ROTATIONAL PREDISSOCIATION OF Ar–HD VAN DER WAALS COMPLEX:
SPACE-FIXED COMPLEX-COORDINATE COUPLED-CHANNEL CALCULATIONS

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The space-fixed complex-coordinate coupled-channel (SFCCCC) method is applied to the accurate determination of the level energies and widths (lifetimes) of predissociating states of Ar–HD ($v = 1, j = 2$) van der Waals molecule, using the Carley–Le Roy BC$_3$(6.8) potential for Ar–H$_2$. The calculated widths are in good harmony with the experimental data of McKellar and in excellent agreement with the close-coupling scattering results of Hutson and Le Roy.

1. Introduction

There is currently much interest in the study of spectroscopy, structure and predissociation dynamics of weakly bound van der Waals (vdW) molecules [1,2]. Reliable anisotropic potential surfaces for several vdW complexes, particularly the rare-gas–H$_2$ systems, are now becoming available. In this paper, we are concerned with accurate calculations of the resonance energies and rotational predissociation (RP) linewidths (lifetimes) of the Ar–HD vdW molecule. This study is prompted by the recent successful experimental determination of the RP linewidths by McKellar [3] from the (improved) IR high-resolution spectra of Ar–HD and Kr–H$_2$ systems. The direct comparison between theoretical and experimental results allows a critical assessment on the quality of the theoretical methods as well as the reliability of the potential surfaces used in the calculations.

Previous theoretical approaches for the treatment of predissociation by internal vibration/rotation have been summarized by Beswick and Jortner [2]. Recently, we have developed two alternative practical and accurate approaches for the study of rotational predissociation of vdW molecules. They are the complex-coordinate coupled-channel (CCCC) methods, one formulated in the space-fixed (SF), the other in the body-fixed (BF) frames of coordinates. The SFCCCC theory [4,5] is more appropriate for the treatment of weak-coupling vdW complexes (such as Ar–H$_2$), whereas the BFCCCC theory [6] more natural for strong-coupling complexes (such as Ar–HCl). The utility and advantage of the CCCC methods may be summarized as follows: (1) It is an ab initio method (given a defined “exact” hamiltonian). (2) Only bound-state structure calculations are required and no asymptotic conditions need to be enforced. (3) The resonance energies are obtained directly from eigenvalue analysis of appropriate non-hermitean matrices, the imaginary parts of the complex eigenvalues being related directly to the lifetimes of the vdW complexes. (4) It is applicable to many (open and closed) channel problems involving multiply coupled continua. These methods have been applied successfully to a number of vdW molecules [4–7].

In section 2, the SFCCCC theory appropriate for the Ar–HD study is briefly outlined. In section 3, we discuss the potential-energy surface chosen in the current study. The predicted RP linewidths are compared with the experimental data as well as other theoretical results in section 4.

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2. Complex-coordinate coupled-channel approach to predissociation by internal vibration and rotation

The hamiltonian of a triatomic vdW molecule A..BC, after separating out the motion of the centre of mass, may be expressed in the SF frame as

$$H(R, r) = (1/2\mu)[-(h^2/2\mu)R^{-1}(\partial^2/\partial R^2)R + I^2(R)/R^2] + H_d(r) + V(R, r, \theta).$$

(1)

Here $\mu = m_A(m_B + m_C)/(m_A + m_B + m_C)$ is the reduced mass, $R$ is the axis of the complex, $r$ that of the diatom BC, $I$ is the angular momentum of BC and A about each other, $H_d$ is the vibration–rotation hamiltonian of the diatom, $V(R, r, \theta)$ is the interaction potential of A and BC, and $\theta = \cos^{-1}(\vec{r}.\vec{R})$. The interaction potential for weak-coupling complexes may be conveniently expressed as an expansion in terms of a Legendre polynomial as well as a power series expansion in the diatom stretching coordinate $\xi(r)$ [8]:

$$V(R, r, \theta) = V(R, \xi, \theta) - \sum \sum \xi^k P_k(\cos \theta) V_{\lambda,k}(R).$$

(2)

where $\xi(r) = (r - r_0)/r_0$ and $r_0$ is an isotope-independent constant. The eigenfunctions of $H_d(r)$ may be written as $\phi_{ij}(r) Y_{jm_j}(r)$, where $v$ and $j$ are respectively the vibrational and rotational quantum numbers of the diatom BC. $Y_{jm_j}$ is the spherical harmonics, and $\phi_{ij}(r)$ satisfies the radial Schrödinger equation

$$\left[-(\hbar^2/2\mu_{BC})r^{-1}(\partial^2/\partial r^2)r - j(j + 1)/r^2 \right] + V_{BC}(r) - E_d(v, j)\phi_{ij}(r) = 0.$$

(3)

In eq. (3), $E_d(v, j)$ are the vibration–rotation eigenvalues of the free diatom, $\mu_{BC}$ is the reduced mass, and $V_{BC}(r)$ is the diatom potential.

In the space-fixed total angular momentum $(J, M)$ representation, $J = I + j$, a convenient angular basis for wavefunction expansion is the total angular momentum eigenfunction defined by

$$\Upsilon^{M}_{m_\ell}(\vec{R}, \vec{r}) = \sum \sum (ljm_lm_j) ljm(JM) Y_{lm_l}(\vec{R}) Y_{jm_j}(\vec{r}),$$

(4)

where $( | )$ is the Clebsch–Gordan coefficient and $Y_{km_k}$ is the spherical harmonics. It is expedient to define a scheme for labeling of the eigenstates of the complex uniquely. In the zero-coupling limit, each isotropic state is an eigenfunction of $H_d, I^2, J^2$ and $J_z$, and may be labelled by $|uvIM\rangle$. The latter may be decomposed into radial and angular functions

$$|uvIM\rangle = \psi^I_{uj}(R) \phi_{ij}(r) \Upsilon^{M}_{m_\ell}(\vec{R}, \vec{r}).$$

(5)

When the coupling is turned on, the state will be only an eigenfunction of $J^2$ and $J_z$ and only $J, M$ and the parity $p = (-1)^{J+M+I}$ will be good quantum numbers in the perturbed state. However, for weak-coupling complexes such as Ar–H$_2$ and Ar–HD, $v, j$ and $l$ remain nearly good quantum numbers. Thus the isotropic function $|uvIM\rangle$ provides a good zeroth-order picture for level energies and widths.

We now discuss the complex-coordinate coupled-channel (CCCC) formulation in the SF frame. According to the theory of dilatation or complex-coordinate transformation [9–11] the energy ($E_R$) and the width ($\Gamma$) associated with a metastable state of vdW molecule may be determined by the solution of the complex eigenvalue of a non-hermitean hamiltonian $H_\alpha(Re^{i\alpha}, r)$, obtained by applying the complex-coordinate transformation [9] to the vdW bond (dissociating) coordinate, $R \to R e^{i\alpha}$. In the CCCC formalism, the total wavefunction of the coordinate-rotated hamiltonian $H_\alpha(Re^{i\alpha}, r)$, for a given $J, M$ and $p$, is expanded in terms of the complete set of the isotropic state functions $|uvIM\rangle$ allowed by the symmetry. We further expand the radial function $\psi^I_{uj}(R)$ in terms of an orthonormalized square-integrable ($L^2$) basis function $|X_n(r)|$. 


\[ \psi_{ij}^{\beta}(r) = \sum_{n=1}^{N_{\gamma}} a_{n}(\gamma) x_{n}(r). \]

where \( \gamma \) specifies the channel quantum numbers, \( \gamma = (ujLM) \), \( N_{\gamma} \) is the size of the truncated radial basis, and \( \langle x_{n} | x_{m} \rangle = \delta_{nm} \). For convenience, let us define the channel basis function to be

\[ \langle \gamma n | \rangle = x_{n}(r) \phi_{ij}(r) \phi_{ij}^{\beta}(\vec{r}, \vec{R}) \]

and arrange the order of the matrix elements of \( H_{\alpha}(Re^{i\alpha}, r) \) in such a way that \( n \) is allowed to vary from 1 to \( N_{\gamma} \) within each channel block \( \gamma = (ujLM) \). The matrix element in the \( |\gamma n \rangle \) representation is then

\[ \langle \gamma' n' | H_{\alpha}(Re^{i\alpha}, r) | \gamma n \rangle = e^{-2 i \alpha (h^2/2\mu)} \langle x_{n'} | R \rangle ^{-1} \langle \partial^2/\partial R^2 \rangle R + i(l+1)/R^2 \delta_{uu'} \delta_{jj'} \delta_{\mu \mu'} \delta_{\nu \nu'} \delta_{jj'} \delta_{\mu \mu'} \]

\[ + E_{d}(v,j) \delta_{uu'} \delta_{jj'} \delta_{\mu \mu'} \delta_{\nu \nu'} \delta_{jj'} \delta_{\mu \mu'} + \sum_{\lambda} \sum_{l} \langle \phi_{u,j'} | \xi_{k} | \phi_{u,j} \rangle \langle x_{n'} | \delta_{\lambda k} \rangle \delta_{ll'} \delta_{\mu \mu'} \delta_{\nu \nu'} \delta_{jj'} \delta_{\mu \mu'}, \]

where \( f_{k} \) is the Percival–Seaton coefficient \([12]\). The resulting matrix of \( H_{\alpha} \) is a symmetric complex one whose complex eigenvalues may be determined via the secular determinant

\[ \text{Det}(H_{\alpha} | \gamma n, \gamma n - \epsilon) = 0. \]

The desired metastable states are then identified by the stationary points \([4-7,10]\) of the \( \alpha \) trajectories of complex eigenvalues.

3. Potential-energy surface

In the present study, the \( \text{Ar–HD} \) potential surface was derived from the Buckingham–Corner-type \( BC_{3}(6,8) \) \( \text{Ar–H}_{2} \) potential of Carley and Le Roy \([8]\). The reasons for this choice are as follows: (i) In one recent SFCCCCC study, we have carried out detailed RP linewidth calculations for the \( \text{Ar–H}_{2} \) system, using six realistic anisotropic potentials obtained recently from experiments \([5]\). It was found that the RP linewidths are sensitive to the surfaces used. In particular, the widths predicted for the three (less accurate) Lennard-Jones (LJ) potentials adopted vary as large as a factor of four. However, the agreement among the more recent potentials (namely, the BC potential of Zandee and Reuss \([13] \), the \( BC_{3} \) potential of Carley and Le Roy \([8]\), and the semi-empirical potential of Tang and Toennies \([14]\)), are much closer to within 30%. (ii) The \( BC_{3}(6,8) \) potential of Carley and Le Roy is the only surface which contains the information about its dependence on the length of the diatom bond. (iii) Recently Hutson and Le Roy \([15]\) have independently performed the RP calculations for the \( \text{Ar–HD} \) system using the \( BC_{3}(6,8) \) potential and the traditional close-coupling scattering method, allowing for a detailed comparison between different theoretical approaches.

The \( BC_{3}(6,8) \) \( \text{Ar–H}_{2} \) potential \([8]\) is expanded in the form

\[ V(R, \xi, \theta) = \sum_{k=0}^{3} \sum_{\lambda=0.2} \xi_{k} P_{\lambda}(\cos \theta) \ V_{\lambda k}(R), \]

where \( \xi = (r - r_{0})/r_{0} \) with \( r_{0} = 0.7666348 \) Å. The radial strength function \( V_{\lambda k}(R) \) has the form

\[ V_{\lambda k}(R) = A_{\lambda k} \exp(-\beta_{\lambda} R) - D(R) (C_{6}^{\lambda k}/R^{6} + C_{8}^{\lambda k}/R^{8}), \]

where

\[ D(R) = \exp[-4(R_{0}/R - 1)^{3}], \quad \text{for } R < R_{0} = R_{c}^{0.0}, \]

\[ = 1, \quad \text{for } R \geq R_{0}. \]
Fig. 1. The diagonal vibrationally preaveraged anisotropy strength radial functions $\bar{V}_\lambda(v,j|R)$ for $Ar-HD(v=1,j=2)$. The parameters ($A^{\lambda k}, B_\lambda$,...etc.) are listed in ref. [6]. To obtain the Ar–HD potential, we first performed the vibrational averaging over the $\xi$ coordinate of eq. (10), using exact $\phi_{ij}(r)$ eigenfunctions of $H_0(r)$. The diatom vibrational wavefunctions $\phi_{ij}(r)$ were obtained by the numerical solutions of the accurate HD potential data of Bishop and Shih [16]. Next we carried out the well-known asymmetric isotope frame transformation [17] to a coordinate system based on the centre of mass of HD, which is located $\approx 0.166556r$ from the bond midpoint. This transformation introduces Legendre terms of odd order into the potential expansion, so that the diagonal vibrationally preaveraged Ar–HD potential, for example, has the form

$$\bar{V}(v,j|R, \theta) = \sum_{\lambda=0,1,2,...}^{\lambda_{\text{max}}} \bar{V}_\lambda(v,j|R) P_\lambda(\cos \theta).$$

The vibrationally averaged anisotropy strength radial functions $\bar{V}_\lambda(v,j|R)$ for the case of current interest ($v=1, j=2$) are plotted in fig. 1.

4. Calculations and discussion

The Ar–HD ($v=1, j=2$) predissociating states have been observed experimentally [3] in the $S_1(0)$ band of the vdW complex, which corresponds to transitions between states of Ar–HD($v''=0,j''=0$) and Ar–HD($v'=1, j'=2$). The allowed transitions consist of four branches:

N branch, $J'' = l'' \rightarrow l' = l'' - 3, J' = J'' + 1$,

P branch, $J'' = l'' \rightarrow l' = l'' - 1, J' = J'' - 1, J'', J'' + 1,$
R branch, \( J'' = J'' + 1 \rightarrow J' = J' + 1 \).

T branch, \( J'' = J'' + 1 \rightarrow J' = J' + 1 \).

Only the N- and T-branch spectral lines are well resolved and their widths can be determined experimentally.

The SFCCCC calculations were carried out for all N- and T-branch predissociating states observed experimentally. The basis set of HD includes all channels corresponding to \( v = 1, j = 0, 1, 2, \) and 3. Channels corresponding to HD(\( v = 0, j \)) states can be safely ignored, as the vibrational predissociation (VP) rates from \( v = 1 \) to \( v = 0 \) states were found to be at least three orders of magnitude smaller than the rotational predissociation (RP) rates in the \( v = 1 \) states [18]. Fig. 2 depicts an example of the isotropic-channel potential curves (specified by \( j \) and \( I \)) corresponding to the case of \( J = 8 \). The experimentally observed Ar–HD(\( v = 1, j = 2 \)) \( S_1(0) \) RP widths correspond to those of the metastable levels associated with the \( j = 2 \) potential curve manifold. Both open (\( j = 0 \) and \( j = 1 \)) and closed (\( j = 3 \)) channels are illustrated here.

Since the Ar–HD surface used in this work was obtained by first vibrational preaveraging [with \( \phi_{v=1, j=2} \)] over the \( \xi \) coordinate, the coupling-matrix elements [the last term in eq. (8)] become

\[
\lambda_{\text{max}} \sum_{\lambda=0,1,\ldots} \langle \chi_{\lambda}(R) | V_{\lambda}(v=1,j=2) | \chi_{\lambda}(R) \rangle I_k(O^j; \lambda; J) \delta_{jj'\delta_{MM'}}.
\]

It was found that \( \lambda_{\text{max}} = 3 \) is sufficient to obtain converged results to within 0.001 cm\(^{-1}\). The matrix of interest
in the \(|\gamma m\rangle\) representation is of \(N_{cc}\) by \(N_{cc}\) block form, where \(N_{cc}\) is the number of isotropic basis channels included in the SFCCCA calculations. Within each diagonal block specified by the channel quantum number \(\gamma (=\nu\ell M)\), we use the orthonormal harmonic-oscillator (HO) \(L^2\) basis \([4-7]\)

\[
\chi_n(R) = (\beta l^{1/2}2^n n!)^{1/2} H_n(\beta x) \exp\left(-\frac{1}{2} \beta^2 x^2\right),
\]

where \(H_n\) is a Hermite polynomial and \(x = R - R_0\) (with \(R_0\) and \(\beta\) being adjustable parameters), to expand the bound as well as to discretize the continuum radial wavefunctions \(\psi_{\nu\ell}^j(R)\) defined in eq. (5). The kinetic matrix elements in the HO basis can be worked out analytically. Since the radial potentials \(V_{\alpha}(R)\) were generated in numerical rather than in analytic form, the radial coupling-matrix elements \(\langle \chi_n(R) | V_{\alpha}(R) | \chi_n(R) \rangle\) were computed most conveniently and accurately using the new computational scheme designed for the extension of complex-coordinate transformation to numerical potentials \([7]\).

Using the abovementioned procedure and the potential surface shown in fig. 1, we have performed the SFCCCA calculations for all N- and T-branch predissociating states of Ar-HD\((\nu = 1, \ell = 2)\) observed experimentally. Shown in fig. 3 is a typical example of the resonance \(\alpha\) trajectory of the complex eigenvalue correlated with the metastable state \([J = 5, \nu = 1, \ell = 2, I = 3]\). The desired resonance position \((E_R, -\Gamma/2)\) is clearly identified by the stationary point in the diagram \([E_R = \text{Re}(E), \Gamma/2 = -\text{Im}(E)]\). The results of the present SFCCCA calculations are summarized in table 1.

Shown in table 1 are also the theoretical results obtained recently by Hutson and Le Roy \([15]\) using the close-coupling scattering method and a similar procedure to generate the Ar-HD surface from the BC3(6,8) Ar-H\(_2\) potential. The overall agreement of the predicted RP widths (\(\Gamma\)) is seen to be excellent (to within 1-2%), providing a mutual check on the reliability of both methods. The predicted resonance energies \((E_R)\) are also in close agreement, except they are uniformly differed by \(\approx 0.15 \text{ cm}^{-1}\). This displacement is mainly attributed to the fact that slightly different diatom level energies were used in both computations. (In our SFCCCA calculations, the HD\((\nu = 1, \ell = 0-3)\) vibration-rotation energies (in cm\(^{-1}\)) used were \(-255.407, -170.073, 0.00, 253.629\), respectively.

Table 1

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\(\text{a)}\) Molecular constants used are \(\mu(\text{Ar-HD}) = 2.8094762\) amu, \(\mu(\text{HD}) = 0.671711245\) amu.

\(\text{b)}\) Ref. \([15]\).

\(\text{c)}\) \(\Delta E_R = E_R^{\text{CCS}} - E_R^{\text{SFCCCA}}\). This approximate constant shift in energies is mainly due to the fact that slightly different diatom level energies were used in both calculations. See text for details.
tively, relative to the \((v = 1, j = 2)\) level. Whereas the corresponding ones used by Hutson and Le Roy were \(-255.54, -170.16, 0.00,\) and 253.77 \(\text{cm}^{-1}\) Since these diatom level energies appear only in the diagonal matrix elements, they have negligible effect on the width calculations.

The SFCCCC calculated N- and T-branch widths are compared with the experimental ones of McKellar \([3]\) in fig. 4. The two sets of data appear in good harmony, considering the sensitivity of the width calculations with respect to potential surfaces used \([5]\). The discrepancy between theoretical and experimental widths \(^\dagger\) as well as the recent hyperfine spectroscopy of \(\text{Ar-H}_2\) \([19]\) suggest that further refinement of the \(\text{BC}_3(6,8)\) anisotropic potential may be possible.

In conclusion, the present work lends further strong supports to previous conclusions \([4-7]\) that the CCCC formalisms provide reliable and highly efficient methods for direct prediction of predissociating resonance energies and widths of vdW molecules.

Acknowledgement

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\(^\dagger\) After the completion of this work, the authors received a preprint from Hutson and Le Roy \([20]\), who reperformed the RP calculations using different procedures to obtain the \(\text{Ar-HD}\) potential. Their new widths differ \(\approx 9.7\%\) from their previous ones \([15]\).

References