Durham Research Online

Deposited in DRO:
19 August 2015

Version of attached file:
Published Version

Peer-review status of attached file:
Peer-reviewed

Citation for published item:

Further information on publisher's website:
http://dx.doi.org/10.1063/1.2371080

Publisher’s copyright statement:
© 2006 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in The Journal of Chemical Physics 125, 184312 (2006) and may be found at http://dx.doi.org/10.1063/1.2371080

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a link is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full DRO policy for further details.
Ab initio potential energy surfaces, bound states, and electronic spectrum of the Ar–SH complex
Richard J. Doyle, David M. Hirst, and Jeremy M. Hutson

Citation: The Journal of Chemical Physics 125, 184312 (2006); doi: 10.1063/1.2371080
View online: http://dx.doi.org/10.1063/1.2371080
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/125/18?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Highly accurate potential energy surface, dipole moment surface, rovibrational energy levels, and infrared line list for 32S16O2 up to 8000 cm−1

A three-dimensional ab initio potential energy surface and predicted infrared spectra for the He – N2O complex

Spectroscopy of Ar–SH and Ar–SD. II. Determination of the three-dimensional intermolecular potential-energy surface

Ab initio intermolecular potential energy surface, bound states, and microwave spectra for the van der Waals complex Ne–HCCCN

The C 3 -bending levels of the C 3 – Ar complex studied by optical spectroscopy and ab initio calculation
J. Chem. Phys. 120, 3189 (2004); 10.1063/1.1641017
I. INTRODUCTION

van der Waals complexes containing open-shell species are of great current interest. In particular, complexes containing atoms or molecules with orbital angular momentum necessarily involve multiple electronic states. They provide a test bed for studying electronically nonadiabatic effects, which are important in the theory of reaction dynamics. In addition, the observation of prereactive van der Waals complexes trapped in bound levels can shed light on intermolecular forces in the entrance and exit channels of chemical reactions. The form of these shallow, long-range wells can be important in determining reaction outcomes and transition-state geometries.

In this paper, we consider the complex consisting of an open-shell SH radical and an Ar atom. New ab initio potential energy surfaces (PESs) for the X 3Π state are presented and used in calculations of the bound rotation-vibration levels. We discuss the possibility of employing an approximate approach in the bound-state calculations, using a single adiabatic PES rather than the two surfaces used in the standard method. Finally, the bound-state energies and wave functions are used to simulate the vibrationally resolved electronic spectrum.

The Ar–SH cluster was first detected experimentally by Yang et al. using laser-induced fluorescence excitation spectroscopy. Subsequently, this group developed empirical PESs for the complex, for both the A state and the X state by fitting model functions to reproduce laser-induced fluorescence results. The region of the A state PES corresponding to the Ar–S–H configuration (Jacobi angles between ~90° and 180°) was determined only approximately, because the fluorescence experiments did not probe this zone. More recently, Hirst et al. have presented a PES for the A state based on ab initio calculations at the restricted coupled cluster with single, double, and noniterative triple excitations level with the aug-cc-pV5Z basis set. This surface was used to predict bound vibrational levels in the Ar–SH configuration which have not, to our knowledge, been observed in experiment so far. A possible reason why these levels have eluded detection is discussed in Sec. IV of this paper.

Sumiyoshi et al. have recorded high-resolution spectra for Ar–S–H in the ground electronic state using Fourier-transform microwave spectroscopy. These authors also produced PESs for the X state based on fitting a function to reproduce their experimental results, and these surfaces were later improved with the aid of some ab initio results. Most recently, results from microwave–millimeter-wave double-resonance spectroscopy were employed to determine new three-dimensional PESs for the X state.

The family of weakly bound clusters containing a rare gas atom and either the OH or SH radical has been reviewed by Carter et al. in 2000 and by Heaven in 2005.

The structure of the present paper is as follows. In Sec. II we present new PESs for Ar–SH (3Π) based entirely on ab initio calculations at the RCCSD(T) level with an aug-cc-pV5Z basis set. In Sec. III we describe bound rotation-vibration level calculations using these surfaces. We also investigate the wave functions and introduce a new adiabatic approximation for the bound states, including spin-orbit coupling. In Sec. IV the results are combined with those of a
previous study of the $A^2Σ^+$ state, in order to produce a high-quality simulation of the vibrationally resolved electronic spectrum.

II. POTENTIAL ENERGY SURFACES

The geometry of the complex is specified in terms of body-fixed Jacobi coordinates $r$, $R$, and $θ$. $R$ is the length of the vector $R$ which links the center of mass of the SH fragment to the Ar nucleus. The vector $r$ links the S nucleus to the H nucleus: its modulus $r$ is the SH bond length. The angle between $R$ and $r$ is $θ$, so that $θ=0°$ corresponds to a linear Ar–H–S configuration. For this work the bond length $r$ was held constant at the experimentally determined equilibrium value of 1.3409 Å, which is justified because the vibrational motion of the diatom is very weakly coupled to the relatively low-frequency van der Waals modes of interest.

Energies were calculated for a regular grid of geometry points using the MOLPRO quantum chemistry program. These points are at every distance $R$ from 3.25 to 5.5 Å in steps of 0.25 Å and for every angle $θ$ from 0° to 180° in steps of 15°. This gives a total of 130 points. We used the RCCSD(T) method with the aug-cc-pV5Z basis set. The counterpoise procedure of Boys and Bernardi was used to correct for basis set superposition error. This is the same level of theory and basis set as were used in recent calculations of the PES for the $A$ state of Ar–SH.

Two potential surfaces were obtained from the ab initio calculations. These correspond to two adiabatic electronic states: one symmetric ($A'$) and one antisymmetric ($A''$) with respect to reflection in the plane of the nuclei. The two states are degenerate at linear geometries but nondegenerate at nonlinear geometries: the splitting is an example of the Renner-Teller effect. The interaction energies for each state were calculated at the RCCSD(T) level, using the smaller aug-cc-pVTZ basis set, and counterpoise correction. A comparison of the positions and energies of the minima on the Ar–SH surfaces presented here with those for X-state He–SH and Ne–SH is given in Table I. For all the $A''$ surfaces there is a global minimum in the linear X-SH configuration (where $X$ is He, Ne, or Ar) and a local minimum in the linear X-HS configuration. The X-HS configurations are saddle points on the $A'$ surfaces, which have shallow local minima at $θ=180°$ and global minima at nonlinear configurations. The $A'$ global minima are deeper than those on the $A''$ surfaces, because in the $A'$ state the SH π hole is directed towards the Ar atom, resulting in reduced repulsion. The global minima for the $A'$ state occur at angles $θ$ that increase with the atomic number of the rare gas atom. Also, as expected, the minima are deeper for clusters containing heavier (and more polarizable) rare gas atoms.

In order to perform dynamical calculations on Ar–SH, we need to evaluate the matrix elements of the potential between electronic states labeled with an angular momentum quantum number $λ$. For this purpose it is convenient to re-express the PESs as the sum ($V_0$) and difference ($V_2$) potentials,

$$V_0(R, θ) = \frac{1}{2} [V_{A'}(R, θ) + V_{A''}(R, θ)],$$

$$V_2(R, θ) = \frac{1}{2} [V_{A'}(R, θ) - V_{A''}(R, θ)].$$

Contour plots of these surfaces are shown in Fig. 2. They are

---

![FIG. 1. Ab initio potential energy surface contour plots for Ar–SH (X) in the $A'$ state (upper plot) and the $A''$ state (lower plot). Solid contour lines are shown at 10 cm$^{-1}$ intervals, ranging from 0 to $−150$ cm$^{-1}$ inclusive for the $A'$ surface and 0 to $−120$ cm$^{-1}$ inclusive for the $A''$ surface. Dashed contour lines are shown at 100 cm$^{-1}$ intervals from $+100$ to $+500$ cm$^{-1}$ inclusive for both surfaces. The linear Ar–H–S conformation corresponds to $θ=0°$.](image)

---

<table>
<thead>
<tr>
<th>Cluster</th>
<th>State</th>
<th>$R$ (Å)</th>
<th>$θ$ (deg)</th>
<th>depth (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar–SH</td>
<td>$A'$</td>
<td>3.678</td>
<td>66.6</td>
<td>157.69</td>
</tr>
<tr>
<td>Ne–SH</td>
<td>$A'$</td>
<td>3.611</td>
<td>57.2</td>
<td>57.05</td>
</tr>
<tr>
<td>He–SH</td>
<td>$A'$</td>
<td>3.639</td>
<td>54.4</td>
<td>25.97</td>
</tr>
<tr>
<td>Ar–SH</td>
<td>$A'$</td>
<td>3.801</td>
<td>180</td>
<td>128.54</td>
</tr>
<tr>
<td>Ne–SH</td>
<td>$A'$</td>
<td>3.593</td>
<td>180</td>
<td>54.27</td>
</tr>
<tr>
<td>He–SH</td>
<td>$A'$</td>
<td>3.593</td>
<td>180</td>
<td>25.27</td>
</tr>
<tr>
<td>Ar–SH</td>
<td>$A''$</td>
<td>4.274</td>
<td>0</td>
<td>125.22</td>
</tr>
<tr>
<td>Ne–SH</td>
<td>$A''$</td>
<td>4.101</td>
<td>0</td>
<td>45.75</td>
</tr>
<tr>
<td>He–SH</td>
<td>$A''$</td>
<td>4.126</td>
<td>0</td>
<td>21.16</td>
</tr>
</tbody>
</table>
FIG. 2. Contour plots for the Ar–SH (X) difference (upper plot) and sum (lower plot) potential energy surfaces. Solid contour lines are shown at 10 cm$^{-1}$ intervals, ranging from 0 to $-300$ cm$^{-1}$ inclusive for the difference surface and from 0 to $-120$ cm$^{-1}$ inclusive for the sum surface. Dashed contour lines are shown at 100 cm$^{-1}$ intervals from $+100$ to $+500$ cm$^{-1}$ for the sum surface only. The linear Ar–H–S conformation corresponds to $\theta=0^\circ$.

III. BOUND-STATE CALCULATIONS

A. Coupled-channel calculations

The bound states of a complex such as Ar–SH (X$^2\Pi$) involve both PESs. In the present work we use a coupled-channel approach to calculate the bound states. In a body-fixed axis system the Hamiltonian operator is

$$H = -\frac{\hbar^2}{2\mu} \sum_{j} R^{-1} \left( \frac{\partial^2}{\partial R^2} \right) R + H_{\text{mon}} + \frac{\hbar^2}{2\mu R^2} \hat{\mathbf{j}} \cdot \hat{\mathbf{j}} + \hat{\mathbf{V}},$$  

where $H_{\text{mon}}$ is the monomer Hamiltonian and $\hat{\mathbf{V}}$ is the intermolecular potential. In a full treatment including overall rotation, the total wave function of the complex may be expanded,$^1$

$$\Psi_n^{JM} = R^{-1} \sum_{jP\lambda\sigma} \Phi_n^{JM}_{jP;\lambda\sigma} \chi_{Pn;j;\lambda\sigma}(R),$$

where the channel basis functions are

$$\Phi_n^{JM}_{jP;\lambda\sigma} = \varphi \varphi(\frac{2j+1}{4\pi}) \left[ \frac{2j+1}{4\pi} \right]^{1/2} D_{\mu\nu}^P(\phi, \theta, 0) \times \left[ \frac{2j+1}{4\pi} \right]^{1/2} D_{\mu\nu}^P(\alpha, \beta, 0).$$

The monomer basis functions are labeled by Hund’s case (a) quantum numbers $\lambda$ and $\sigma$, the projections of the electronic orbital and spin angular momentum along the SH axis, and $\omega=\lambda+\sigma$. The latter were fitted to reproduce experimental results, with starting values for the potential parameters obtained from $ab$ initio calculations [RCCSD(T)/aug-cc-pVTZ]. The form of our sum potential is also qualitatively similar to those recently presented by Sumiyoshi and Endo.$^2$ The latter were fitted to reproduce experimental results, with starting values for the potential parameters obtained from $ab$ initio calculations [RCCSD(T)/aug-cc-pVTZ]. The form of our sum potential is also qualitatively similar to those recently presented by Sumiya et al.$^3$
using the BOUND program of Hutson. The wave function log-derivative matrix is propagated outwards from a boundary point at short range \( R_{\text{min}} \) and inwards from a boundary point at long range \( R_{\text{max}} \) to a matching point \( R_{\text{mid}} \) in the classically allowed region. If \( E \) is an eigenvalue of the Hamiltonian, the determinant of the difference between the two log-derivative matrices at \( R_{\text{mid}} \) is zero. The BOUND program locates eigenvalues by searching for zeros of the derivative sector size of 0.02 Å. The basis set includes all SH functions up to \( j = 15/2 \) in both spin-orbit orbit manifolds.

The energies obtained from full close-coupling calculations for the lowest few \( J = 3/2 \) levels of Ar–SH (actually carried out in the equivalent space-fixed basis set) are shown in Table II. These levels all correlate with SH \( ^2\Pi_{3/2}, J=3/2 \) and are labeled with the projection quantum number \( P \) and parity doubling constant \( B \). All energies are relative to the dissociation energy to form SH \((X^2\Sigma^+_1, j = 3/2)\). All energies are given as wave numbers in cm\(^{-1}\).

### Table II. Bound-state energies for \( J = 3/2 \) levels of Ar–SH from full close-coupling calculations (average \( E_{\text{CC}} \) and parity splitting \( \Delta E_{\text{CC}} \)), helicity decoupling calculations \( (E_{\text{HD}}) \), and single-surface calculations on the lower adiabatic surface including spin-orbit coupling \( (E_{\text{ul}}) \). All energies are relative to the dissociation energy to form SH \((X^2\Sigma^+_1, j = 3/2)\). All energies are given as wave numbers in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>( P )</th>
<th>( n )</th>
<th>( E_{\text{CC}} )</th>
<th>( \Delta E_{\text{CC}} )</th>
<th>( E_{\text{HD}} )</th>
<th>( E_{\text{ul}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3/2</td>
<td>0</td>
<td>-102745</td>
<td>+3.5 \times 10^{-5}</td>
<td>-102652</td>
<td>-102725</td>
</tr>
<tr>
<td>+1/2</td>
<td>0</td>
<td>-97766</td>
<td>+0.144</td>
<td>-97593</td>
<td>-97667</td>
</tr>
<tr>
<td>-3/2</td>
<td>0</td>
<td>-94940</td>
<td>-1.1 \times 10^{-3}</td>
<td>-94894</td>
<td>-95035</td>
</tr>
<tr>
<td>-1/2</td>
<td>0</td>
<td>-92116</td>
<td>-0.138</td>
<td>-92222</td>
<td>-92293</td>
</tr>
<tr>
<td>+3/2</td>
<td>1</td>
<td>-77292</td>
<td>+2.6 \times 10^{-5}</td>
<td>-77111</td>
<td>-77258</td>
</tr>
<tr>
<td>+1/2</td>
<td>1</td>
<td>-72276</td>
<td>+0.134</td>
<td>-72100</td>
<td>-72148</td>
</tr>
<tr>
<td>-3/2</td>
<td>1</td>
<td>-69356</td>
<td>-1.3 \times 10^{-3}</td>
<td>-69265</td>
<td>-69382</td>
</tr>
<tr>
<td>-1/2</td>
<td>1</td>
<td>-67207</td>
<td>-0.124</td>
<td>-67291</td>
<td>-67315</td>
</tr>
</tbody>
</table>

**B. Wave functions**

The full wave functions [Eq. (2)] contain contributions from all possible values of \( P \) and \( \omega \) and are not separable between the body-fixed angles \((\theta, \phi)\) and the space-fixed angles \((\beta, \alpha)\). This makes them hard to visualize. In addition, since the mixings depend on the total angular momentum \( J \), they are not convenient for calculating band intensities. We therefore introduce two approximations to simplify the description of the wave functions for this purpose. First, we introduce the helicity decoupling approximation, where matrix elements of \((\hat{J} - \hat{j})^2\) off-diagonal in \( P \) are neglected. Secondly, we neglect matrix elements of \( H_{\text{mon}} \) off-diagonal in \( \sigma \) (spin-uncoupling terms). The coupled equations then simplify to

\[
\begin{align*}
-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dR^2} + & \frac{\hbar^2}{2\mu R^2} \left( J(J+1) + j(j+1) - 2\omega^2 \right) - E_{P,0} \\
& \times \chi_{\rho,\sigma;\lambda}^{\frac{1}{2},j,j}(R) \\
= & -\sum_{j' \neq j} (JM;j'P\lambda';\sigma)^{\frac{1}{2},j,j}(R) \chi_{\rho,\lambda;\sigma}^{j,j}(R).
\end{align*}
\]

Since all matrix elements off-diagonal in \( P \) and \( \sigma \) have been neglected, states with quantum numbers \((P, \omega)\) and \((-P, -\omega)\) are uncoupled and it is not necessary to take combinations of definite total parity. However, states with \((P, \omega)\) and \((-P, \omega)\) or \((-P, -\omega)\) have different potential energies and are nondegenerate.

The energy levels obtained from helicity decoupling calculations for Ar–SH are included in Table II. The approxi-
mation is accurate to about 0.2 cm\(^{-1}\) for \(n=0\) and 1 but is less reliable for higher states. In particular, the region between \(-60\) and \(-40\) cm\(^{-1}\) contains both \(j=3/2, n=2\) and \(j=5/2, n=0\) levels. In the presence of the resulting near degeneracies, the terms that are omitted in the approximate Hamiltonian can cause quite significant level shifts.

In the helicity decoupling approximation, \(P\) is a good quantum number. However, \(\omega\) is not because \(V_2\) mixes levels with \(\Delta \lambda = \pm 2\) (but \(\Delta \sigma = 0\)) and thus mixes \(\omega = +3/2\) with \(-1/2\) and \(\omega = +1/2\) with \(-3/2\). However, in the absence of terms off-diagonal in \(n\) the two sets are not mixed with one another. Each wave function thus has only two components corresponding to different values of \(\omega\). The wave functions may be written as

\[
\Psi_{Pn}^I = \sum_{\omega} \chi_{Pn,\omega}(R, \theta) P_{\lambda,\sigma}^{\lambda M}(R, \theta) \Phi_{P\lambda,\sigma}^{\lambda M}(\alpha, \beta, \phi),
\]

where the basis functions now exclude the \(\theta\) dependence,

\[
\Phi_{P\lambda,\sigma}^{\lambda M} = \varphi_{\alpha,\lambda}(2J + 1) \frac{1}{8\pi^2} D_{JM}^{\lambda}(-1/2)^{JJ_{\sigma}}(\alpha, \lambda, \beta, \phi),
\]

and the 2D functions that characterize the components of the wave function for each \(\omega\) are

\[
\chi_{Pn,\omega}(R, \theta) = \sum_{j} (j + 1/2)^{1/2} d_{j\sigma}^{\omega}(\theta) \chi_{Pn,\omega; j,\sigma}(R),
\]

where \(d_{j\sigma}^{\omega}(\theta)\) is a reduced rotation matrix.\(^{39}\)

We have adapted the BOUND program\(^{41}\) to calculate wave functions for this case by backsubstituting into the log-derivative propagation equations, as described for the closed-shell (single-surface) case by Thorne and Hutson.\(^{42}\) Examples of the resulting wave functions \(\chi_{Pn,\omega}(R, \theta)\) are shown in Fig. 3. It may be seen that the components for different values of \(\omega\) have quite different radial and angular distributions.

The Ar–SH wave functions are qualitatively similar to those for Ne–SH obtained by Cybulski et al.\(^{5}\) Since the potential anisotropy for Ar–SH is only a few tens cm\(^{-1}\) in the well region, there is only weak mixing of SH rotational functions with different values of \(j\). For this reason the wave functions are dominated by the functions \(\tilde{d}_{j\sigma}^{\omega}(\theta)\), as described by Dubernet et al.\(^{1}\) for the case of Ar–OH. The \(d\) functions are shown, for example, in Fig. 7 of Ref. 1 and the angular parts of the wave functions of Fig. 3 follow them quite closely.

### C. Adiabatic approximations

In a basis set of Hund’s case (a) functions with signed values of \(\lambda = \pm 1\) and \(\sigma = \pm 1/2\), we can define new adiabatic surfaces (adiabats) including spin-orbit coupling as eigenvalues of the Hamiltonian matrix at each value of \(R\) and \(\theta\),

\[
\begin{pmatrix}
V_0 + \frac{1}{2}a & 0 & V_2 & 0 \\
0 & V_0 - \frac{1}{2}a & 0 & V_2 \\
V_2 & 0 & V_0 - \frac{1}{2}a & 0 \\
0 & V_2 & 0 & V_0 + \frac{1}{2}a
\end{pmatrix},
\]

where again the spin-orbit Hamiltonian is taken to be simply \(a\lambda\sigma\). This clearly factorizes into two equivalent \(2 \times 2\) matrices, one containing \(\omega = +3/2\) and \(-1/2\) and the other containing \(\omega = +1/2\) and \(-3/2\). The resulting adiabats may be designated \(V_4(R, \theta)\) and \(V_6(R, \theta)\) with corresponding electronic functions \(\psi_4(R, \theta)\) and \(\psi_6(R, \theta)\) given by

\[
\begin{pmatrix}
\psi_4(R, \theta) \\
\psi_6(R, \theta)
\end{pmatrix} = \left(\begin{array}{cc}
\cos \alpha_{ad}(R, \theta) & \sin \alpha_{ad}(R, \theta) \\
-\sin \alpha_{ad}(R, \theta) & \cos \alpha_{ad}(R, \theta)
\end{array}\right) \left(\begin{array}{c}
\varphi_{\pm 3/2} \\
\varphi_{\mp 1/2}
\end{array}\right),
\]

where \(\varphi_{\pm \omega} = \varphi_{\pm \lambda \sigma}\). The adiabats for Ar–SH are shown in Fig. 4. Since for Ar–SH \(V_2(R, \theta)\) is small compared to \(a\) in the well region, the lower adiabat is always predominantly \(\omega = \pm 3/2\) in character and the upper adiabat is always predominantly \(\omega = \pm 1/2\) in character. The corresponding mixing angle \(\alpha_{ad}\) is 0 at \(\theta=0^\circ\) and \(180^\circ\) [where \(V_2(R, \theta=0)\)] and less than \(20^\circ\) at other angles for \(R > 3.5\) Å. A contour plot of the mixing angle is shown in Fig. 5.

A further consequence of the large spin-orbit coupling constant is that both adiabats resemble the sum potential \(V_0(R, \theta)\) much more than the \(A^1\) and \(A^2\) potentials. The spin-orbit coupling has in effect quenched the splitting between the \(A^1\) and \(A^2\) states. This explains why there is no tendency for the wave functions shown in Fig. 3 to “fall into” the nonlinear minimum of the \(A^1\) state.

The existence of adiabats including spin-orbit coupling suggests a Born-Oppenheimer separation in which the total wave functions are written approximately as

\[
\Psi_{Pn} = R^{-1}\psi(P, \theta)\chi_{Pn}(R, \theta),
\]

where \(\psi\) is one of the functions of Eq. (14) and \(\chi_{Pn}(R, \theta)\) is a solution of an effective Schrödinger equation of the form

\[
\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + H_{rot} + \frac{\hbar^2}{2\mu R^2} \frac{\partial^2}{\partial \theta^2} + V_4(R, \theta) - E_{Pn} = 0.
\]

However, the appropriate angular operator \(H_{rot}\) to use in such a calculation is hard to define. The reduced rotation matrices \(d_{j\sigma}^{\omega}(\theta)\) that describe the free SH molecule are eigenfunctions of \(H_{rot} = b(\hat{j}^2 - 2a^2)\), where

\[
\hat{j}^2 = -\frac{1}{\sin^2 \theta} \frac{\partial}{\partial \theta} \left( \frac{\partial}{\partial \theta} \right) + \frac{P^2 + \omega^2 - 2P\omega \cos \theta}{\sin^2 \theta}.
\]

This contains singularities at \(\theta=0^\circ\) and/or \(180^\circ\) that depend on the values of \(P\) and \(\omega\). However, there is no single value of \(\omega\) that is appropriate at all configurations. The simplest approach is to replace \(\omega\) in Eq. (17) with the value that is appropriate at \(\theta=0^\circ\) and \(180^\circ\) and solve Eq. (16) in a basis set of \(d\) functions for each value of \(P\). This is equivalent to solving the coupled equations using a basis set containing...
only functions with a single value of $\omega$. The results obtained with this approximation are included in Table II. It may be seen that it gives energies that are generally slightly too low (compared to the helicity decoupling results), by 0.05–0.15 cm$^{-1}$. A slightly better but significantly more complicated approximation would be to replace $\omega$ with $\langle \omega \rangle$ and $\omega^2$ with $\langle \omega^2 \rangle$ in Eq. (17) to give an improved effective potential.

One approach that is clearly not appropriate is to carry out a bound-state calculation on a single adiabat $V_\pm(R, \theta)$ assuming that the SH molecule behaves as a closed-shell rigid rotor. Such a calculation would give substantially incorrect energies and wave functions.

It is in fact true that no wave function of the form (15) can have the correct behavior near both linear geometries. To see this, consider an alternative definition of the mixing....

FIG. 3. (Color online) Contour plots of the wave function components, superimposed on the average potential.
angle that can be obtained from a single wave function in the helicity decoupling approximation,

$$\tan \alpha_{Pn}^J(R, \theta) = \frac{X_{Pn;+\frac{1}{2}}(R, \theta)}{X_{Pn;+\frac{3}{2}}(R, \theta)}.$$  \hspace{1cm} (18)

This quantity is plotted for \(n=0\) and all four \(P\) values corresponding to \(J=3/2\) in Fig. 6. The mixing angles for \(P=+3/2\) and \(P=+1/2\) bear some similarity to \(\alpha_{ad}(R, \theta)\) (Fig. 5) at small \(\theta\), but tend to 90° instead of zero at \(\theta=180°\). Conversely, the mixing angles for \(P=-3/2\) and \(P=-1/2\) tend to 90° at \(\theta=0°\). This is easy to explain in terms of the reduced rotation matrices that appear in Eq. (12). For example, the functions \(d_{a3/2,a3/2}(\theta)\) all behave as \(\cos^3(\theta/2)\) as \(\theta \to 180°\), while the functions \(d_{\pm 1/2, \pm 3/2}(\theta)\) behave as \(\cos(\theta/2)\). This corresponds to \(\tan \alpha_{3/2,n}^J \to \infty\) as \(\theta \to 180°\) so \(\alpha_{3/2,n} \to 90°\) in that limit. The point here is that the component of the \(P=+3/2\) wave function on the \(\omega=-1/2\) surface goes to zero more slowly than that on the \(\omega=+3/2\) surface as \(\theta \to 180°\). Figure 5 shows that the coupled-channel wave functions (10) for \(P=+3/2\) and \(+1/2\) are predominantly in the \(\omega=-1/2\) state near \(\theta=180°\), which corresponds to the upper adiabat rather than the lower one. The \(P=+3/2\) and \(-1/2\) wave functions show similar behavior around \(\theta=0°\). This is not the behavior implied by Eq. (15).

IV. ELECTRONIC SPECTRUM CALCULATION

A. Transition wave numbers

In order to calculate the line positions in the vibrationally resolved \(A^2\Sigma^+ \rightarrow X^2\Pi\) electronic spectrum, we require the bound-state energies for the excited electronic state, as well as those for the ground state. For the \(A^2\Sigma^+\) state we make use of the recent PES presented by Hirst et al.\(^{22}\) This surface has a global minimum of \(-742.5\) cm\(^{-1}\) at the linear Ar–HS conformation (\(\theta=0°\)) and a secondary minimum of \(-673.7\) cm\(^{-1}\) for linear Ar–SH (\(\theta=180°\)). The two minima are separated by a barrier more than 600 cm\(^{-1}\) high and the lowest-energy vibrational levels are localized within one or the other of the two wells.

The bound states of this PES have been analyzed previously\(^{22}\) and only a brief discussion is given here. Bound-state energies were calculated as eigenvalues of the spin-free triatomic Hamiltonian in Jacobi coordinates. Discrete variable representations (DVRs) were employed for both the intermolecular distance \(R\) and the angle \(\theta\). For \(R\), 120 sinc-DVR functions\(^{24}\) were used, with DVR points ranging from 2.5 to 8.5 Å. For \(\theta\), a 64-point DVR based on Legendre polynomials was used. With this basis set, the bound levels of interest were converged to at least seven significant figures. The resulting levels are labeled by quantum numbers \((v_{SH}, b^K, n)\), where \(v_{SH}\) and \(n\) are quantum numbers for the SH stretch and the atom-diatom stretch, respectively. \(K\) is the
projection of the total angular momentum of the diatom, neglecting spin, onto the body-fixed z axis, and b is the number of nodes in the intermolecular angle θ. The resulting energies for levels with total angular momentum N=0 (neglecting spin) are in precise agreement with previous results. To facilitate the calculation of band intensities, for N=1 the helicity decoupled approximation was employed, in which the Coriolis terms coupling different K levels are ignored. The helicity decoupled energies are within 0.5 cm⁻¹ of the full close-coupled results.

For the purpose of calculating transition frequencies, the asymptotic separation of the potentials is taken to be the experimental excitation energy from the v=0, j=3/2 level of the 3Π₂ state to the lowest v=0, j=1/2 level of the 2Σ⁺ state of isolated SH, which is 30 832.68 cm⁻¹. All transitions of the complex were assumed to originate from the P=+3/2 level of Ar–SH (1Π₁). The lowest-energy transition frequency for the complex is calculated to be 30 488.5 cm⁻¹, which is 31.5 cm⁻¹ greater than the experimental value of 30 457 cm⁻¹. This agreement is reasonable, considering the level of theory used in the calculation of the potentials.

B. Transition dipole moments

Calculations of spectroscopic intensities require transition dipole moments µ_{if}^{tot}, where

\[ µ_{if}^{tot} = ⟨i|μ_el|f⟩. \tag{19} \]

The integrals involve the initial (i) and final (f) wave functions as determined from bound-state calculations. In this work we evaluated transition dipoles over internal coordinates (R, θ), neglecting overall rotation. This gives transition dipoles that correspond to band intensities between intermolecular vibrational states. The electronic dipole moment µ_{el} is in general a parametric function of the nuclear coordinates. In the body-fixed frame it may be expanded in terms of reduced rotation matrices,

\[ µ_{el}(R, θ) = \sum_j µ_{el,j}(R)δ^{Δλ}_{P,j}(θ), \tag{20} \]

where ΔP=P_f−P_i and Δλ=λ_f−λ_i. In the excited electronic state, P=K±½. In this work it is assumed that µ_{el} consists purely of contributions from the SH monomer, so that only j=1 contributes in Eq. (20) and the coefficients µ_{el,j} are independent of R. Since we are dealing with a perpendicular transition in SH, Δλ=±1. The transition dipoles were calculated as one-dimensional Gaussian quadratures in θ, then integrated over R.

C. Intensities and lifetime factors

The signals in a pulsed-laser fluorescence excitation experiment decay exponentially following each pulse, with a lifetime equal to that of the excited state being probed. Intensities are typically measured as the area under the decay curve, and so the experimental intensities are proportional to the lifetime of the excited state. Ar–SH is somewhat unusual in the large range of lifetimes exhibited by different vibrational levels in the A state. It is known that the presence of the Ar atom blocks the electronic predissociation of the SH radical, leading to a greatly increased lifetime of up to 600 ns for low-lying bound levels, compared to ~1 ns for the uncomplexed species. However, the actual lifetime depends on the degree of vibrational excitation, and lifetimes specific to particular levels have been calculated by McCoy.20

The top panel of Fig. 7 shows a spectrum calculated directly from the squares of transition dipoles, while the center panel shows a spectrum in which the intensities have been multiplied by McCoy’s lifetime values. Clearly this is possible only for levels for which lifetime data exist, and transitions to other levels are omitted in the center panel (i.e.,
it is assumed that their lifetimes are small). Also shown is an experimental spectrum from Ref. 20. The spacings between the peaks in the calculated Ar–SH spectrum are consistently \(\sim 5\%\) smaller than in experiment. It is clear that the intensity distributions are significantly different in the two calculated spectra, and that the one that includes lifetime factors gives considerably better agreement with experiment. The agreement in intensities is quite good, especially considering that the experimental spectrum was most likely not normalized for dye laser power.\(^{51}\) From our results it seems likely that the small peak at \(\sim 30 \text{ 810 cm}^{-1}\) in the experimental spectrum can be assigned to the transition to \((0,0^3,6)\).

Even without the lifetime weighting, transitions to levels localized in the \(\theta=180^\circ\) well of the \(A\) state, which are labeled with + + symbols in Fig. 7, are weak in the simulated spectrum. This arises because of poor overlap with the \(P=+3/2\) ground-state wave function (which is concentrated around \(\theta=0^\circ\)). In addition, it is likely that such levels have short lifetimes close to that of uncomplexed SH (Ref. 22) and so will have even lower intensities in the fluorescence excitation spectrum. These levels have not been observed experimentally to our knowledge.

V. SUMMARY

We have obtained new \textit{ab initio} PESs for the Ar–SH complex in its ground \(2^3\Pi\) electronic state and used them to calculate bound-state energies and wave functions using coupled-channel methods. We have also described a new adiabatic approximation that includes spin-orbit coupling and can be used to calculate bound states on a single PESs. However, the adiabatic wave functions fail to reproduce some features of the true wave functions. We have used our results to simulate the vibrationally resolved laser-induced fluorescence excitation spectrum of Ar–SH, with intensities modeled using calculated transition dipole moments and calculated lifetimes. The inclusion of the lifetime factor is important to obtain satisfactory agreement with the experimental intensities.

ACKNOWLEDGMENTS

The authors would like to thank Terry Miller for providing his experimental spectrum. One of the authors (R.J.D.) also thanks Dr. Stuart Mackenzie for helpful discussions, and is grateful to the Engineering and Physical Sciences Research Council (EPSRC) for funding.

51 T. A. Miller (private communication).
52 We adopt the convention of using lowercase letters for all quantities that refer to monomers and reserve uppercase letters for quantities that refer to the complex as a whole.