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Ab Initio Treatment of the Chemical Reaction Precursor Complex Br(2P)–HCN. 1. Adiabatic and Diabatic Potential Surfaces

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The three adiabatic potential surfaces of the Br(2P)–HCN complex that correlate to the 2P ground state of the Br atom were calculated ab initio. With the aid of a geometry-dependent diabatic mixing angle, also calculated ab initio, these adiabatic potential surfaces were transformed into a set of four diabatic potential surfaces required to define the full 3 × 3 matrix of diabatic potentials. Each of these diabatic potential surfaces was expanded in terms of the appropriate spherical harmonics in the atom-linear molecule Jacobi angle θ. The dependence of the expansion coefficients on the distance R between Br and the HCN center of mass and on the CH bond length was fit to an analytic form. For HCN in its equilibrium geometry, the global minimum with Δ0 = 800.4 cm⁻¹ and RCH = 6.908a₀ corresponds to a linear Br–NCH geometry, with an electronic ground state of C2v symmetry. A local minimum with Δ1 = 415.1 cm⁻¹, RCH = 8.730a₀, and a twofold degenerate Π ground state is found for the linear Br–HCN geometry. The binding energy, Δe, depends strongly on the CH bond length for the Br–HCN complex and much less strongly for the Br–NCH complex, with a longer CH bond giving stronger binding for both complexes. Spin–orbit coupling was included and diabatic states were constructed that correlate to the ground 2P3/2 and excited 2P1/2 spin–orbit states of the Br atom. For the ground spin–orbit state with electronic angular momentum j = (3/2) the minimum in the potential for projection quantum number α = ±(3/2) coincides with the local minimum for linear Br–HCN of the spin-free case. The minimum in the potential for projection quantum number α = ±(1/2) occurs for linear Br–NCH but is considerably less deep than the global minimum of the spin-free case. According to the lowest spin–orbit coupling included adiabatic potential the two linear isomers, Br–NCH and Br–HCN, are about equally stable. In the subsequent paper, we use these potentials in calculations of the rovibronic states of the Br–HCN complex.

1. Introduction

The weakly bound complexes X–HY with electronegative atoms or groups X, Y = F, Cl, Br, O, OH, CN occur in the entrance and exit channels of the hydrogen exchange reactions X + HY →HX + Y. It appeared experimentally in the reaction of Cl with HD and theoretically in the reaction Cl + OH →HCl + O that this occurrence may have significant effects on the rate of the reaction, on the product branching ratios, and so forth. Therefore, it is important to know the stability and structure of these weakly bound complexes. Experimentally, a series of these radical complexes was investigated by Merritt et al. They were prepared in cold superfluid helium clusters in a supersonic molecular beam setup and studied by high-resolution infrared spectroscopy in the range of the HY stretch frequency. Theoretically, some of these complexes were investigated by Meuwly and Hutson, who used empirical potentials. Our group made detailed studies of the bound states and spectra of Cl–HCl and Cl–HF on the basis of ab initio potentials. A complex that was recently studied spectroscopically by Merritt et al. is Br–HCN. This species is particularly interesting because it was found to occur in two isomeric forms: Br–HCN and Br–NCH, both linear.

Theoretical investigations on the open-shell species X(2P)–HY with halogen atoms X = F, Cl, Br in their 2P ground state are complicated because of electronic degeneracies, which lead to the breakdown of the Born–Oppenheimer approximation. Multiple electronic states that are asymptotically degenerate have to be included simultaneously, and the nonadiabatic coupling between these states must be taken into account. In ref 11, building on earlier work by Alexander and by Dubernet and Hutson, we described a diabatic model in which this is taken care of. The diabatic states of the complex labeled P_1, P_0, P_1 correlate to the spatial components of the threefold degenerate X(2P) atomic ground state. Spin–orbit coupling is included as well, and a new set of diabatic states is constructed that correlates asymptotically with the X(2P) states with j = (3/2) and j = (1/2). The diabatic potentials are obtained from three adiabatic potential surfaces V_1(A), V_2(A'), V_3(A'') for states of reflection symmetry A' and A'' through symmetry adapted diabatic states labeled P_1, P_2, P_3 that are easily transformed into the complex states P_1, P_2, P_3. The symmetry adapted diabatic state P_3 coincides with the adiabatic state of A'' symmetry. Only...
a single mixing angle, \( \gamma \), transforming the two adiabatic states of \( \Delta' \) symmetry into the diabatic states \( P_\mu P_\nu \) of the same symmetry, is needed to obtain the full 3 \( \times \) 3 matrix of complex diabatic potential surfaces \( V_{\mu\nu}(r) \) with \( \mu, \nu = -1,0,1 \). In the present two papers (henceforth called paper 1 and paper 2), we applied this method to the Br–HCN complex. Paper 1 describes the ad initio calculation and analytic fit of the potential surfaces; paper 2 describes the application of the diabatic potentials in a computation of the rovibronic states and properties of the complex, with the inclusion of spin–orbit coupling. Paper 2 also includes a comparison of the ad initio computed results with the spectroscopic data.\(^4\)

The computation and analytic fit of the potentials is described in Section 2 of paper 1. The adiabatic potentials \( V_1(A'), V_2(A'), V(A'') \) were obtained from the partially spin-restricted coupled cluster [RCCSD(T)] method including single and double excitations and, noniteratively, triples.\(^5\) To obtain the mixing angle, \( \gamma \), we performed complete active space self-consistent field (CASSCF) plus multireference configuration interaction (MRCI) calculations that provided the wave functions from which this mixing angle was extracted. After transformation to the diabatic potentials, \( V_{\mu\nu}(r) \), the latter were expanded in the appropriate spherical harmonics, according to the theory in ref 11. The dependence of the expansion coefficients on the CH bond length, \( r_{\text{CH}} \), in the HCN monomer and on the distance \( R \) between the Br nucleus and the center of mass of HCN was fitted analytically. In Section 3, we discuss these potentials. In Section 4, we construct new diabatic states by inclusion of the important spin–orbit coupling on the Br atom and we discuss the effect of spin–orbit coupling on the diabatic and adiabatic potentials.

2. Computation and Fits of the Potential Surfaces

Three-dimensional nonrelativistic adiabatic potential energy surfaces were obtained from RCCSD(T) calculations in an atomic orbital basis of augmented correlation-consistent polarized-valence functions of double-\( \zeta \) quality (aug-cc-pVDZ)\(^{16,17} \) supplemented with a \( \{322\} \) set of uncontracted bond functions (exponents sp:0.9,0.3,0.1 and d:0.6,0.2) centered halfway between the Br nucleus and the center of mass of HCN. The equilibrium geometries of the complex were also investigated with the corresponding triple- and quadruple-\( \zeta \) (aug-cc-pVTZ and aug-cc-pVQZ) basis sets, with the same midbond functions. The 1s electrons on C and N and the 1s,2s,2p,3s,3p,3d electrons on Br were left uncorelated. The computer program molpro\(^{18} \) was used in all of the calculations. The origin of a Cartesian frame was chosen on the Br nucleus, and the positive \( z \) axis along the vector \( \mathbf{R} \) that points from the Br nucleus to the center of mass of HCN. The atomic masses are: \( m_N = 1.0078250321 \) u, \( m_C = 12 \) u, and \( m_B = 14.0037040052 \) u. To examine the experimentally observed\(^4 \) red shift in the CH stretch frequency due to the complex formation, we varied the CH bond length, \( r_{\text{CH}} \), but froze the CN bond at the calculated equilibrium distance of \( r_{\text{CN}} = 2.2220a_0 \) and kept HCN linear. The vector \( \mathbf{r} \), which points from the N to the H nucleus, lies in the \( xy \) plane of the frame and makes an angle \( \theta \) with the positive \( z \) axis. Hence, \( \theta = 0^\circ \) corresponds to the linear Br–NCH conformation and \( \theta = 180^\circ \) corresponds to linear Br–HCN. The coordinates that were varied in addition to \( r_{\text{CH}} \) are \( R \), the length of the vector \( \mathbf{R} \), and the angle \( \theta \). The calculations were carried out on a \( 16 \times 12 \times 5 \)-dimensional grid. The \( R \) values were 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 12.5, 15.0, 20.0, and 25.0\( a_0 \). For \( \theta \) we used a 12-point Gauss–Legendre quadrature grid, and the \( r_{\text{CH}} \) grid includes the following values: 1.6661, 1.8551, 2.0440, 2.2330, and 2.4220\( a_0 \). The value \( r_1 = 2.0440a_0 \) is the equilibrium CH bond length in a geometry optimization of HCN at the CCSD(T)/aug-cc-pVDZ level. The other grid values correspond to an increase/decrease of \( 0.1 \) \( a_0 \).

The adiabatic and diabatic potential surfaces: 1. Adiabatic and Diabatic Potential Surfaces

The adiabatic and diabatic potential surfaces were constructed from the adiabatic potentials \( V_1(A'), V_2(A'), V(A'') \) by applying the expression

\[
\gamma(R, \theta, r_{\text{CH}}) = \arctan \left( \frac{\langle \Psi_2(A') | L_z | \Psi_1(A') \rangle}{\langle \Psi_1(A') | L_z | \Psi_2(A') \rangle} \right)
\]

for each grid point from the matrix elements of the electronic angular momentum operator, \( L_z \).

This expression, proposed by Alexander\(^{12} \), was used earlier in studies on \( \text{H}_2\text{O}\)，\(^{20} \text{Cl}–\text{HCl}^{21} \) and \( \text{Cl}–\text{H}\).\(^{5} \)

The transformation from the adiabatic potentials to the diabatic ones, with the use of this mixing angle \( \gamma \), is described in detail in ref 9. The 3 \( \times \) 3 Hermitian matrix of diabatic potentials contains four different substates of Br) and possesses three potential energy surfaces that correlate to the \( \text{P} \) ground state of the free bromine atom: two of \( \Delta' \) symmetry (correlating to mixed \( P_u \) and \( P_d \) substates of Br) and one of \( \Delta'' \) symmetry (correlating to \( P_p \)). The potentials \( V_1(A') \) and \( V_1(A'') \) correspond to the ground states of the two symmetries, but the potential \( V_2(A') \) corresponds to an excited \( \Delta' \) state. The RCCSD(T) method is normally used only to obtain ground-state energies. The procedure to correct the interaction energies for the basis set superposition error (BSSE), which is nontrivial especially for the two \( \Delta' \) states, is described in detail in ref 9.

In a few of the grid points, the RCCSD iterations did not converge. The \( V(\Delta'') \) potential did not cause any problems; all points gave convergence. However, for the \( V_1(A') \) potential about 0.1% of the points and for the \( V_2(A') \) potential about 3% of the points did not converge. The values of the potentials at these points were obtained from neighboring points by interpolation.

For interpolation in the \( R \) coordinate, we used the reproducing kernel Hilbert space (RKHS)\(^{19} \) method with a kernel for distancelike variables; for interpolation in \( r_{\text{CH}} \) and \( \theta \) we used quadratic functions. The accuracy of these interpolations was checked by applying them to similar points for which converged RCCSD(T) interaction energies were available. Moreover, we checked this accuracy by simultaneous interpolation in more than one of the coordinates. In general, we can say that possible errors caused by interpolation are comparable with or smaller than the errors in the analytic fit. The latter are given at the end of this section.

The wave functions of the three adiabatic states \( \Psi_1(A'), \Psi_2(A'), \) and \( \Psi(A'') \) needed to compute the mixing angle, \( \gamma \), were obtained from CASSCF plus MRCI calculations on the same grid and with the same basis. The angle \( \gamma \) was obtained for each grid point from the matrix elements of the electronic angular momentum operator, \( L_z \):

\[
\gamma(R, \theta, r_{\text{CH}}) = \arctan \left( \frac{\langle \Psi_2(A') | L_z | \Psi_1(A') \rangle}{\langle \Psi_1(A') | L_z | \Psi_2(A') \rangle} \right)
\]

As shown in ref 11, the diabatic potentials can be expanded in spherical harmonics \( C_{\mu L}(\theta,0) \), which are Racah-normalized such that

\[
C_{\mu L}(\theta,0) = \delta_{\mu L} \delta_{\ell 0}
\]

and

\[
V_{\mu\nu}(R,\theta,r_{\text{CH}}) = \sum_{L=|\mu-\nu|}^{\ell_{\text{max}}} C_{\mu L}(\theta,0) C_{\nu L}^{*}(R,r_{\text{CH}})
\]

The expansion coefficients were calculated by numerical integration, according to eq 9 of ref 9. We used the 12-point
Gauss–Legendre quadrature grid in the angle \( \theta \) on which the
ab initio data were computed. Just as in ref 9, the expansion
coefficients \( \tilde{V}_{ij}(R,r_{CH}) \) were obtained as functions of \( R \) and
\( r_{CH} \) by application of the RKHS method\(^{19} \) to the points in the
\( R \) and \( r_{CH} \) grids, with the use of a two-dimensional kernel for
distancelike variables. The parameters \( \eta_{RKHS} \) and \( \eta_{RKHS} \) were
chosen in the same way as in ref 9.

Because for the smallest values of \( R \) the potential becomes
extremely repulsive especially at the linear Br–HCN geometry,
one would need very many terms in the spherical harmonic
expansion of eq 2. To avoid this, the diagonal potentials \( V_{0,0} \) and
\( V_{1,1} \) were damped in these strongly repulsive regions by
means of a tanh function up to a value of \( V_{\text{max}} \)

\[
\tilde{V}_{ij} = \begin{cases} 
V_{ij} & \text{for } V_{ij} \leq V_0 \\
V_0 + \beta^{-1} \tanh [\beta(V_{ij} - V_0)] & \text{for } V_{ij} > V_0
\end{cases}
\]

where \( \beta = [V_{\text{max}} - V_0]^{-1} \). With this scheme, the damped
potentials \( \tilde{V}_{ij} \) are continuous around \( V_0 \) up to the second
derivative. Care was taken to use sufficiently high values of \( V_0 \) and
\( V_{\text{max}} \) so that the potentials were affected only in regions
that are not of any practical importance in bound-state and low-
energy scattering calculations. The actual values used were \( V_0 = 10000 \text{ cm}^{-1} \), and \( V_{\text{max}} = 2V_0 \). At those grid points where
the diagonal potentials were damped, the off-diagonal potential,
\( V_{0,1} \), was scaled by the factor \( V_{0,0}/V_0 \) and the off-diagonal
potential, \( V_{1,-1} \), by the factor \( V_{1,1}/V_{1,1} \).

To check the quality of the fits, we used the analytically
expressed diabatic potentials and recomputed the lowest adiabatic
potential by diagonalization of the \( 3 \times 3 \) matrix of diabatic
potentials. When we compared that with the original ab
initio points for this adiabat, we found a root-mean-square relative
deviation of 1.8% in the short range for \( R = 5a_0 \), 0.5% in the
region of the minimum for \( R = 8.5a_0 \), and 1.3% in the long
range for \( R = 12.5a_0 \).

3. Results and Discussion

All plots of the potentials shown in the figures are cuts at
the calculated equilibrium distance \( r_{CH} = 2.044a_0 \) of HCN,
which is close to the experimental value \( r_{CH} = 2.0135a_0 \). Figure
1 shows plots of the adiabatic and diagonal diabatic potentials
as functions of the angle \( \theta \). Although the distance \( R \) is not
optimized in this figure but is fixed at \( R = 8.5a_0 \), one can already
see that both linear structures are minima. One also observes
how the Br–HCN interaction splits the Br(2P) state for the linear
geometries into a \( \Sigma \) and a \( \Pi \) state. For linear Br–NCH (\( \theta = 0^\circ \)), the \( \Sigma \) state is lowest in energy, whereas for linear Br–
HCN (\( \theta = 180^\circ \)) the \( \Pi \) state is lowest. This holds for the entire
range of the \( R \) variable. The adiabatic \( \Sigma \) state always correlates
with one of the \( \Pi \) states, whereas the other \( \Pi \) component
coincides with the adiabatic \( \Sigma \) state. Such a
degeneracy gives rise to a nonadiabatic Renner–Teller coupling.\(^{22} \) Because the \( \Pi \) state is the ground state for linear Br–
HCN, we expect to see the effects of this coupling in the lower
rovibronic levels of this complex. This was indeed found and
will be discussed in paper 2.

Figure 2 shows contour plots of the adiabatic potentials as
functions of \( R \) and \( \theta \). The two prominent minima in \( V(\theta') \)
coincides with the minimum in the potential \( V(\theta) \) and
\( V(\theta) \) is very similar to \( V(\theta') \). To check the quality of the fits, we used the analytically
expressed diabatic potentials and recomputed the lowest adiabatic
potential by diagonalization of the \( 3 \times 3 \) matrix of diabatic
potentials. When we compared that with the original ab
initio points for this adiabat, we found a root-mean-square relative
deviation of 1.8% in the short range for \( R = 5a_0 \), 0.5% in the
region of the minimum for \( R = 8.5a_0 \), and 1.3% in the long
range for \( R = 12.5a_0 \).
much more sensitive to variation of $r_{\text{CH}}$. This is what might be expected from the structures of the two complexes.

The fact that linear $\text{Br}-\text{HCN}$ has a ground state of $\Pi$ symmetry, whereas linear $\text{Br}-\text{NCH}$ has a $\Sigma$ ground state can be well understood from electrostatic considerations. The $\text{Br}$ atom in its $^3\text{P}$ ground state has a large quadrupole moment. The interaction of this quadrupole with the dipole of HCN is the dominant contribution to the interaction energy. The $\Sigma$ and $\Pi$ components of this quadrupole moment are the expectation values of the quadrupole operator $Q_{2,0} = \sum r_i^2 C_{2,0}(\theta_i, \phi_i)$ over

![Figure 2. Adiabatic potential surfaces $V_{1}(A^\prime)$, $V(A''')$, and $V_2(A')$ (in cm$^{-1}$) for $r_{\text{CH}} = 2.0440\text{a.u.}$](image)

![Figure 3. Diabatic potential surfaces $V_{0,0}$, $V_{1,1}$, and $V_{0,1}$ (in cm$^{-1}$) for $r_{\text{CH}} = 2.0440\text{a.u.}$](image)
the Br(P0) and Br(P±1) substrates, respectively, where (r,θ,φi) denote the electronic coordinates. The Br atom is isoelectronic to the rare gas atom Kr with one electron taken out of the 4p shell. In the Σ state, this electron is taken out of a 4p↑ orbital along the bond axis; in the Π state it is taken out of a 4p↓ or 4p↓−1 orbital. Or, equivalently, out of 4p↓ or 4p↑. Therefore, it is not surprising that the Σ quadrupole has a positive value, whereas the Π state quadrupole moment is negative. The Σ quadrupole interacts most favorably with the negative N side of HCN, giving Br—HCN, the Π quadrupole interacts most favorably with the positive H side of HCN, giving Br—HCN. This agrees with the equilibrium structures found in the full ab initio calculations.

Finally, let us compare Br—HCN with some similar complexes of which the interaction potentials were recently computed ab initio. The complex Cl—HF9,10 has a global minimum at the linear Cl—HF structure. This structure has a ground state of Π symmetry, just as linear Br—HCN. The value of D0 = 676.5 cm−1 for Cl—HF at the equilibrium bond length of HF is larger than that for Br—HCN. The global minimum for linear Br—HCN with its Σ electronic ground state corresponds to a local minimum with D0 = 237.4 cm−1 for Cl—FH. For Cl—HCl,7,8,21 two deep minima were also found, and the minimum for linear Cl—HCl is qualitatively similar to those of linear Br—HCN and Cl—HF. The second minimum, with a Σ electronic ground state, occurs in Cl—HCl for a T-shaped structure. This is probably related to the above considerations about the dominance of electrostatic interactions. For HCl, it is usually not only the dipole that plays a role in such interactions but also the quadrupole. Interaction of this quadrupole with the quadrupole of Cl(P↑) leads to maximum binding for a T-shaped Cl—HCl complex. Similar T-shaped equilibrium structures were found for OH—HCl,23 HCl—HCl,24 and HCN—HCl.25 For F—HF three minima were found,26 one for each of the two linear geometries and a T-shaped one. The linear F—HF minimum was the deepest, then the T-shaped one, while the linear F—FH minimum is the shallowest. The barriers between these minima are small, however. In Br—HBr,26 the situation is qualitatively similar to Cl—HCl: a linear Br—HBr minimum and a T-shaped minimum, with the first one being deeper. The linear Br—BrH complex corresponds to a saddle point, just as Cl—CHH.

4. Effect of Spin—Orbit Coupling

The spin—orbit states of the Br atom are split by $D_{SO} = E(3P_{1/2}) - E(3P_{3/2}) = 3685.5$ cm$^{-1}$. We assume that the spin—orbit coupling in the Br atom is not affected by the relatively weak interaction with the HCN molecule so that we may use for the Br—HCN complex the spin—orbit coupling term AĀS with the operators $\lambda$ and $\tilde{S}$ representing the orbital and spin angular momenta of the Br(3P) atom and the constant parameter $A = -(\lambda^2)D_{SO}$. Because we expect that this large splitting has an important effect on the properties of the complex, we constructed a new set of diabatic electronic states with the inclusion of spin—orbit coupling. These states are denoted by $|j_\lambda\omega,\lambda\rangle$, where the quantum number $j_\lambda$ is the total angular momentum on the Br atom $\lambda$ and $\omega_\lambda$ is the projection of $j_\lambda$ on the dimer axis $\mathbf{R}$. They are obtained from the original, spin-free, diabatic states $|\lambda,\mu\rangle$ and the spin functions $|S,\sigma\rangle$ by Clebsch—Gordan coupling

$$|j_\lambda\omega_\lambda\rangle \equiv (|\lambda S\rangle |j_\lambda\omega_\lambda\rangle) = \sum_{\mu,\sigma} |\lambda,\mu\rangle |S,\sigma\rangle |\lambda,\mu; S,\sigma; j_\lambda,\omega_\lambda\rangle$$

(4)

where $|\lambda,\mu; S,\sigma; j_\lambda,\omega_\lambda\rangle$ is a Clebsch—Gordan coefficient. Because $\lambda = 1$ and $S = (1/2)$, the total atomic angular momentum of Br takes on the values $j_\lambda = (1/2)$ with projections $\omega_\lambda = \pm(1/2)$ on the z axis and $j_\lambda = (3/2)$ with projections $\omega_\lambda = \pm(3/2), \pm(1/2)$. Diabatic states with $j_\lambda = (3/2)$ correlate to the $3P_{3/2}$ ground state of the Br atom, states with $j_\lambda = (1/2)$ with the excited $3P_{1/2}$ state. Because the atomic spin—orbit splitting is so large, the $j_\lambda = (3/2)$ basis functions will probably not play a significant role in the lower rovibrational levels of the complex. Diagonal and off-diagonal spin—orbit coupled diabatic potentials, labeled by $j_\lambda,\omega_\lambda$, are obtained from the diabatic potentials $V_{\mu,\mu'}$ in the spin-free diabatic basis $|\lambda,\mu\rangle$ by a similarity transformation according to eq 4.

Figure 4 shows the two diagonal spin—orbit diabatic potentials $V_{j_\lambda,\omega_\lambda}$ with $j_\lambda = (1/2)$. The potential for $|\omega_\lambda\rangle = (1/2)$ has a minimum at $\theta = 180^\circ$, which corresponds to the linear Br—HCN configuration. For linear geometries, this potential coincides with the spin-free diabatic potential $V_{1,1}$ in Figure 3 because the spin—orbit coupled state with $|\omega_\lambda\rangle = (1/2)$ contains only the spin-free diabatic states $P_{\lambda} \equiv |\lambda,\mu\rangle$ with $\lambda = 1,\mu = \pm 1$ and the diabatic coupling potential $V_{1,-1}$ vanishes for linear geometries. Also, for nonlinear geometries the spin—orbit coupled potential for $|\omega_\lambda\rangle = (1/2)$ is very similar to $V_{1,1}$ because the off-diagonal diabatic potential $V_{1,-1}$ is very small everywhere. The potential for $|\omega_\lambda\rangle = (1/2)$ has a minimum at $\theta = 0^\circ$, which corresponds to the linear Br—HCN configuration. Such a minimum also occurs in the spin-free diabatic potential $V_{0,0}$, which is the dominant contribution to $V_{32(12),(12),(22),(22),2}$, but there it is considerably deeper, cf. Figure 3. This is due to the fact (which one may easily check by inspection of the Clebsch—Gordan coefficients) that the spin—orbit coupled state with $j_\lambda = (1/2)$ and $|\omega_\lambda\rangle = (1/2)$ has only $\gamma_1$ of $P_{\lambda} (\mu = 0)$ character and $\gamma_3$ of $P_{\lambda 1} (\mu = \pm 1)$ character. The deep minimum in $V_{0,0}$ for linear Br—HCN is partly damped because $V_{1,1}$ is repulsive in this region. With the inclusion of spin—orbit coupling, the minimum for linear Br—HCN ($\theta = 180^\circ$) with $|\omega_\lambda\rangle = (1/2)$ is deeper than the minimum for linear Br—NCH ($\theta = 0^\circ$) with $|\omega_\lambda\rangle = (1/2)$, whereas without spin—orbit coupling the linear Br—NCH conformation was much more stable.

The spin—orbit coupled diabatic potentials are elements of a 6 × 6 matrix. These elements are obtained from the similarity transformation of the spin-free diabatic potentials $V_{\mu,\mu'}$ according to eq 4, and the addition of $A(j_\lambda(\lambda + 1) - \lambda(\lambda + 1) - S(S + 1))/2$ with $\lambda = 1, S = (1/2)$, and $j_\lambda = (1/2)$ or $(3/2)$ on the diagonal. These diagonal terms represent the spin—orbit coupling operator $A\hat{S}^2 = A(j_\lambda^2 - \lambda^2 - \tilde{S}^2)/2$, which is diagonal in the basis $|j_\lambda\omega_\lambda\rangle$. Diagonalization of this 6 × 6 matrix produces spin—orbit coupling included adiabatic potentials, more briefly called

$$A = -(\lambda^2)D_{SO}.$$
spin–orbit adiabatic potentials. Figure 5 shows the spin–orbit adiabatic potential that is the lowest eigenvalue of this matrix, for each geometry of the complex. Here, we find both minima, one for linear Br–HCN that originates from the $j_A = |\omega_A| = (3/2)$ contribution and one for linear Br–NCH originating from $j_A = (3/2), |\omega_A| = (1/2)$. Because of the effect of spin–orbit

Figure 4. Diabatic potential energy surfaces including spin–orbit coupling for $j_A = (3/2)$. Energy (in cm$^{-1}$) relative to the Br($^3P_{3/2}$) and HCN ground states.
coupling, the two minima have become about equally deep, in contrast with those in the lowest spin-free adiabatic potential in Figure 2.

5. Conclusions

The three adiabatic potentials of the Br–HCN complex that correlate to the $^2P$ ground state of the Br atom were calculated ab initio at the RCCSD(T) level of theory as functions of the intermolecular distance $R$, the atom-linear molecule Jacobi angle $\theta$, and the length $r_{CH}$ of the CH bond in HCN. Two of these potentials, $V_1(A')$ and $V_2(A')$, correspond to the lowest states of even ($A'$) reflection symmetry, the third one, $V(A'')$, to the ground state of odd ($A''$) symmetry. From CASSCF and MRCI calculations for the same set of geometries of the complex, we obtained the corresponding wave functions and the diabatic potential energy surface. Energy (in cm$^{-1}$) relative to the Br$(^2P_{\overline{2}})$ and HCN ground states.

Figure 5. Lowest spin–orbit adiabatic potential energy surface. Energy (in cm$^{-1}$) relative to the Br$(^2P_{\overline{2}})$ and HCN ground states.

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References and Notes

1. Adiabatic and Diabatic Potential Surfaces


