

Predissociation of HD-Ar van der Waals molecules by internal rotation

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Accurate close-coupling calculations of level energies and widths of predissociating levels of HD-Ar have been carried out using the Le Roy-Carley BC_3 potential for H_2 -Ar. The calculated widths agree well with the experimental data of McKellar. The principal product from predissociation of HD($v = 1, j = 2$)-Ar is HD in its $v = 1, j = 1$ state. This channel is symmetry forbidden for $H_2(1, 2)$ -Ar, and its presence accounts for the much larger spectroscopic linewidths found for HD-Ar.

I. INTRODUCTION

When one of the monomers in a van der Waals molecule is vibrationally or rotationally excited, the energy of excitation is frequently larger than the dissociation energy of the van der Waals bond. The complex can then predissociate and the resultant reduction in the lifetime of the excited state leads to observable broadening of spectroscopic lines. The predissociation phenomenon is of interest because it is in effect a simple unimolecular reaction; the excited van der Waals molecule may be viewed as an activated complex, capable of fragmenting to form products in several possible internal states.

The most intensively studied van der Waals molecule is undoubtedly H_2 -Ar, for which LeRoy and Carley¹ have obtained an accurate three-dimensional potential energy surface from the spectroscopic data of McKellar and Welsh.² Predissociation linewidths have not yet been measured for H_2 -Ar itself, but McKellar³ has recently reported widths for predissociating levels of HD-Ar, whose potential surface is readily obtained from that for H_2 -Ar.⁴ The states involved correlate with the ($v = 1, j = 2$) level of HD, and can predissociate by converting HD rotational energy into relative translational energy of the fragments. The purpose of this paper is to present accurate calculations of the predissociation process, allowing comparison with experiment and giving information on the distribution of the dissociation products among the possible rotational levels.

II. THE POTENTIAL ENERGY SURFACE

The calculations in this paper were performed using the $BC_3(6, 8)$ H_2 -Ar potential of Carley and LeRoy.¹ This is expanded in the form

$$V(R, \xi, \theta) = \sum_{k=0}^3 \sum_{\lambda=0, 2} \xi^k P_\lambda(\cos \theta) V_{\lambda k}(R), \quad (1)$$

where R is the distance between the atom and the diatom center of mass, the diatom bond length is represented by the stretching coordinate $\xi = (r - r_0)/r_0$ with $r_0 = 0.7666438 \text{ \AA}$, and θ is the angle between R and the axis of the diatom. The radial strength functions $V_{\lambda k}(R)$ all have the form

$$V_{\lambda k}(R) = A^{\lambda k} \exp(-\beta_\lambda R) - D(R) [C_8^{\lambda k}/R^8 + C_6^{\lambda k}/R^6], \quad (2)$$

where

$$D(R) = \exp[-4(R_0/R - 1)^3] \text{ for } R < R_0 \equiv R_0^{00} \\ = 1 \text{ for } R \geq R_0 \quad (3)$$

and the constants $A^{\lambda k}$ and $C_8^{\lambda k}$ are defined by the values of the depth $\epsilon^{\lambda k}$ and position $R_0^{\lambda k}$ of the minimum of $V_{\lambda k}(R)$. The parameters defining the H_2 -Ar surface are listed in Table V of Ref. 1.

For calculations on HD-Ar, the potential surface must be transformed to a coordinate system based on the center of mass of HD,⁴ which is located 0.16655635367 from the bond midpoint. The center-of-mass transformation introduces Legendre terms of odd order into the potential expansion, so that in the new coordinate system the potential is

$$V(R, \xi, \theta) = \sum_{k=0}^{k_{\max}} \sum_{\lambda=0}^{\lambda_{\max}} \xi^k P_\lambda(\cos \theta) V_{\lambda k}(R). \quad (4)$$

In the present work, the transformation was carried out using the Gaussian quadrature method of Liu *et al.*,⁴ with the summations truncated at $k_{\max} = \lambda_{\max} = 8$. The resonance energies and widths are converged to better than 10^{-3} cm^{-1} with respect to the number of terms in this expansion.

It is important to realize that it is not the radial strength functions $V_{\lambda k}(R)$, but rather the vibrational matrix elements of the full potential $\langle v, j | V(R, \xi, \theta) | v', j' \rangle$, integrated over the diatom stretching coordinate ξ , which are physically significant. The diagonal terms differ significantly from one (v, j) state to another and the off-diagonal terms also depend on the states being coupled. For HD-Ar the averaging over the diatom stretching coordinate ξ should be performed *after* the center-of-mass transformation: this was done in the calculations reported below.⁵

The diatom matrix elements $\langle v, j | \xi^k | v', j' \rangle$ used to define the potential matrix were generated using exact (numerical) radial wave functions for HD calculated from a smoothed potential curve obtained by Bishop and Shih⁶ from the *ab initio* points of Kořos and Wolniewicz.⁷ The HD vibration-rotation energy levels were also taken from calculations on this potential: for $v = 1, j = 0-3$ the level energies were -255.54 ,

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-170.16, 0.00, and 253.77 cm^{-1} , respectively, relative to the ($v=1, j=2$) level.

III. COMPUTATIONAL METHOD

Metastable states of HD-Ar were characterized by performing close-coupled scattering calculations as a function of energy and analyzing the energy dependence of the S matrix as described by Ashton *et al.*⁸ In this formulation, a predissociating state appears as a resonant perturbation in the S -matrix eigenphase sum^{8,9} $\sigma(E)$, which rises sharply by π across the width of the resonance. Each resonance is characterized by its energy E_m , full width at half-maximum Γ_m , and partial widths Γ_{mi} for each open channel i . The partial widths are related to the total width by

$$\Gamma_m = \sum_i \Gamma_{mi} \quad (5)$$

and the fraction of the products asymptotically in channel i is given by Γ_{mi}/Γ_m .

The coupled equations were formulated in the space-fixed representation of Arthurs and Dalgarno¹⁰ and solved using the R -matrix propagator algorithm of Light and Walker.¹¹ The basis set of HD rotational functions included all channels corresponding to $v=1, j=0$ to 3. Channels corresponding to HD in its $v=0$ vibrational state were omitted, since predissociation to them is expected to be several orders of magnitude slower.¹²

The fundamental constants used here are specified by the single number $\hbar^2/2 = 16.857\,630 \text{ amu cm}^{-1} \text{ \AA}^2$. The collision reduced mass for HD-Ar was taken to be 2.809\,476\,2 amu.

IV. PREDISSOCIATION ENERGIES AND WIDTHS

In the space-fixed representation, each channel is characterized by the total angular momentum J , the diatomic angular momentum j , and the end-over-end angular momentum of the complex l . The good quantum numbers are J and the parity label $p = (-)^{j+l+J}$. In addition,

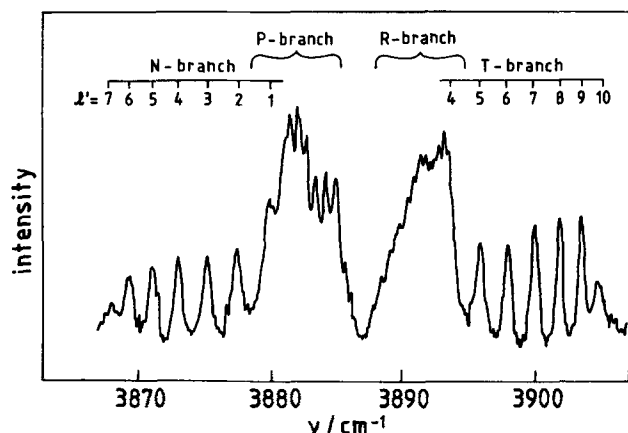


FIG. 1. Experimental spectrum of the $S_1(0)$ band of HD-Ar, with assignments of the quantum number l' for the upper levels. J' is $l' + 2$ for N-branch lines and $l' - 2$ for T-branch lines. Adapted from Ref. 3.

j and l are nearly good quantum numbers for HD-Ar, and provide a good zeroth-order picture for discussing the level energies and widths.

Predissociating states of HD-Ar have been observed experimentally in the $S_1(0)$ band of the complex,³ which is reproduced in Fig. 1. This band involves transitions between states of HD($v=0, j=0$)-Ar and HD($v=1, j=2$)-Ar, with the selection rules

$$\Delta l = \pm 1, \pm 3,$$

$$\Delta J = 0, \pm 1.$$

The lower states involved in these transitions have $J'' = l''$, since the HD molecule is in its ground rotational state, so that the allowed transitions form four branches corresponding to the upper states:

$$\begin{array}{ll} N \text{ branch } l' = l'' - 3 & J' = J'' - 1 \\ P \text{ branch } l' = l'' - 1 & \begin{cases} J' = J'' - 1 \\ J' = J'' \\ J' = J'' + 1 \end{cases} \\ R \text{ branch } l' = l'' + 1 & \begin{cases} J' = J'' - 1 \\ J' = J'' \\ J' = J'' + 1 \end{cases} \\ T \text{ branch } l' = l'' + 3 & J' = J'' + 1 \end{array}$$

The N - and T -branch progressions appear as a series of well-separated lines on the low and high frequency sides of the band origin, as shown in Fig. 1, and their widths can be measured experimentally.³ The P - and R -branch lines are much more closely spaced and individual lines cannot be resolved.

Calculations were carried out for all spectroscopically observed levels of HD(1, 2)-Ar and the resulting level energies, widths, and partial widths are shown in Table I. The calculated N - and T -branch widths are compared with the experimental ones in Fig. 2. The calculated widths for states of (+) parity are typically 10–20 times greater than the widths for corresponding levels of H_2 -Ar.¹³ This is principally because predissociation to the $j=1$ level is possible for HD-Ar, since the transformed potential contains Legendre terms of odd order, while for H_2 -Ar the only open channel is that for $j=0$. The $j=1$ open channels are indeed the most important for predissociation of HD-Ar, as may be seen from the partial widths in Table I. For (-) parity states there is no $j=0$ channel, so that for HD-Ar predissociation by internal rotation occurs exclusively to the $j=1$ channel. Odd parity (-) states of H_2 -Ar cannot predissociate by internal rotation at all.

Since the dominant process is HD(1, 2)-Ar \rightarrow HD(1, 1) + Ar, the $P_1(\cos \theta)$ anisotropy in Eq. (4) is clearly the term principally responsible for predissociation. This term arises in the center-of-mass transformation and contains significant contributions from both the isotropic and anisotropic parts of the H_2 -Ar potential. In order to establish the contribution of these two terms to the predissociation widths, the calculations for the $l' = 0, J' = 2$ state were repeated using only the isotropic

part of the H_2 -Ar potential; under these circumstances, the only anisotropy in HD-Ar is that arising from the coordinate transformation. The width obtained was 0.338 cm^{-1} , which is approximately half that obtained with the full potential. It thus appears that the anisotropy of the untransformed potential does contribute significantly to the predissociation widths, and that a "loaded sphere" approximation would not provide an adequate explanation of the widths. The predissociation process is effectively inelastic scattering below the rotational threshold, so that this conclusion should also apply to low-energy inelastic cross sections.

The matrix elements of $P_1(\cos \theta)$ between space-fixed

TABLE I. Resonance energies E_m , widths Γ_m , and partial widths Γ_{mj} for predissociating levels of HD(1,2)-Ar. The partial widths are summed over different l values contributing to each j .

l'	J'	E_m	Γ_m	Γ_{m0}^a	Γ_{m1}	Γ_{m2}^b
0	2	-26.169	0.713	0.105	0.607	...
1	1	-25.657	0.995	0.159	0.836	...
1	2	-25.050	0.166	...	0.166	...
1	3	-25.465	0.778	0.119	0.659	...
2	0	-24.140	1.457	0.369	1.088	...
2	1	-24.115	0.542	...	0.542	...
2	2	-23.601	0.381	0.080	0.301	...
2	3	-23.537	0.210	...	0.210	...
2	4	-23.944	0.801	0.125	0.676	...
3	1	-21.840	1.076	0.203	0.872	...
3	2	-21.586	0.361	...	0.361	...
3	3	-21.191	0.352	0.079	0.273	...
3	4	-21.220	0.226	...	0.226	...
3	5	-21.645	0.795	0.125	0.670	...
4	2	-18.742	0.888	0.156	0.732	...
4	3	-18.419	0.293	...	0.293	...
4	4	-18.057	0.326	0.075	0.252	...
4	5	-18.132	0.228	...	0.228	...
4	6	-18.590	0.769	0.121	0.648	...
5	3	-14.931	0.758	0.128	0.630	...
5	4	-14.549	0.249	...	0.249	...
5	5	-14.198	0.297	0.068	0.230	...
5	6	-14.305	0.224	...	0.224	...
5	7	-14.804	0.723	0.114	0.610	...
6	4	-10.433	0.643	0.104	0.539	...
6	5	-9.990	0.210	...	0.210	...
6	6	-9.642	0.264	0.060	0.204	...
6	7	-9.774	0.212	...	0.212	...
6	8	-10.322	0.663	0.103	0.560	...
7	5	-5.287	0.535	0.084	0.452	...
7	6	-4.785	0.172	...	0.172	...
7	7	-4.437	0.227	0.050	0.176	...
7	8	-4.590	0.191	...	0.191	...
7	9	-5.187	0.587	0.090	0.497	...
8	6	0.453	0.425	0.058	0.361	0.006
8	7	0.994	0.135	...	0.135	0.0005
8	8	1.339	0.193	0.041	0.148	0.004
9	7	6.598	0.329	0.042	0.261	0.026
9	8	7.186	0.131	...	0.094	0.037
10	8	12.966	0.726	0.026	0.169	0.531

^aThe $j=0$ channel exists only for states of (+) parity.

^bThe $j=2$ channels are open for $l' \geq 8$.

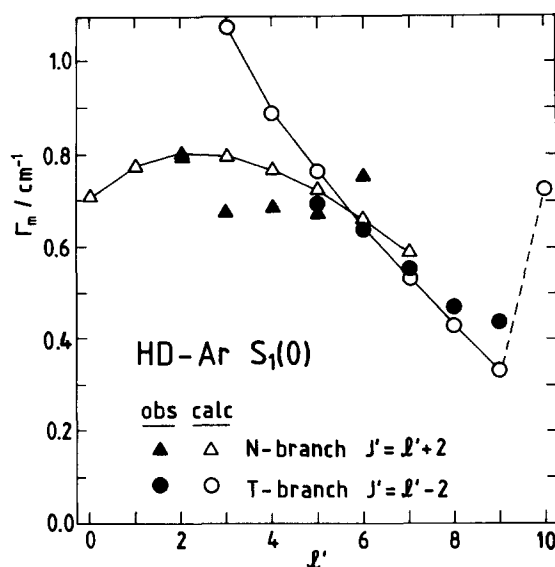


FIG. 2. Comparison of calculated and experimental widths for predissociating states of HD(1,2)-Ar. The calculated widths (open symbols) are from this work, and the experimental widths (closed symbols) are taken from Ref. 3. The calculated N -branch point for $l'=2$ and the T -branch point for $l'=6$ lie directly underneath the corresponding experimental points. Note: The experimental N -branch points were plotted incorrectly in Ref. 3; they are correct here.

basis functions are Percival-Seaton coefficients,¹⁴ $f_1(jl; j'l'; J)$

$$f_1(jl; j'l'; J) = \langle jJM | P_1(\cos \theta) | j'l'JM \rangle \quad (6)$$

and it is principally these coefficients which determine the relative widths of the different levels. If the mixing of states of different l' by the $P_2(\cos \theta)$ anisotropy is neglected, the predissociation processes allowed by a $P_1(\cos \theta)$ anisotropy for states of (+) parity are

$$j' = 2, \quad l' = J' + 2 - j = 1, \quad l = J' + 1 \quad (a)$$

$$j' = 2, \quad l' = J' - j = 1, \quad l = J' + 1 \quad (b)$$

$$j' = 2, \quad l' = J' - j = 1, \quad l = J' - 1 \quad (c)$$

$$j' = 2, \quad l' = J' - 2 - j = 1, \quad l = J' - 1 \quad (d)$$

and for states of (-) parity

$$j' = 2, \quad l' = J' + 1 - j = 1, \quad l = J' \quad (e)$$

$$j' = 2, \quad l' = J' - 1 - j = 1, \quad l = J' \quad (f)$$

Except for $J=1$, the Percival-Seaton coefficients associated with processes (a) and (d) are considerably larger than those for the other four processes, so that levels with $J' = l' \pm 2$ are usually much broader than those with $J' = l'$ and $J' = l' \pm 1$. The unresolved P- and R-branch structures in the center of Fig. 1 include lines corresponding to these narrower upper states, and it may be seen that there are indeed some sharp features in this region. However, the lines are too closely spaced to allow accurate width measurements.

Superimposed on the width pattern due to Percival-Seaton coefficients is a trend to decreasing width with increasing end-over-end angular momentum l' . This simply reflects the increasing centrifugal term in the

effective potential: for higher values of l' the radial wave function is displaced to larger intermolecular distances where the potential anisotropy is relatively weak.

Levels with $l' \geq 8$ lie above the $v=1, j=2$ threshold and so can also dissociate by tunneling through the centrifugal barrier in the effective potential. For $l'=8$ and 9 this process contributes only a small amount to the total width, as may be seen from the relevant $j=2$ partial widths in Table I; indeed, the transitions terminating on these levels give the sharpest lines in the N and T branches of the HD-Ar $S_1(0)$ spectrum.³ However, for $l'=10$ the bound state lies quite close to the maximum in the effective potential, and the tunneling mechanism contributes over 0.5 cm^{-1} to the total width. This is again in accord with experiment; the T -branch line corresponding to $l'=10$ in Fig. 1 is clearly much broader than the others, although its low intensity makes the width difficult to measure accurately.

V. CONCLUSION

Accurate calculations of level energies and widths of predissociating levels of HD-Ar have been carried out using the LeRoy-Carley BC_3 potential for H_2 -Ar. The calculated widths agree well with experimental data.

The principal product from predissociation of HD($v=1, j=2$)-Ar is HD in its $v=1, j=1$ state. This channel is symmetry forbidden for predissociation of $H_2(1,2)$ -Ar and its presence accounts for the much larger spectroscopic linewidths found for HD-Ar. The relative widths of different states of HD-Ar can be qualitatively explained in terms of predissociation induced by the $P_1(\cos \theta)$ anisotropy introduced by the center-of-mass transformation; in particular, states with $J'=l' \pm 2$ are considerably broader than those with $J'=l'$ and $J'=l' \pm 1$. However, the *absolute* widths are not well represented by a "loaded sphere" model, in which the entire anisotropy is taken to arise from the isotropic part of the

H_2 -Ar potential; in order to obtain good agreement with experiment, it is necessary to include the full anisotropic potential.

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