The effect of the interaction between pentaerythritol and polycaprolactone in the adhesives.

The effect of the interaction between pentaerythritol and polycaprolactone in the adhesives.

The effect of the interaction between pentaerythritol and polycaprolactone in the adhesives.

The effect of the interaction between pentaerythritol and polycaprolactone in the adhesives.

The effect of the interaction between pentaerythritol and polycaprolactone in the adhesives.

The effect of the interaction between pentaerythritol and polycaprolactone in the adhesives.
fitting available experimental RKR turning points or the calculated SEC energies.

The paper is organized as follows. In Section 2, we provide a description of the EHFACE2(U) models. The ab initio calculations and the main features of the SEC method are given in Section 3. Section 4 reports the calculated EHFACE2(U) potential energy curves, and compares them with the available experimental and theoretical data. The concluding remarks are in Section 5.

2. Method

In the EHFACE2 method, the potential energy is written as

\[ V = V_{\text{EHF}}(R) + V_{\text{dc}}(R) \]  

where EHF denotes the extended Hartree–Fock type energy, and dc the dynamical correlation which includes the asymptotic long-range dispersion energy. As usual, we maintain the designation \( V_{\text{dc}} \) even when this term accounts also for the long-range electrostatic and induction energies, which appear in the EHF part of the interaction energy.

The EHF part of the potential assumes the form,

\[ V_{\text{EHF}} = -DR^{-1}(1+\sum_{i=1}^{3} a_i \bar{r}_i \exp(-\gamma(r)r)) \]  

where

\[ \gamma = \gamma_0[1+\gamma_1\tanh(\gamma_2r)] \]  

In this equation, \( r = R - R_0 \) is the displacement coordinate from the equilibrium geometry \( R_0 \), and \( D, \gamma_0, \gamma_1, \gamma_2 \), and \( a_i \) (\( i = 1-3 \)) are parameters to be determined from a least-squares fit to ab initio or experimental data. For simplicity, no attempt is made to reproduce the correct behavior of the asymptotic exchange energy (ref 18, and references therein). This appears justified for consistency reasons given the approximations involved in scaling the external correlation of the excited-state curves.

In turn, the dynamical correlation energy is approximated by

\[ V_{\text{dc}} = -\sum_n C_n \chi_n(R)R^{-n} \]  

where the damping functions for the dispersion coefficients are defined by

\[ \chi_n(R) = [1 - \exp(-A_nR/\rho - B_nR^2/\rho^2)]^n \]  

and the auxiliary functions \( A_n \) and \( B_n \) assume the form

\[ A_n = \alpha_n R^{-\alpha_1} \]  

\[ B_n = \beta_n \exp(-\beta_1 R) \]  

with \( \alpha_1 \) and \( \beta_1 \) being universal and dimensionless parameters determined from a fit to the ab initio results for \( \Sigma + \Sigma \) : \( \alpha_0 \) = 16.366 06, \( \alpha_1 = 0.701 72, \beta_0 = 17.193 38, \text{and} \beta_1 = 0.095 74 \). Moreover, \( \rho \) is a scaling distance (in atomic units) by \( \rho = (5.5 + 1.25R_0) \), where \( R_0 = 2\langle r_X^2 \rangle^{1/2} + \langle r_Y^2 \rangle^{1/2} \) is the Le Roy parameter 27 and \( \langle r_X^2 \rangle \) is the expectation value of the squared radii for the outermost electrons in atom X (similarly for atom Y). To obtain the values of the \( C_n \) and \( C_{00} \) dispersion coefficients, we have employed the universal correlation 13

\[ C_nC_6 = \kappa_0 R_0^{(n-2)/2} \]  

where \( \kappa_0 = 1, \kappa_0 = 1.31, \text{and} a = 1.54 \) are universal parameters. All expectation values necessary to evaluate \( R_0 \) have been taken from the tabulations of Bunge et al. 28 In turn, the \( C_n \) dispersion coefficients for the title systems have been calculated from those of \( H_2, \text{Cl}_2, \text{and} \text{O}_2 \) by using the combination rule 29

\[ C_{n}^{XY} \approx \left( C_n^{XX} C_n^{YY} \right)^{1/2} \]  

The numerical values of the calculated dispersion coefficients are reported in Table 1.

For ions or neutral systems with permanent electric multipole moments, one may also need to consider the electrostatic and induction energies. It has been suggested that the corresponding damping functions can be obtained from those originally obtained for the dispersion energy simply by using the appropriate powers of \( n \). 13 17 This is the procedure followed here to deal with the two electronic states of OCl, since both the Cl- \( (\bar{p}) \) and O \( (\bar{p}) \) possess a permanent quadrupole moment. It turns out 30 that, for the \( X^2 \Pi, \text{quadrupole−quadrupole} C_5 \) coefficient vanishes, while for the excited \( A^2 \Sigma^+ \) state it has the value \( C_5 = 11.55 \ E_{\text{int}} \). Since the \( C_6 R^{-5} \) term is expected to dominate at large interatomic separations, one then expects the \( A^2 \Sigma^+ \) state to be lowest at such interatomic distances.

Often, due to the unavailability of sufficient input data to define the shallow van der Waals minimum in repulsive states, we find it useful to represent the EHF part of their potential energy curves by the generalized screened-Coulomb form 13 18

\[ V_{\text{EHF}} = D' R^{-1} \exp(-\sum_{i=1}^{m} \alpha_i R_i) \]  

where the parameters are obtained from the calculated ab initio energies through a linear least-squares fitting procedure of \( \ln(V_{\text{ab initio}} - V_{\text{dc}}) \) vs \( R \). Of course, the asymptotic behavior of the EHF curve cannot be reproduced, since the decay rate is dictated by the highest power of \( R \) in the exponential. An alternative is to use 13

\[ V_{\text{EHF}} = \tilde{D} R^{-1}(1 + \sum_{i=1}^{n} \tilde{a}_i R_i) \exp(-\tilde{\gamma} R) \]  

where the coefficients are obtained from a least-squares fitting procedure to the calculated ab initio energies. In fact, by fixing \( \tilde{\gamma} = \gamma_0 \), one may impose the asymptotic behavior of \( V_{\text{EHF}} \) to be equal to that of the ground-state curve, as one might expect. Clearly, depending on the calculated value of \( D \), the cusp behavior in eq 10 or 11 at the united-atom limit may be only approximately satisfied.

3. Ab Initio Calculations

To construct the potential energy curve for the considered states of the HCl and OCl systems (\( \Sigma^+ \) and \( \Sigma^+ \) for HCl, and \( \Pi^+ \) and \( \Sigma^+ \) for OCl), ab initio calculations have been carried out at the MRCI 13 32 level using FVCAS 33 34 wave functions as a reference. In this study, the aug-cc-pvqz (AVQZ) basis sets of Dunning 35 37 were employed. They consist of (6s,3p,2d,1f)/ (4s,3p,2d,1f) contracted functions augmented by diffuse (1s,1p,1d,1f) orbitals for the hydrogen atom, and (12s,6p,3d,2f,1g)/(5s,4p,3d,2f,1g) and (16s,11p,3d,2f,1g)/(6s,5p,3d,2f,1g) contracted functions with diffuse (1s,1p,1d,1f) orbitals for the oxygen and chlorine atoms, respectively. All calculations have

\[ C_nC_6 = \kappa_0 R_0^{(n-2)/2} \]
TABLE 1: Values of $R_a$ and Long-Range Dispersion Coefficients Used in this Work$^a$

<table>
<thead>
<tr>
<th>system</th>
<th>$R_a$/Å</th>
<th>$C_d/E_h$</th>
<th>$C_o/E_h$</th>
<th>$C_o/E_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>7.493528</td>
<td>25.12</td>
<td>558.52</td>
<td>16267.66</td>
</tr>
<tr>
<td>OCl</td>
<td>6.840157</td>
<td>34.77</td>
<td>747.10</td>
<td>18908.15</td>
</tr>
</tbody>
</table>

$^a$ These parameters assume the same value for all states of HCl and OCl. $^b$ For the electrostatic coefficients in the case of OCl, see the text.

been carried out on a DEC Alpha 600 workstation using the MOLPRO$^{38}$ ab initio package. A total of 56, 32, 42, and 48 geometries have been considered for HCl($^1\Sigma^+$), HCl($^3\Sigma^+$), OCl($^2\Pi$), and OCl($^2\Sigma^+$).

The ab initio energies so obtained were then corrected by scaling the dynamical correlation. Note that the nondynamical correlation is system specific and in this sense nontransferable.$^{39-42}$ It is also geometry specific, and hence nonscaleable.$^{24,25}$ The external correlation can be obtained by including in the CI wave function the various excitations from the FVCAS reference configuration to the virtual orbital space.$^{19,39}$ However, convergence of the CI expansion with respect to including high-order excitations is difficult.$^{19,20}$ and most MRCI$^{43-46}$ calculations include only single and double replacements from the FVCAS wave function. Although this procedure may recover a large fraction of the dynamical correlation, such calculations often yield bond energies which may be several kcal mol$^{-1}$ too low and saddle point heights too high. On the other hand, since the specifically geometry-dependent effects are included in the FVCAS wave function, it is expected that the external correlation will be approximately transferable$^{19,39-42}$ and scaleable.$^{23,24}$ It has therefore been suggested$^{23,24}$ that the missing dynamical correlation due to triple and higher excitations as well as due to the incompleteness of the one-electron basis set can be estimated semianalytically by scaling the external correlation energy which is recovered at the FVCAS-CISD level. Such a scheme has been referred to as the SEC (scaled-external correlation) method, and is based on the assumption that the core correlation effects are geometry independent (for a generalization to polyatomic interactions within the context of a many-body expansion, see ref 24).

According to the SEC method, the total energy is written$^{23,24}$

$$E_{\text{SEC}}(R) = E_{\text{FVCAS}}(R) + \frac{[E_{\text{MRCI}}(R) - E_{\text{FVCAS}}(R)]}{\omega}$$  \hspace{1cm} (12)

with the empirical factor $\omega$ being usually defined by

$$\omega = \frac{V_{\text{MRCI}} - V_{\text{FVCAS}}}{V_d - V_{\text{FVCAS}}}$$  \hspace{1cm} (13)

so as to reproduce the bond energy of the diatomic molecule. Thus, $V_d$ is the experimental dissociation energy of the diatomic, and $V_{\text{MRCI}}$ and $V_{\text{FVCAS}}$ are the energies calculated at the MRCI and FVCAS levels, respectively. We make the further assumption that the value of $\omega$ can be transferred without modification to scale the external correlation of the excited electronic states considered in the present work. Although one may expect to recover different percentages of the dynamical correlation for open and closed shell reference states, it is also true that on average such a single scaling parameter may still be used. Note that the FVCAS calculations for both the ground and excited states include open shell configuration state functions. Moreover, such a use of a single scaling parameter for both the ground and excited diatomic states seems justified by the fact that such states dissociate to the same set of ground-state atoms. Table 2 gathers the values of $\omega$, and the parameters employed for their calculation.

4. Results and Discussion

Figures 1–4 show the EHFACE2U potential energy curves calculated for the title molecules. We observe that the excited states ($^2\Sigma^+$ for the HCl and $^2\Sigma^+$ for the OCl) considered are repulsive for both molecules, and bound only by weak van der
Waals forces. It is interesting to describe in some detail the fitting procedure which has been used for the various systems. For the ground states, where RKR turning points are available, these have been employed to obtain the fitting procedure which has been used for the various systems.

Figure 3. Interatomic potential for HCl(A^2Σ^+).

Figure 4. Interatomic potential for OCl(A^2Σ^+).

The incorporation of information referring to both such asymptotic limits has the merit of transforming the fitting procedure into an interpolation scheme which utilizes the fitted data points to guide the curve at intermediate regions. Clearly, the smooth curves obtained by fitting the experimental RKR points mimic quite well the ab initio points calculated in the present work. Note that the calculated root-mean-square deviations are (in 10^{-4} cm^{-1}) 0.54, 2.64, 0.93, and 1.48 cm^{-1} respectively for the A^2Σ^+, B^2Σ^+, C^2Π, and D^2Σ^+ states of HCl (first two states) and OCI. For the ground-state curves, this corresponds to 12 cm^{-1} for HCl and 2 cm^{-1} for OCI. The present results corroborate the validity of the SEC approach even for regions quite far away from the equilibrium geometry of the diatomic molecule. The numerical values of the parameters obtained through the calibration process are gathered in Table 3.

To obtain the potential energy curves for the excited states, we have used our own SEC points, since no spectroscopic information seems to be available for such systems. Moreover, we have employed both eqs 10 and 11 to carry out the fits. Yet, for brevity, we give in Table 3 only the numerical information required to reproduce the Coulombic cusp at the united-atom limit, and the agreement with experiment, with the average deviations being 21 cm^{-1} (0.2%) for HCl and 13 cm^{-1} (0.4%) for OCI. To our

<table>
<thead>
<tr>
<th>coefficient</th>
<th>HCl</th>
<th>OCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>D, D/E_h</td>
<td>0.370 391</td>
<td>0.246 085</td>
</tr>
<tr>
<td>a_1, a_3/a_0^{-1}</td>
<td>1.882 657</td>
<td>2.498 213</td>
</tr>
<tr>
<td>a_2, a_3/a_0^{-2}</td>
<td>0.745 380</td>
<td>1.466 852</td>
</tr>
<tr>
<td>a_5, a_3/a_0^{-3}</td>
<td>0.307 348</td>
<td>0.787 479</td>
</tr>
<tr>
<td>a_6/a_0^{-4}</td>
<td>0.006 800 24</td>
<td>0.776 447</td>
</tr>
<tr>
<td>a_7/a_0^{-5}</td>
<td>-0.141 087</td>
<td></td>
</tr>
<tr>
<td>a_8/a_0^{-6}</td>
<td>0.009 242 53</td>
<td></td>
</tr>
<tr>
<td>γ_0, γ_1/a_0^{-1}</td>
<td>1.399 596</td>
<td>1.962 760</td>
</tr>
<tr>
<td>γ_1</td>
<td>12.067 036</td>
<td>0.517 858</td>
</tr>
<tr>
<td>γ_2/a_0^{-1}</td>
<td>0.008 154 30</td>
<td>0.301 390</td>
</tr>
</tbody>
</table>

* N = 4 in eq 11. b N = 6 in eq 11.
knowledge, no spectroscopic experimental information is available for the excited states investigated in the current work. Although the calculated values reported in Table 6 and Table 7 are very sensitive to small errors in the potential function (and hence should be viewed with some caution), they may be helpful to localize the corresponding spectral lines.

5. Conclusions

We have shown that the physically motivated EHFACE2(U) models are most adequate to describe the electronic states of HCl and OCI considered in the present work. To obtain the fitting parameters when experimental data was unavailable, or else to test the theory, we have also reported accurate ab initio MRCl calculations for those electronic states by employing a full valence complete active space construction of the reference state and a large basis set (AVQZ). The calculated energies were then corrected through scaling of the external correlation to compensate for the truncation of the CI expansion and for the basis set incompleteness.

The model potential energy curves reported in the present work have shown high reliability when compared with the input data. Thus, they may be useful for molecular dynamics studies, particularly those referring to the photodissociation and predissociation of hypochlorous acid in ozone chemistry. The present study offers also a new test of the EHFACE2U model. The quality of the results achieved, together with the simplicity of the functional form, clearly recommend it to represent the two-body fragments of polyatomic potential-energy surfaces within the double many-body expansion method. In fact, this is currently being used to obtain a global two-valued potential energy surface for HCl, with accurate ab initio electronic structure calculations at the levels reported in this work having already been completed. This ongoing work will hopefully be reported in a future publication.

Acknowledgment. A.P.G. thanks the Fundación Gil Dávila, Spain, for a scholarship. This work has been supported by the Fundación para la Ciencia e Tecnologia, Portugal, under program PRAXIS XXI.

References and Notes

(42) Sinanoğlu, O.; Brueckner, K. A. Three Approaches to Electron Correlation in Atoms; Yale University: New Haven, CT, 1970.