV \AA}^6$, $B = 10^6 \text{ eV \AA}^{12}$, $\gamma_{\text{bond}} = 20 \text{ eV \AA}^3$, $\beta_{\text{sep}} = 12 \times 10^3 \text{ eV \AA}^9$ and $\gamma_{\text{sep}} = 12.5 \text{ eV \AA}^3$. The dotted line labeled BE represents the binding energy of the molecular pair in free space.

4.2. The retarded region

The analysis for the retarded region is similar to that for the non-retarded region, except that it is possible to approximate the Hamiltonian for the system by

$$H_{\text{bond}}^{\text{real}}(\rho) = \frac{B}{\rho^{12}} - \frac{A F_{\text{ret}}(2z/\rho, \rho)}{\rho^6} - \frac{\gamma_{\text{bond}}}{z^4}. \quad (36)$$

Here z is only a parameter, and the above Hamiltonian is minimized with respect to ρ only. The parameter γ_{bond} is given by $\hbar c \alpha_{\text{bond}}(0)/4\pi$. By the same reasoning as in the non-retarded region we can expand $H_{\text{bond}}^{\text{real}}$ around ρ_{mp} to second order. If we let

$$a = \left. \frac{\partial H_{\text{bond}}^{\text{real}}}{\partial \rho} \right|_{\rho_{\text{mp}} z_{\text{sur}}} \quad b = \left. \frac{\partial H_{\text{bond}}^{\text{real}}}{\partial z} \right|_{\rho_{\text{mp}} z_{\text{sur}}} \quad (37)$$

The bond length in this case is

$$\rho_{\text{mp}+\text{sur}} = \rho_{\text{mp}} - \frac{a}{2b}. \quad (38)$$

This result can be substituted into the above Hamiltonian, which can then be compared with the Hamiltonian

$$H_{\text{sep}} = \frac{-2\gamma_{\text{sep}}}{z^4} \quad (39)$$

which will yield a criterion given symbolically by

$$\frac{-2\gamma_{\text{sep}}}{z^4} < H_{\text{bond}}^{\text{real}}\left(\rho_{\text{mp}} - \frac{a}{2b}\right). \quad (40)$$

This yields the retarded region criterion for bond breakup involving only the parameters γ_{sep} , γ_{bond} , z , A and B .

5. Discussion

In the non-retarded region we can see, by examining $H_{\text{bond}}^{\text{real}}$ and H_{sep} , that when the intermolecular Lennard-Jones interaction is in general an order of magnitude less than the molecular-pair surface interaction, bond breakup is possible if the species is such that $2\gamma_{\text{sep}} > \gamma_{\text{bond}}$. In figure 2 we show the difference in surface potentials felt by a molecular pair and two dissociated molecules in this region. Note that as $z \rightarrow \infty$ the molecular-pair potential energy approaches their binding energy in free space, while the potential energy curve representing the dissociated pair naturally asymptotes to zero in this limit. Figure 2 shows that as the molecular pair approaches the surface, it becomes energetically favourable for dissociation to occur. The choice of parameters is $A = 400 \text{ eV } \text{\AA}^6$, $B = 10^6 \text{ eV } \text{\AA}^{12}$, $\gamma_{\text{bond}} = 20 \text{ eV } \text{\AA}^3$, $\beta_{\text{sep}} = 12 \times 10^3 \text{ eV } \text{\AA}^9$ and $\gamma_{\text{sep}} = 12.5 \text{ eV } \text{\AA}^3$. This combination of parameters (typical of small molecules) is such that they satisfy the criterion for bond breakup to occur, i.e. the potential felt by the two separated molecules produces a lower minimum energy than the bonded case. The energies are calculated using the above method to be $H_{\text{bond}}^{\text{real}}(\text{min}) = -0.26 \text{ eV}$, compared to $H_{\text{sep}}(\text{min}) = -0.31 \text{ eV}$.

In the retarded region the weakening of the bond is naturally very small, so for bond breakup to occur in this region each molecule species, when dissociated, must have a large polarizability and thus a significant interaction with the surface which therefore lowers the energy. However, when they exist as a molecular pair the van der Waals bond must be weak and the pair polarizability be such that $\gamma_{\text{bond}} < 2\gamma_{\text{sep}}$. The most appropriate species likely to fulfill these requirements are the fullerenes and hyperfullerenes. Their anomalously large polarizabilities [2] make the attraction with the surface at 100 \AA significant, if their bond energy is of the same order of magnitude (of order eV). For these large molecules, retardation between the molecules themselves may further weaken their bond.

As stated before, the analysis conducted so far has ignored the dynamical or other processes that constitute the real system. This paper has been a consideration of statics alone; however, it is worthwhile to discuss what additional processes are required for dissociative physisorption in our model system.

One process which seems an obvious candidate is simply the thermal contribution to the total energy. A gas of paired van der Waals bonded molecules will have an accompanying Maxwell–Boltzmann distribution. The fraction of molecules with enough thermal energy to overcome the energy barrier may dissociate. It is also possible that dissociation may occur purely through quantum mechanical tunneling (depending on the width of the barrier), or that vibrational energies of the bond are enough to get over the barrier. While a knowledge of the actual size of the energy barrier requires a more sophisticated quantum mechanical calculation, an estimate can be obtained from a graph like figure 2. One can see that for favourable cases such a barrier is quite small in view of the small differences in energies and between z_{sur} and $z_{\text{mp+sur}}$.

6. Conclusion

By utilizing the theory of Mahanty and March, and extending it to take retardation into account (for large z) between one molecule and the image of another, we have examined the stability of molecular pairs bonded parallel to a metallic surface and derived a criterion for the possibility of dissociative physisorption to occur, in both retarded and non-retarded regions.

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