Quantum dynamics of ArI2 vibrational predissociation including low total angular momenta: The role of intramolecular vibrational energy redistribution

Octavio Roncero and Stephen K. Gray

Citation: *J. Chem. Phys.* **104**, 4999 (1996); doi: 10.1063/1.471267

View online: <http://dx.doi.org/10.1063/1.471267>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v104/i13>

Published by the American Institute of Physics.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Instruments for advanced science

Gas Analysis

- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science

- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics

- plasma source characterization
- etch and deposition process
- reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis

- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

HIDEN
ANALYTICAL

info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue

Quantum dynamics of ArI₂ vibrational predissociation including low total angular momenta: The role of intramolecular vibrational energy redistribution

Octavio Roncero

Instituto de Matemáticas y Física Fundamental, C.S.I.C., Serrano 123, 28006 Madrid, Spain

Stephen K. Gray

Theoretical Chemistry Group, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 19 October 1995; accepted 26 December 1995)

Full-dimensional quantum dynamics calculations on ArI₂(*B*, *v_i*) vibrational predissociation with total angular momenta *J*=0, 1, and 2 are presented. Models based on a few interacting states are shown to reproduce important aspects of the dynamics, confirming that vibrational predissociation is mediated by a few-state intramolecular vibrational energy redistribution effect. As a consequence, vibrational predissociation rate constants exhibit large oscillations with *v_i*, the initial I₂ vibrational quantum number in the complex. The qualitative effect persists when alternative choices for the interaction potential parameters are considered. Similarly, despite the importance of Coriolis coupling, the effect persists as *J* is varied from 0 to 2. We also discuss how the effect may be difficult to observe in typical experiments that involve higher *J* values. © 1996 American Institute of Physics. [S0021-9606(96)00313-2]

I. INTRODUCTION

Photodissociation and relaxation of I₂ surrounded by Ar atoms is a simple model for chemical dynamics in condensed media.¹⁻⁸ We focus on dynamics of the simplest limit, the triatomic van der Waals (vdW) complex ArI₂. When I₂ is excited to the *B* electronic state,¹⁻⁴ vibrational predissociation (VP),

competes with electronic predissociation (EP),

VP is transfer of vibrational energy from I₂ to the ArI bonds which subsequently break. EP involves transitions between electronic states and can be viewed as intersystem crossing.

Burke and Klemperer,^{4(b)} measured the VP efficiency (VPE), the VP rate divided by the total (vibrational plus electronic) predissociation rate for ArI₂. The VPE oscillates with *v_i* (Refs. 1, 2, and 4) and Burke and Klemperer suggested that the oscillations are due to EP induced by the presence of the Ar atom. A recent wave packet study⁹ is also consistent with EP in ArI₂ being oscillatory. Combining their VPE data and real-time measurements of the total predissociation rate,³ Burke and Klemperer obtained rates for the two processes in Eq. (1).^{4(b)} Furthermore, they showed that the fluorescence intensities for the ground and first two excited vdW levels are qualitatively similar as a function *v_i* which they associated with the absence of intermediate resonances in the VP process.^{4(b)} Based on their results, they conjectured that, in contrast to EP, the VP rate increases smoothly with *v_i* in agreement with the energy gap law.^{10,11}

A question still to be resolved is whether it is theoretically possible for the ArI₂ VP rate to vary monotonically with *v_i*. When transfer of one vibrational quantum from the

diatom is enough to break the vdW bond, the VP rate increases smoothly with *v_i*.^{10,11} However, when more than one vibrational quantum is needed to break the vdW bond, intramolecular vibrational energy redistribution (IVR) competes with direct coupling to the dissociative continuum. The initial zero-order bright state is then coupled to a manifold of zero-order dark states and VP depends strongly on the density of states of the dark manifold.^{12,13} For high densities, the dark states behave as a continuum and the VP rate is expected to increase smoothly.^{12,13} For low dark state densities, however, VP strongly depends on energy differences and couplings between bright and dark states. Examples include NeI₂ (Ref. 14) and ArCl₂ (Ref. 15). VP in ArCl₂ (Ref. 15) can occur via sequential transfer of two vibrational quanta from Cl₂ to the vdW modes, with a dark state intermediate. Janda and co-workers used this to explain how experimental Cl₂ rotational distributions are structured and sensitive to *v_i*.¹⁵

In ArI₂ three vibrational quanta are needed to break the vdW bond and a sequential mechanism is likely. Time-dependent quantum studies of ArI₂ VP with zero total angular momentum (*J*=0) indicate a few dark states mediate the dissociation,^{16,17} and the VP rate oscillates with *v_i*.¹⁷ These results appear to conflict with the conclusions reached based on the experimental work^{4(b)} discussed earlier. The experiments involve nonzero *J* states, so it is natural to suspect *J* plays an important role. Often VP rates are not very sensitive to *J*.¹⁸ However, when VP is mediated by IVR with excited dark states there may be strong couplings between rotational and vibrational motion.^{15(b)} The energetics of ArI₂ is such that dark states with a lot of bending excitation occur. Coriolis coupling is probably important and a rigorous, but computationally intensive treatment, is required. We present such a treatment using time-independent and time-dependent quantum dynamics methods, for several values of *J*. We also

use IVR models based on a few interacting states to interpret our results, and consider the sensitivity of results to potential parameters.

Section II outlines methods. Section III discusses $J=0$ resonances and IVR model results. Details of the models are in the Appendix. Section III also shows how resonance widths depend on the potential parameters. Section IV presents $J>0$ results, IVR model results, and compares with experimental data. Section V concludes the paper.

II. THEORY

We study resonances associated with complexes on the (first excited) B electronic state, which dominate the VP dynamics. The Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\mathbf{l}^2}{2\mu R^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\mathbf{j}^2}{2mr^2} + V_B(r, R, \theta). \quad (2)$$

$\mathbf{R}$ is the vector between Ar and the center of mass of I₂, $\mathbf{r}$ is the I₂ internuclear vector, and θ is the angle between $\mathbf{R}$ and $\mathbf{r}$. $\mathbf{l}$ and $\mathbf{j}$ are angular momentum operators associated with $\mathbf{R}$ and $\mathbf{r}$, $\mu = 2m_{\text{Ar}}m_{\text{I}}/(m_{\text{Ar}} + 2m_{\text{I}})$ and $m = m_{\text{I}}/2$. V_B is taken to be

$$V_B(r, R, \theta) = V_{\text{II}}(r) + W(r, R, \theta), \quad (3)$$

where V_{II} is the isolated I₂ potential¹⁶ and W is the interaction potential. A sum of atom-atom Morse potentials model is used.¹⁶ Section III C discusses W .

The I₂ vibrational wave functions satisfy

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{\text{II}}(r) - \epsilon_v \right) \chi_v(r) = 0. \quad (4)$$

The χ_v are used to partition the Hamiltonian as $H = H_0 + V$, where

$$H_0 = \sum_v |\chi_v\rangle H_v \langle \chi_v| \quad \text{with} \quad H_v = \langle \chi_v | H | \chi_v \rangle, \quad (5)$$

$$V = \sum_v \sum_{v' \neq v} |\chi_v\rangle V_{vv'} \langle \chi_{v'}| \quad \text{with} \quad V_{vv'} = \langle \chi_v | H | \chi_{v'} \rangle.$$

Each zero-order Hamiltonian $H_v(\mathbf{R}, \hat{r})$ has a set of discrete Φ_{vn}^J eigenfunctions, where n denotes vdW ro-vibrational modes, and a continuous set of dissociative eigenfunctions $\Phi_{vj\Omega E}^J$ corresponding asymptotically to I₂ in states (v, j, Ω) .

We determine resonances in the time-independent case by examining energy variation of the absolute square of scattering wave functions overlapped with certain discrete wavefunctions. Consider $R \rightarrow \infty$, where diatomic fragments are described by $\chi_v(r) \Theta_{j\Omega}^{JMp}(\hat{r}, \hat{R})$. $\Theta_{j\Omega}^{JMp}$ are rotational functions in a body-fixed (BF) frame with the z axis attached to $\mathbf{R}$,¹⁹

$$\Theta_{j\Omega}^{JMp}(\hat{r}, \hat{R}) = \left(\frac{2J+1}{4\pi} \right)^{1/2} c_{\Omega} [D_{M\Omega}^{J*}(\phi_R, \theta_R, 0) Y_{j\Omega}(\theta, \phi) + p(-1)^J D_{M-\Omega}^{J*}(\phi_R, \theta_R, 0) Y_{j-\Omega}(\theta, \phi)]. \quad (6)$$

M and Ω are projections of total angular momentum on the z axis of the space-fixed and BF frames, respectively, $p = \pm 1$ is parity under nuclear coordinates inversion and $c_{\Omega} = [2(1 + \delta_{\Omega 0})]^{-1/2}$. $\hat{r} \equiv (\phi, \theta)$ denotes polar angles for $\mathbf{r}$ in the BF frame and $\hat{R} \equiv (\phi_R, \theta_R)$ denotes polar angles for $\mathbf{R}$ in the space-fixed frame. $D_{M\Omega}^{J*}$ and $Y_{j\Omega}$ are Wigner functions and spherical harmonics.²⁰ Scattering wave functions consistent with (v, j, Ω) final states are¹⁵

$$\Psi_E^{J,v,j,\Omega}(\mathbf{r}, \mathbf{R}; E) = \sum_{v'j'\Omega'} \varphi_{v'j'\Omega'}^{J,v,j,\Omega}(R; E) \chi_{v'}(r) \Theta_{j'\Omega'}^{JMp}(\hat{r}, \hat{R}), \quad (7)$$

where the coefficients $\varphi_{v'j'\Omega'}^{J,v,j,\Omega}$ are solutions with “incoming” boundary conditions¹⁵ of

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + B_{vv}j(j+1) - E \right) \varphi_{vj\Omega}^{J,v,j,\Omega}(R; E) = - \sum_{v'j'\Omega'} \left(V_{vj\Omega, v'j'\Omega'}(R) + \frac{\delta_{jj'}\delta_{v'v'}}{2mR^2} \langle \Theta_{j\Omega}^{JMp} | \mathbf{l}^2 | \Theta_{j'\Omega'}^{JMp} \rangle \right) \varphi_{v'j'\Omega'}^{J,v,j,\Omega}(R; E) \quad (8)$$

with $B_{vv} = (\hbar^2/2m) \langle \chi_v | r^{-2} | \chi_v \rangle$. As in related time-independent work,^{14,15,18} terms proportionate to $B_{vv'}$ with $v \neq v'$ are not included in the coupled equations, facilitating imposition of boundary conditions. Such couplings, of magnitude 0.003 cm⁻¹ or less, do not appreciably influence the dynamics. The $\mathbf{l}^2$ matrix elements include the Coriolis terms that couple Ω with $\Omega \pm 1$ (with $v = v'$ and $j = j'$). The $\mathbf{l}^2$ matrix elements and other technical details are found in numerous other references.^{18,19}

Absorption cross sections can be approximated from the square of the overlap of B state scattering wave functions with bound states of the X state. In order to simply determine

the relevant B state resonances, it suffices to examine the square of the overlap of the B state scattering wave functions with discrete states associated with the very same B state. In such vdW systems, the X and B interaction potentials are sufficiently similar that the discrete states associated with the B state are similar to the bound states associated with the X state. The discrete states are¹⁵

$$\Phi_{vn}^J(\mathbf{R}, \hat{r}) = \sum_{j\Omega} \sum_k a_{j\Omega}^{J,v,n} \varphi_k(R) \Theta_{j\Omega}^{JMp}(\hat{r}, \hat{R}), \quad (9)$$

where $\varphi_k(R)$ is a suitable (e.g., harmonic oscillator) basis

set. Introducing Eq. (9) into the time-independent Schrödinger for H_v in Eq. (5) leads to a Hamiltonian matrix that is diagonalized to yield the discrete states.

The relevant squared overlaps, which we call spectra, are

$$A_{v_n}^J(E) = \sum_{\Omega', v', j'} |A_{v_n}^{Jj'v'\Omega'}(E)|^2 \quad (10)$$

with

$$A_{v_n}^{Jj'v'\Omega'}(E) = \langle \Phi_{v_n}^J \chi_v | \Psi_E^{Jj',v',\Omega'} \rangle. \quad (11)$$

To obtain estimates of the resonances associated with an initial excitation v_i in I_2 , and n_i in the vdW degrees of freedom, we consider $A_{v_i, n_i}^J(E)$. (Most work focuses on the ground vdW excitation $n_i=0$, although for $J=0$ we give some $n_i=1$ results.)

The I_2 product distribution associated with a resonance near energy E is

$$P_{v_i, n_i}^{Jj'v'\Omega'}(E) = \frac{|A_{v_i, n_i}^{Jj'v'\Omega'}(E)|^2}{A_{v_i, n_i}^J(E)}, \quad (12)$$

where v_i, n_i is the main discrete component of the resonance and $v' \leq v_i - 3$ due to the relatively large vdW bonding energy ($\approx 222 \text{ cm}^{-1}$).

The A_{v_i, n_i}^J can also be found from time evolution of the initial discrete state,²¹

$$A_{v_i, n_i}^J(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} \langle \Psi(\mathbf{r}, \mathbf{R}; t=0) | \Psi(\mathbf{r}, \mathbf{R}; t) \rangle, \quad (13)$$

where

$$\begin{aligned} \Psi(\mathbf{r}, \mathbf{R}; t=0) &= \chi_{v_i} \Phi_{v_i, n_i}^J(\hat{r}, \mathbf{R}), \\ \Psi(\mathbf{r}, \mathbf{R}; t) &= e^{-iHt/\hbar} \Psi(\mathbf{r}, \mathbf{R}; t=0). \end{aligned} \quad (14)$$

The wave packet $\Psi(t)$ is

$$\Psi(\mathbf{r}, \mathbf{R}; t) = \sum_{v', j', \Omega'} \varphi_{v', j', \Omega'}^J(R; t) \chi_{v'}(r) \Theta_{j', \Omega'}^{JMp}(\hat{r}, \hat{R}) \quad (15)$$

with the $\varphi_{v', j', \Omega'}^J(R; t)$ satisfying

$$\begin{aligned} i\hbar \frac{\partial \varphi_{v', j', \Omega'}^J(R; t)}{\partial t} &= \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + B_{vv} j(j+1) \right) \varphi_{v', j', \Omega'}^J(R; t) \\ &+ \sum_{v'', j'', \Omega''} \left(\delta_{\Omega''} V_{v', j', \Omega'}(R) \right. \\ &+ \left. \frac{\delta_{jj'}}{2mR^2} \langle \Theta_{j', \Omega'}^{JMp} | \mathbf{I}^2 | \Theta_{j'', \Omega''}^{JMp} \rangle \right) \\ &\times \varphi_{v'', j'', \Omega''}^J(R; t). \end{aligned} \quad (16)$$

The time-dependent probabilities for different (v, j, Ω) channels are

$$P_{v, j, \Omega}^J(t) = \int_0^\infty |\varphi_{v, j, \Omega}^J(R; t)|^2 dR. \quad (17)$$

Summing Eq. (17) over j and Ω yields I_2 vibrational probabilities. For closed vibrational channels, a given vibrational probability can initially oscillate, reflecting internal transitions, but tends to zero in the long time limit. Open channel probabilities first increase monotonically with time and then become constants in the long time limit. The sum of the probabilities over the open channels ($v \leq v_i - 3$) is directly related to the dissociation probability.

The Hamiltonian matrix elements factor into four uncoupled blocks,²² labeled $e+$, $e-$, $o+$, and $o-$; e or o denotes even or odd j I_2 rotational states, and $+$ or $-$ denotes parity $p = +1$ or -1 . Due to computational limitations, most of our work focuses on just one block for each J . For $J=0$, we examine the $j=\text{even}$ ($e+$) case. For $J>0$ we examine in detail even j states with $p=(-1)^J$, i.e., for $J=1$ the $e-$ block and for $J=2$ the $e+$ block.

Calculations probing initial excitation v_i in ArI₂(v_i) include five I_2 v states, v_i-4 , v_i-3 , v_i-2 , v_i-1 , v_i , and forty j states, 0, 2, 4, ..., 78. The symmetry blocks studied in detail have $\Omega=0, 1, \dots, J$. Since the $\Theta_{j, \Omega}^{JMp}$ have $j \geq \Omega$, there are $N=200$, 395, and 590 coupled equations for $J=0$, 1, and 2, respectively. We use the Fox–Godwin–Numerov method²³ to solve the time-independent equations, Eq. (8), and the Lanczos method²⁴ to solve the time-dependent equations, Eq. (16). The grid for the time-independent equations consists of 1500 points between $R=2$ and 15 Å. A coarser grid of 128 evenly spaced points in the same range suffices for the time-dependent calculations.^{16,17} Wave packet amplitude approaching the outer edge of the R grid is removed via periodic absorption in real time.^{16,17} (Somewhat smaller grids with absorption closer to the interaction region could probably also be used). Note that the vibrational probabilities are given by the instantaneous evaluation of Eq. (17) plus the accumulated probability lost via absorption.¹⁶ One energy for a $J=0$ time-independent run requires 5–10 CPU minutes on an IBM RISC 6000 workstation, but 25–100 energies are needed to characterize all the relevant resonances in a given v_i excitation region. Several CPU hours are thus required to study a particular excitation v_i . The $J=0$ wave packet calculations are more time consuming, e.g., require 12–24 h for each v_i . However, these calculations reveal information about resonances outside the range of the time-independent calculations, and allow mechanistic features to be easily seen. As J is increased from 0 to 2, the time-independent calculations become much more time consuming, scaling as roughly N^3 . The wave packet calculations tend to scale more favorably, roughly as N^2 . By $J=2$, both types of calculations require roughly equal but substantial amounts (on the order of several days) of CPU time.

III. TOTAL ANGULAR MOMENTUM $J=0$

A. Resonance properties

Some $J=0$ results have already been given.^{16,17} We present a more extensive list of resonances to serve as reference for modeling IVR mediated dissociation (Sec. III B), and for comparison with $J>0$ results (Sec. IV). We focus on the ground ($n_i=0$) and first excited ($n_i=1$) vdW states with

TABLE I. Positions E_k , half widths Γ_k , and weights w_k for $J=0$, $e+$ resonances associated with $v_i, n_i=0$. Positions are given relative to the isolated $I_2(v_i)$ energies, ϵ_{v_i} . $\epsilon_{v_i} = 126.621 (v_i + 1/2) - 0.8713 (v_i + 1/2)^2$ relative to the I_2 potential minimum with the Morse parameters of Ref. 16.

v_i	$(E_k - \epsilon_{v_i}) (\text{cm}^{-1})$	$\Gamma_k (\text{cm}^{-1})$	w_k
16	-222.342	0.000 02	≈ 1.00
17	-222.220	0.0002	0.967
18	-222.781	0.0321	0.022
	-222.524	0.0570	0.097
	-222.192	0.0580	0.152
	-222.011	0.0038	0.743
19	-221.974	0.000 24	0.959
	-221.064	0.0634	0.012
	-220.596	0.0292	0.011
20	-223.760	0.0164	0.013
	-222.355	0.0146	0.018
	-222.035	0.0800	0.041
	-221.775	0.0019	0.920
21	-222.240	0.0540	0.117
	-221.892	0.0530	0.232
	-221.509	0.0105	0.619
22	-223.856	0.0279	0.002
	-223.683	0.0346	0.002
	-222.201	0.0688	0.002
	-221.563	0.0134	0.967
	-220.123	0.0246	0.027
23	-221.940	0.0155	0.058
	-221.334	0.0008	0.903
	-221.148	0.1327	0.016
24	-221.191	0.0014	0.948
	-220.786	0.1759	0.018
	-219.998	0.0369	0.012

$j=\text{even}$. The ground vdW resonance position is $\approx -222 \text{ cm}^{-1}$ relative to the energy of isolated $I_2(v_i)$. The first vdW excitation is roughly the stretching mode and is $\approx 23 \text{ cm}^{-1}$ higher in energy. (There is also bending character present in this state because it is one component of a Fermi resonance.¹⁷) The spectra show several peaks which arise from oscillator strength of the bright state, corresponding to v_i , being shared with several zero-order dark states corresponding to v_i-1 and v_i-2 . Normalized spectra are fit to a sum of Lorentzian functions, $\sum_k w_k L(E; E_k, \Gamma_k)$, $L(E; E_k, \Gamma_k) = (\Gamma_k/\pi) / [(E - E_k)^2 + \Gamma_k^2]$, to infer the resonance positions E_k , halfwidths Γ_k , and relative weights w_k . Tables I and II list results for $n_i=0$ and $n_i=1$, respectively. Analysis of wave packet autocorrelation functions with Pro-

TABLE II. Resonance properties for $J=0$, $e+$ resonances associated with $v_i, n_i=1$. See Table I caption for additional details.

v_i	$(E_k - \epsilon_{v_i}) (\text{cm}^{-1})$	$\Gamma_k (\text{cm}^{-1})$	w_k
18	-198.813	0.0001	≈ 1
19	-198.673	0.005	0.650
	-198.606	0.019	0.350
20	-198.471	0.0006	0.954
21	-199.541	0.0411	0.030
	-199.084	0.1185	0.023
	-198.237	0.0145	0.896

TABLE III. Zero-order analytical model parameters used to fit the numerical data $v_i=21$, $n_i=0$, and $J=0$. See the Appendix for more details. $\Gamma_{v-1, v-2} = \Gamma_{v-2, v-1} = 0.45 (\Gamma_{v-1, v-1} \Gamma_{v-2, v-2})^{1/2}$; $V_{v, v-1} = V_{v-1, v} = -0.2392 \text{ cm}^{-1}$; $V_{v, v-2} = V_{v-2, v} = 0.088 65 \text{ cm}^{-1}$; $V_{v-1, v-2} = V_{v-2, v-1} = -0.1558 \text{ cm}^{-1}$.

v	$(E_v - \epsilon_{v_i}) (\text{cm}^{-1})$	$\Gamma_{vv} (\text{cm}^{-1})$
21	-221.735	0.000
20	-222.400	0.044
19	-221.859	0.074

ny's method²⁵ yields similar results.¹⁷ (The main purpose of also carrying out wave packet calculations here is to obtain time-dependent vibrational probabilities.)

For each v_i in Tables I and II there is a dominant resonance with weight $w_i > 0.5$. Its halfwidth varies dramatically with v_i suggesting VP mediated by IVR. In order to analyze the energy flow pathways and verify the IVR picture, we show how IVR-based models with just a few parameters reproduce the spectra and time-dependent probabilities.

B. Analysis of the VP dynamics using IVR models

VP in ArI₂ requires loss of at least three I_2 vibrational quanta. Several mechanisms are possible: direct dissociation,

and the more probable dissociation mediated through IVR, for which we distinguish between a sequential mechanism

and more complicated patterns

We analyze some $n_i=0$ resonances from Table I. (A similar analysis applies equally to the $n_i=1$ resonances.) In Table I, the maximum mixing occurs for the case $v_i=21$. An estimate of the direct dissociation contribution is obtained by carrying out calculations with $\Delta v=1$ couplings neglected. For $v_i=21$ a width of $\approx 10^{-7} \text{ cm}^{-1}$ is found, which is 5 orders of magnitude smaller than the exact width. We thus neglect the contribution of Eq. (18) in modeling the dynamics. We use a model based on three coupled zero-order states, each associated with a well defined vibrational quantum number v . As described in the Appendix, the model parameters are chosen to reproduce the main features of both the spectrum and time-dependent probabilities. Parameters for this model are in Table III, and comparisons with the exact results are shown in Figs. 1 and 2 for the spectrum and vibrational probabilities. The agreement of exact (symbols) and model (dashed and solid lines) spectra in Fig. 1 is good. (The three-resonance model cannot reproduce a weak, asymmetric fourth resonance feature at $\approx -221.7 \text{ cm}^{-1}$.) The exact and model time-dependent probabilities, Figs. 2(a) and 2(b) are also qualitatively similar. We show all three closed

FIG. 1. Spectrum for initial $v_i=21$, $n_i=0$, and $J=0$: symbols denote the numerical results, while solid and dashed lines denote the zero-order model analytical fit.

channels, but only the first open vibrational channel, v_i-3 . The v_i-4 channel, included in the calculations, parallels v_i-3 but is typically too small to see clearly on the scale of such figures. (All model results labeled v_i-3 are actually the dissociation probabilities of the Appendix, since there is little difference between the dissociation probability and the v_i-3 probability.) Figure 2 is consistent with a sequential mechanism: the initially excited vibrational state ($v=v_i=21$) and next available ($v=20$) state are roughly correlated, with loss in one corresponding to gain in the other. Growth in the $v=19$ state also roughly correlates with loss in $v=20$. Beat frequencies in the closed vibrational channels are related to the energy differences of participating resonances. The non-zero value for $\Gamma_{v_i-1,v_i-1} = \Gamma_{20,20}$ in Table III suggests that $v_i=21$ is a case where the more complicated Eq. (20) mechanism competes with the sequential mechanism Eq. (19).

At the other extreme are cases such as $v_i=19$, $n_i=0$, where IVR mixing is much smaller, giving rise to a main resonance with $w_i > 0.95$. This happens when there is accidentally relatively poor energetic alignment between zero-order bright and dark states. Due to the small mixing, the direct VP mechanism might be expected to compete with VP mediated by IVR. However, a three-state model similar to that used for $v_i=21$ describes the $v_i=19$ situation reasonably well. The results are similar in spirit to those for $v_i=21$, so we do not display them. Such a model involves no contribution from a direct VP mechanism.

For $v_i=18$, $n_i=0$ the IVR picture is again operative, but the simple picture of three coupled states is less adequate and a five state model is necessary. As outlined in the Appendix, the fitting procedure is simplified by using a first-order model based on linear combinations of zero-order states. Parameters used in the first-order model are in Table IV. Figure 3 shows numerical and model spectra. (The model uses two overlapping resonances, $i=3$ and 4 in Table IV, to describe a broad, asymmetric resonance feature near -222.5 cm⁻¹.) Figure 4 shows the numerical and model I₂ time-dependent

FIG. 2. I₂ vibrational probabilities for initial $v_i=21$, $n_i=0$, and $J=0$: (a) Numerical results and (b) zero-order model analytical fit.

probabilities, which are also in good agreement. (One cannot easily extract intermediate v_i-1 and v_i-2 probabilities out of our first-order model. The model results in Fig. 4 are thus only the $v=18$ and 15 probabilities.)

C. Effect of the ArI₂(B) interaction potential surface

In our work we take the ArI₂(B) potential to be

$$W(r, R, \theta) = V_{\text{ArI}}(R_{\text{ArI}_A}) + V_{\text{ArI}}(R_{\text{ArI}_B}), \quad (21)$$

TABLE IV. First-order model parameters used to fit the numerical data obtained for initial $v_i=18$, $n_i=0$, and $J=0$. See the Appendix for more details. $\Gamma_{12}=\Gamma_{21}=-1.0$ ($\Gamma_{11}\Gamma_{22}$)^{1/2}; $\Gamma_{13}=\Gamma_{31}=0.5$ ($\Gamma_{11}\Gamma_{33}$)^{1/2}; $\Gamma_{23}=\Gamma_{32}=-0.2$ ($\Gamma_{22}\Gamma_{33}$)^{1/2}; $\Gamma_{k4}=0$ for $k \neq 4$; $\Gamma_{k5}=0$ for $k \neq 5$.

k	$(E_k - \epsilon_{v_i})(\text{cm}^{-1})$	$\Gamma_{kk}(\text{cm}^{-1})$	α_k
1	-222.009	0.0043	0.749
2	-222.199	0.0490	0.132
3	-222.519	0.0400	0.051
4	-222.580	0.0650	0.054
5	-222.781	0.0250	0.014

FIG. 3. Spectrum for initial $v_i=18$, $n_i=0$, and $J=0$: Symbols denote the numerical results, while solid and dashed lines denote the first-order analytical model fit.

where V_{ArI} is a Morse potential and R_{ArI_A} and R_{ArI_B} are atom-atom distances. Column 1 in Table V lists the Morse parameters used in most of this paper. They yield vdW bond energy $D_0 \approx 222 \text{ cm}^{-1}$, and vdW stretch frequency $\approx 23 \text{ cm}^{-1}$. Levy and co-workers¹ found D_0 to be between 220 and 226 cm^{-1} and vdW stretch frequency 24 cm^{-1} . However, other parameters can be chosen to be consistent with this limited data. Assuming Eq. (21), we investigate the sensitivity of our results to the V_{ArI} parameters. Table V lists three other sets of Morse parameters in columns 2–4. Column 2 has larger D_{ArI} and α_{ArI} values than our original ones. One thus expects the potential couplings and also decay widths to be larger. These parameters still yield $D_0 \approx 222 \text{ cm}^{-1}$. The vdW stretching excitation becomes 28 cm^{-1} , which while a little high compared to experiment¹ is still reasonable. Column 3 in Table V yields $D_0 \approx 225 \text{ cm}^{-1}$, towards the upper end of the experimental range of

TABLE V. Morse parameters used to describe ArI₂(B). The first column of parameter values corresponds to the potential used throughout most of this work.

Parameters	1	2	3	4
R_{ArI} (Å)	4.2	4.2	4.2	4.0
D_{ArI} (cm^{-1})	122	124.7	123.5	122.0
α_{ArI} ($\text{\AA}^{-1}$)	1.3228	1.6063	1.3228	1.3228

possibilities,¹ and a vdW excitation frequency within 1 cm^{-1} of experiment. Column 4 in Table V involves a smaller R_{ArI} than previously used. This should increase decay widths somewhat, but does not change D_0 and the vdW excitation frequency significantly.

Figure 5 displays the main resonance halfwidths for $J=0$, $n_i=0$ resonances obtained with the various potential parameters in Table V. While decay widths can differ by an order of magnitude or more when using alternative parameters, it is still the case that strong oscillatory behavior is observed. The details of the interaction potential alter the positions and number of the zero-order bound states and their couplings, so changes in the parameters produce variations in VP widths. However, it is difficult to avoid non-monotonic behavior in $\Gamma(v_i)$ for $J=0$ because the density of dark states remains low when the potential is described by Eq. (21). Monotonic VP rate constants should result if the density of dark states and associated couplings are sufficiently large to bring about a statistical IVR limit.^{12,13} State densities and couplings can also be altered by total angular momentum, as we show in Sec. IV.

IV. EFFECT OF OVERALL ROTATION

A. Rotational structure of the ArI₂(v_i) discrete states

We discuss the ArI₂ rotational energy states, in a fashion similar to a previous treatment of (rare gas)-Cl₂ systems.²² For fixed I₂ vibrational quantum number $v=v_i=21$, we de-

FIG. 4. I₂ vibrational probabilities for initial $v_i=18$, $n_i=0$, and $J=0$: Solid lines are the numerical results, while dashed lines are the first-order model analytical fit.

FIG. 5. Vibrational predissociation halfwidths for the various vdW interaction potential parameters of Table VI. Results are for $J=0$, $n_i=0$ and the halfwidth associated with the main resonance (largest w_i) is displayed.

TABLE VI. Discrete energy levels for $v_i=21$ [relative to isolated I₂($v_i=21$)]. J_{K_a,K_c} is the usual asymmetric rotor label (Ref. 20). The rigid asymmetric rotor levels from Eq. (22) are also listed. These energies include constant vibrational terms; the vibrational energy of the vdW ground state is -222.062 cm^{-1} and the energy of the first excited bend is -208.535 cm^{-1} to make the lowest $J=1$ rotor levels exactly match the corresponding discrete level energies.

J	Symmetry and J_{K_a,K_c}	Discrete state energy (cm ⁻¹)	Rigid asym. rotor energy (cm ⁻¹)
1	$o-, 1_{01}$	-222.024	-222.024
	$e-, 1_{11}$	-222.017	-222.016
	$o+, 1_{10}$	-222.006	-222.006
	$e-, 1_{01}$	-208.497	-208.497
	$o-, 1_{11}$	-208.493	-208.489
	$e+, 1_{10}$	-208.479	-208.479
	$e+, 2_{02}$	-221.952	-221.953
	$o+, 2_{12}$	-221.950	-221.950
	$e-, 2_{11}$	-221.916	-221.920
	$o-, 2_{21}$	-221.896	-221.896
2	$e+, 2_{20}$	-221.889	-221.891
	$o+, 2_{02}$	-208.428	-208.426
	$e+, 2_{12}$	-208.423	-208.423
	$o-, 2_{11}$	-208.391	-208.393
	$e-, 2_{21}$	-208.371	-208.369
	$o+, 2_{20}$	-208.366	-208.364

termine the lowest lying discrete energy states, Eq. (9), via matrix diagonalization (Sec. II). Table VI presents the resulting energy levels for $J=1$ and 2, including all symmetry blocks. Our calculations do not correspond to a rigid ArI₂ molecule, but we show that the patterns in Table VI are consistent with a rigid asymmetric rotor with a slight oblate tendency.

Consider rigid T-shaped ArI₂ in the x - y plane with origin taken to be the center of mass. Placing Ar on the y axis and I atoms parallel to the x axis, the x , y , and z axes are associated with the a , b , and c principal axes.²⁰ Employing average distances for ground vdW stretching motion and I₂($v_i=21$), $\langle R \rangle = 7.4$ a.u. and $\langle r \rangle = 6.26$ a.u., we find rotational constants $A = \hbar^2/(2I_a) = 0.032\text{ cm}^{-1}$, $B = \hbar^2/(2I_b) = 0.024\text{ cm}^{-1}$, $C = \hbar^2/(2I_c) = 0.014\text{ cm}^{-1}$. The asymmetry parameter is²⁰ $\kappa = (2B - A - C)/(A - C) \approx 0.2$. Since $\kappa = +1$ in the oblate limit and $\kappa = -1$ in the prolate limit, rigid ArI₂ is only marginally in the oblate limit. There are $2J+1$ asymmetric rotor levels for a given J , and Table VI shows, for both $J=1$ and 2, two clumps of $2J+1$ relatively closely spaced discrete levels. The lowest energy clump of levels near -222 cm^{-1} corresponds to zero-point motion in the vdW degrees of freedom. The higher energy clump near -208 cm^{-1} corresponds to asymmetric rotor structure superimposed on the first excited vdW bending state. There is a rough oblate structure within clumps. Oblate symmetric top energy levels increase with $K_c = J, J-1, \dots, 0$ and, except for the highest $K_c=0$ level are doubly degenerate. K_c is magnitude of the projection of total angular momentum on the c -axis, which is out of the molecular plane.

Similar patterns, but with broken degeneracies, are seen in Table VI.

The level patterns within clumps are described quantitatively with a general rigid asymmetric rotor model,²⁰ which leads to a $(2J+1) \times (2J+1)$ Hamiltonian matrix

$$H_J(K, K) = (1/2)(A+B)[J(J+1) - K^2] + CK^2,$$

$$H_J(K, K \pm 2) = (1/4)(A-B)[J(J+1) - K(K \pm 1)]^{1/2} \times [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}, \quad (22)$$

where we assume zero-order rotor states $K = -J, -J+1, \dots, J$ that are eigenstates of the c -axis angular momentum operator. It is straightforward to numerically diagonalize Eq. (22). For low J the eigenvalues of Eq. (22) are also tabulated.²⁰ The last column of Table VI corresponds to these rigid asymmetric rotor levels, which agree very well with the actual discrete levels.

We now compare asymmetric rotor eigenvectors with the corresponding discrete state eigenvectors. K_c is the absolute magnitude of K , and so the relative contribution of K_c in an eigenstate is the sum of the squares of the associated $K = \pm K_c$ components of the eigenvectors of Eq. (22). For $J=1$, the lowest two asymmetric rigid rotor levels are purely $K_c=1$ states and the highest level is a pure $K_c=0$ state. For $J=2$, the lowest rotor level is approximately a 95/5 mixture of $K_c=2/K_c=0$, the next three levels are pure $K_c=2, 1$, and 1 states, and the highest level is a 5/95 mixture of $K_c=2/K_c=0$. The eigenvectors are thus close to what would be expected from an oblate limit. K_c is not the same as Ω used in our dynamics work. Ω , the projection of total angular momentum on $\mathbf{R}$, is more akin to the projection of total angular momentum on the b axis, K_b . To infer the corresponding K_b decomposition, we redo the rigid rotor calculations with the b -axis and c -axis rotational constants exchanged. The same energy levels result, but eigenstate decompositions are consistent with K_b . The $J=1$ levels, in increasing energetic order, correspond to pure $K_b=1, 0$, and 1 states. The $J=2$ levels correspond to a 55/45 mixture of $K_b=0/K_b=2$, pure $K_b=1, 2$, and 1 states, and finally a 45/55 mixture of $K_b=0/K_b=2$. With minor differences of less than 1%, the actual discrete state levels, when analyzed in terms of Ω , agree well with the rigid rotor estimates based on K_b . For example, our lowest $J=2$, $v_i=21$ discrete state is 54.7% $\Omega=0$, 0.5% $\Omega=1$, and 44.8% $\Omega=2$, with the small amount of $\Omega=1$ due to Coriolis coupling.

B. $J>0$ quantum dynamics

Our main results focus on resonances pertinent to various excitations v_i and the lowest levels of either the $e-$ ($J=1$) or $e+$ ($J=2$) symmetry blocks (Sec. II). (For $J=1$ we also briefly mention some results for other relevant symmetry blocks.) For $J=1$, the discrete $e-$ state is the 1_{11} state of Table VI, which is mostly an $\Omega=0$ state. For $J=2$, the corresponding discrete $e+$ state is the 2_{02} state of Table VI; a 55/45 mixture of $\Omega=0/\Omega=2$ for $v_i=21$.

Helicity decoupling^{15(b)} is analyzed by carrying out dynamical calculations for $v_i=21$, $J=1$ including only $\Omega=0$

FIG. 6. Spectra calculated for $v_i=21$, $n_i=0$, and $J=1$. The open squares connected by dashed lines correspond to the helicity decoupling approximations with only $\Omega=0$ being included in the dynamics calculation. The smaller diamond symbols correspond to the full dynamics calculation including both $\Omega=0$ and 1. The solid line that closely follows the full dynamics results represents the first-order analytical model fit to the full dynamics results.

and comparing with a full treatment with $\Omega=0$ and 1 Coriolis coupled. (The $J=1$ e^- initial state is $\approx 99.9\% \Omega=0$.) The halfwidth of the main resonance is 0.0097 cm^{-1} in helicity decoupling and 0.018 cm^{-1} in the full dynamics. The factor of 2 discrepancy suggests helicity decoupling is not well suited to this problem. This is further illustrated in Fig. 6, which compares helicity decoupled and full dynamics spectra.

We must study VP in ArI₂ including all possible (Coriolis coupled) Ω . Results for $J=1$ (e^- block) are in Table VII and results for $J=2$ (e^+ block) are in Table VIII. In both cases various energy regions are examined consistent with v_i quanta in I₂ and $n_i=0$ in the vdW modes. For both $J=1$ and

TABLE VII. Resonance properties for $J=1$, e^- resonances associated with $v_i, n_i=0$. See Table I caption for additional details.

v_i	$(E_k - \epsilon_{v_i}) (\text{cm}^{-1})$	$\Gamma_k (\text{cm}^{-1})$	w_k
16	-222.296	0.00015	≈ 1.00
17	-222.173	0.0024	≈ 1.00
18	-222.609	0.017	0.080
	-222.285	0.057	0.087
	-221.980	0.0022	0.833
19	-221.930	0.0040	0.982
20	-222.585	0.1148	0.0004
	-222.308	0.0132	0.019
	-221.728	0.0093	0.922
	-221.051	0.0814	0.0002
21	-222.304	0.0800	0.080
	-221.947	0.0280	0.170
	-221.654	0.0650	0.220
	-221.427	0.0181	0.530
22	-221.510	0.0080	0.930
23	-221.291	0.0013	0.905
24	-221.138	0.0074	0.959

TABLE VIII. Resonance properties for $J=2$, e^+ resonances associated with $v_i, n_i=0$. See Table I caption for additional details.

v_i	$(E_k - \epsilon_{v_i}) (\text{cm}^{-1})$	$\Gamma_k (\text{cm}^{-1})$	w_k
18	-221.917	0.0017	0.847
	-222.166	0.0600	0.040
	-222.466	0.0213	0.096
	-222.630	0.0400	0.017
19	-221.861	0.0006	0.959
20	-221.668	0.0010	0.890
	-222.197	0.0369	0.034
	-222.665	0.0323	0.001
21	-221.437	0.0273	0.770
	-221.650	0.0500	0.030
	-221.800	0.0500	0.030
	-222.107	0.0242	0.170

2, just as for $J=0$ (Table I), several secondary resonances appear in a v_i excitation region as a consequence of IVR. However, the widths for $J=0, 1$, and 2 can be quite different. For example, contrast the main resonances for $v_i=19$ in Tables I, VII, and VIII. The differences are likely due to changes in the nature of participating dark states in the IVR. We show below that Ω mixing in these states due to Coriolis coupling is very important.

We often find in Tables VII and VIII three or four resonances in each v_i excitation regime, just as with $J=0$. The numbers of dark states participating for $J=1$ and 2 are comparable to $J=0$, and the IVR models of the Appendix are applicable. Typically, the first-order model with four bound states suffices to describe the $J=1$ and 2 results. (For brevity, we do not display parameter values, which are similar in spirit to those in Table IV.) For example, numerical and model spectra for $v_i=21$ shown in Fig. 6 for $J=1$ are in excellent agreement. The I₂ time-dependent probabilities are also described by these models and Figs. 7(a) and 7(b) display exact and first-order model probabilities for the $v_i=21$ and 18 initial states, respectively.

Figure 8 shows the I₂(v_i-3) final rotational distribution for $v_i=21$, $J=1$. Summed over j , the $\Omega=0$ probability is 55% and the $\Omega=1$ probability is 45%, indicating the two allowed Ω states are about equally populated. However, the detailed rotational distributions associated with each Ω in Fig. 8 are distinct. The initial $J=1$ discrete $v_i=21$ state is an almost pure $\Omega=0$ state. Since the potential does not couple states with different v and Ω , the significant probability for $\Omega=1$ is due to the presence of dark states with, in addition to an $\Omega=0$ component, a significant $\Omega=1$ component due to Coriolis coupling. A similar situation occurs for $J=2$. The $J=2$ initial states, in contrast to the $J=1$ ones, are almost 50/50 mixtures of $\Omega=0$ and 2, with a small amount (less than 1%) of $\Omega=1$. However, the final I₂(v_i-3) rotational distribution has a significant $\Omega=1$ contribution. For example, the $v_i=18$ resonance at $E=-221.917 \text{ cm}^{-1}$ has final I₂(v_i-3) distribution with 37%, 54%, and 9% in $\Omega=0, 1$ and 2, respectively. The appearance of large amounts of $\Omega=1$ products in the $J=2$ calculations, as in the $J=1$ calculations, indicates dark states with significant $\Omega=1$ components and

FIG. 7. I₂ vibrational probabilities as a function of time: (a) for $v_i=21$, $n_i=0$, and $J=1$; (b) for $v=18$, $n_i=0$, and $J=1$. Solid lines correspond to numerical results while the analytical model results are dashed lines.

Coriolis coupling are playing important dynamical roles.

We also examined the time-dependence of the Ω contributions to the vibrational state probabilities, $P_{v,\Omega}$. (Our figures show sums over all allowed Ω values, and so do not reveal the Ω dependence.) We do not display detailed results, but note that typically $P_{v,\Omega=1}(t)$ show characteristic IVR beat patterns with the $v=v_i-2$ dark probability tending to be larger than the v_i-1 one. This is also consistent with Coriolis coupling in the dark states being very important.

Figure 9 displays the final I₂(v_i-3) rotational distribution for the $v_i=21$, $J=2$ resonance, showing again different behavior for different final Ω . The rotational distributions are more structured than those for $J=1$. This suggests that the nature of the dark states participating in VP for $J=1$ and 2 is different. As noted earlier, IVR models based on four bound states can also describe the $J=2$ VP dynamics reasonably well. For example, Figs. 10(a) and 10(b) present numerical and model results for the spectrum and the I₂ vibrational probabilities versus time for the case $v_i=18$.

The aforementioned results are associated with one symmetry block for each J . Other symmetry blocks will contrib-

FIG. 8. Final rotational distribution of the I₂ fragments in the v_i-3 vibrational state for $v_i=21$, $J=1$ at -221.66 cm^{-1} , and different asymptotic Ω values.

ute to experimental results. For $J=0$ there are two relevant symmetry blocks, $e+$ and $o+$. The lowest state of the $J=0$, $o+$ block is the vdW bend excitation, $\approx 14 \text{ cm}^{-1}$ above the low lying $e+$ levels studied in Sec. III. However, for $J=1$ and 2, Table VI shows that other symmetry blocks are more relevant. For example, the ground vdW vibrational state for $J=1$ consists of a clump of three very close levels ($o-$, $e-$, and $o+$). The calculations above focused only on the $J=1$, $e-$ case. For $J=2$, the situation is more complicated, with all four symmetry blocks leading to energy levels associated with the ground vdW vibrational state. For $J=1$ we performed dynamics calculations for $v_i=18-21$ of resonance properties for the two other symmetry blocks ($o-$ and $o+$) of relevance to the vdW ground vibrational state. We do not present detailed results but note that the qualitative IVR effect also occurs for these symmetry blocks (see also Sec. IV C).

FIG. 9. Final rotational distribution of the I₂ fragments in the v_i-3 vibrational state for $v_i=21$, $J=2$ at -221.434 cm^{-1} , and different asymptotic Ω values.

FIG. 10. The $v_i=18$, $n_i=0$, and $J=2$ results: (a) The spectrum, with symbols denoting the numerical results and solid and dashed lines denoting the analytical model results, and (b) the I_2 vibrational probabilities versus time, with solid lines denoting the numerical results and dashed lines (corresponding to $v=15$ and 18 only) denoting the first-order analytical model results.

C. Vibrational predissociation rate constants

The experimental VP rate constant estimates are averages over various resonances in a v_i excitation region, as well as averages over J . It is difficult to determine theoretical quantities that directly correlate with such data. Our main

concern is to obtain an approximate idea of the effect of averaging. We define an average VP rate constant

$$K_{v_i, n_i}^J = \frac{2}{\hbar} \sum_k w_k \Gamma_k, \quad (23)$$

where the sum is over resonances associated with a given I_2 excitation v_i and vdW mode excitation n_i . Equation (23) is an effective rate constant associated with bright state v_i, n_i which, in turn, is composed of several resonances. It results from linearizing the approximate dissociation probability, $1 - \sum_k w_k \exp(-2\Gamma_k t/\hbar)$, and is thus an initial decay rate. Of course, a single rate constant is not correct at moderate times, and in the long time limit the smallest Γ_k dominates. Comparisons with time-dependent calculations show, however, that Eq. (23) provides a reasonable measure of the effective dissociation rate over the time scale (≤ 200 ps from Figs. 2, 4, and 7) where appreciable dissociation occurs.

It's unlikely that the first vdW excitation contributes to the experimental results, and so we discuss $n_i=0$. Table IX lists results for $J=0, 1$, and 2 . Experimental estimates for $v_i=18$ and 21 , due to Burke and Klemperer,^{4(b)} are also listed. $K_{v_i, n_i=0}^J$ parallels the behavior of the major resonances (those with largest w_i) in Tables I, VII, and VIII. For example, Table IX also includes the rate constants associated with the major resonances for $J=0$, and we see that the average over other resonances, $K^{J=0}$ in the next column, is qualitatively similar. However, averaging over the other resonances generally produces larger rate constants, and also tends to smooth out the oscillations with v_i a bit. The $J=1$ and 2 results in Table IX are quantitatively different, but qualitatively similar to the $J=0$ results. For example, $v_i=19$ is always a local minimum. This suggests that despite sensitivity to details, important features of the IVR effect persist in the low J limit. We also note, at least for $J=1$, that averaging over all relevant symmetry blocks still does not average out the oscillations. The $J=1$ rate constants, averaged over $n_i=0$ resonances in the $o-$, $e-$, and $e+$ symmetry blocks, are $\approx 4, 1, 3$, and 11 ns^{-1} , for $v_i=18, 19, 20$, and 21 . These results are similar to just the $e- J=1$ results of Table IX.

The experimental results in Table IX for $v_i=18$ and 21 are surprisingly close to our $K_{v_i, n_i=0}^J$ results. However, the

TABLE IX. Approximate VP rate constants for $J=0, 1$, and 2 . $2\Gamma_m^{J=0}/\hbar$ denotes the rate constant associated with the largest weight $J=0$ resonance from Table I. K^J denotes the average given by Eq. (23) over resonances near a v_i ($n_i=0$) bright excitation. Experimental values are from Burke and Klemperer [Ref. 4(b)].

v_i	$(2\Gamma_m^{J=0}/\hbar) (\text{ns}^{-1})$	$K^{J=0} (\text{ns}^{-1})$	$K^{J=1} (\text{ns}^{-1})$	$K^{J=2} (\text{ns}^{-1})$	Expt. (ns^{-1})
16	0.008	0.008	0.06		
17	0.08	0.08	0.9		
18	1.4	6.7	3.1	2.5	4.5
19	0.09	0.5	1.5	0.2	
20	0.7	2.1	3.4	0.8	
21	4.0	9.5	13.2	10.6	7.8
22	5.0	5.2	2.8		
23	0.3	1.4	0.4		
24	0.5	1.8	2.7		

experiments are carried out in supersonic beams with finite temperatures perhaps on the order of 5–10 K. This corresponds to $kT \approx 1\text{--}3\text{ cm}^{-1}$ and allows for many J states to contribute. The average rotational constant for ArI₂ is $\approx 0.023\text{ cm}^{-1}$, which suggests that J values as large as 10 (and probably much larger) could be important. We thus have insufficient information to construct a proper statistical average over J . As noted in Sec. II, higher J dynamics calculations are computationally demanding. However, parallel computer architectures do allow such calculations to be considered and future work²⁶ will address explicitly whether or not higher J values will lead to more smoothly varying average VP rate constants.

V. CONCLUDING REMARKS

We presented a detailed quantum study of ArI₂(v_i) VP for several values of v_i and total angular momenta $J=0, 1$, and 2. On a theoretical level, our results are useful benchmarks for the development of both approximate and accurate dynamical methods for studying resonances and rotational effects in chemical reactions. With respect to ArI₂ itself, we find VP is always mediated by IVR in the sparse limit and direct fragmentation of the complex is unlikely. The degree of mixing between the zero-order states is sensitive to v_i , producing large oscillations in the VP rate. As seen in Sec. IV C, our low J results for the $v_i=18$ and 21 VP rate constants are in reasonable accord with experimental estimates.^{4(b)} However, Sec. I noted secondary experimental evidence^{4(b)} that the VP rate constant may increase monotonically with v_i , which is not the case in our calculations.

The theoretical VP oscillations should disappear if IVR occurs in a statistical limit.^{12,13} Sec. III C showed, despite sensitivity of the results to potential parameter variations, that it is unlikely plausible changes of the potential parameters can accomplish the required increase in dark state density. However, recent work²⁷ on HeCl₂ poses questions regarding the accuracy of atom-atom forms for the potential. While it is unclear if such conclusions can be transferred to a more bonded system such as ArI₂, it may be that a more drastic change in the form of the potential could significantly alter the density of states and intramolecular coupling. For example, an inadequacy of the current potential is that it does not allow for a collinear minimum. A linear isomer may exist, although it may not be as deep on the B state as the X state.^{4(a)} Depending on the barrier between linear and T-shaped geometries, a linear minimum could affect the density of states.

The VP resonance widths can change significantly as J is increased from 0 to 2. This implies an average over many J could wash out oscillations of the VP rate constants. However, as shown in Sec. IV C, $J \leq 2$ is insufficient to accomplish it, at least for the symmetry blocks considered. Inclusion of other, relevant symmetry blocks in defining average rate constants, particularly at the higher J values, will help to average out the oscillations. In addition, as J increases, the density of states also increases. Since (Sec. IV) Coriolis coupling strongly mixes different Ω , the IVR could become sta-

tistical in the limit of higher J . Thus, even for a given symmetry with high J it might be possible to achieve a more smoothly varying VP rate constant. Of course, as the statistical limit is approached the resonances become not only energetically denser, but their widths begin to overlap, leading to potentially interesting features.^{28,29} Our current work is aimed at addressing such issues.²⁶

It is also possible that coupling VP with EP might also have a smoothing effect. However, as noted in Sec. I, EP is itself very sensitive to v_i . Furthermore, in a first approximation the effect of EP would be to lead to certain energy shifts and other changes in the details of the IVR mechanism, but it would not destroy the qualitative phenomenon.

Assuming our model is correct, VP in ArI₂ at low J always takes place via a few state IVR mechanism that should lead to large oscillations in VP rate constants. Our model and conclusions could be checked by performing experiments at very low temperatures. In particular, real-time studies³ of the total predissociation rate for a variety of initial vibrational excitations v_i would be very helpful.

ACKNOWLEDGMENTS

O.R. was supported by DGICYT Grant No. PB92-0053. S.K.G. was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under Contract No. W-31-109-ENG-38. O.R. also thanks the Comunidad Autónoma de Madrid for financial support for a short stay at ANL.

APPENDIX: ANALYTICAL MODEL FOR IVR MEDIATED DISSOCIATION

We generalize previous IVR mediated VP models¹⁵ to include $n_b > 2$ bound states. We use Green's operator and projection operator ideas similar to treatments of related problems.^{29–31} In the zero-order picture one has n_b "bound" states associated with certain of the discrete states, Eq. (9), that are close in energy. For example, the zero-order picture for ArI₂ involves $n_b=3$ bound states with one discrete state corresponding to v_i quanta in I₂ and zero-point motion in the vdW degrees of freedom, and the other two bound states corresponding to v_i-1 and v_i-2 quanta in I₂ and substantial excitations in the vdW modes. The model allows for intramolecular coupling between these states, and allows for each state to have a decay width associated with fragmentation. In the first-order model, the discrete states are taken to be linear combinations of the zero-order ones that make the intramolecular coupling zero.

Discrete, Φ_k , and dissociative, $\Phi_{\beta E}$, states are used to define projection operators P and Q , respectively, which satisfy the usual rules $P+Q=1$, $PQ=0$, $P^2=P$, $Q^2=Q$. The functions inside the discrete subspace P are coupled by V , Eq. (5), so that we consider the coupling scheme,

$$\begin{aligned} \langle \Phi_k | H | \Phi_k \rangle &= \langle \Phi_k | H_0 | \Phi_k \rangle = E_k, \\ \langle \Phi_k | H | \Phi_j \rangle &= \langle \Phi_k | V | \Phi_j \rangle = V_{kj} \quad \text{with } k \neq j. \end{aligned} \quad (\text{A1})$$

We assume the continuum subspace is such that

$$\langle \Phi_{\beta E} | H | \Phi_{\beta' E'} \rangle = \langle \Phi_{\beta E} | H_0 | \Phi_{\beta' E'} \rangle = E \delta(E - E') \delta_{\beta\beta'} \quad (\text{A2})$$

In ArI₂, β labels asymptotic quantum numbers associated with Ar+I₂ (e.g., v , j , and Ω), and we assume n_c such continua are present. In this case the v_i-3 vibrational channel is the most important one, and there is little error in associating the n_c continua with v_i-3 and the various possible j and Ω values. The two subspaces are coupled by V

$$\langle \Phi_k | H | \Phi_{\beta E} \rangle = \langle \Phi_k | V | \Phi_{\beta E} \rangle = V_{k,\beta E} \quad (\text{A3})$$

The bright state is expanded as $\phi = \sum_k^{n_b} \alpha_k \Phi_k$, and the spectrum is

$$\sigma(E) \propto \sum_{\beta}^{n_c} \left| \sum_k^{n_b} \alpha_k \langle \Phi_k | \Psi_{\beta E} \rangle \right|^2, \quad (\text{A4})$$

where $\Psi_{\beta E}$ are exact solutions of the total Hamiltonian, which can be expressed in terms of the zero-order solutions using the Lippmann–Schwinger equation³² as

$$\Psi_{\beta E} = \Phi_{\beta E} + \sum_k^{n_b} G(E) \Phi_k V_{k,\beta E} \quad (\text{A5})$$

with $G(E)$ being the Green's or resolvent operator.³² Equation (A4) becomes

$$\sigma(E) = \sum_{\beta}^{n_c} \left| \sum_j^{n_b} \sum_k^{n_b} \alpha_j \langle \Phi_j | G(E) | \Phi_k \rangle V_{k,\beta E} \right|^2. \quad (\text{A6})$$

The time evolution of the bright state is

$$\Psi(t) = e^{-iHt/\hbar} \phi = \sum_k \alpha_k e^{-iHt/\hbar} \Phi_k. \quad (\text{A7})$$

The amplitudes

$$g_{kj}(t) = \langle \Phi_k | e^{-iHt/\hbar} | \Phi_j \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} dE e^{-iEt/\hbar} \langle \Phi_k | G(E) | \Phi_j \rangle \quad (\text{A8})$$

are used to construct the relevant time-dependent probabilities. For example, the probability of remaining in the bright state is $|\langle \phi | \Psi(t) \rangle|^2$, and the dissociation probability is $1 - P_P(t)$, where $P_P(t) = \sum_k |\langle \Phi_k | \Psi(t) \rangle|^2$ is the probability of remaining in the discrete subspace. Equations (A6) and (A8) require the resolvent operator matrix elements in the discrete subspace. These matrix elements are obtained from

$$PG(z)P = \frac{1}{P[z - H_0 - R(z)]P}, \quad (\text{A9})$$

where the $R(z)$ is the displacement operator, which has matrix elements

$$\begin{aligned} \langle \Phi_k | R(z) | \Phi_j \rangle &= V_{kj} + \sum_{\beta}^{n_c} \int dE \frac{V_{k,\beta E}^* V_{j,\beta E}}{z - E} \\ &\approx V_{kj} - i\Gamma_{kj}. \end{aligned} \quad (\text{A10})$$

V_{kj} , Eq. (A1), accounts for direct coupling between discrete zero-order states. $\Gamma_{kj} = \pi \sum_{\beta} V_{k,\beta E}^* V_{j,\beta E}$ has two meanings: for $k=j$ it is the halfwidth associated with an isolated state coupled to a manifold of continuum states, while for $k \neq j$ it is an indirect coupling between different zero-order bound states due to their dissociation in the same continuum. The indirect coupling has been discussed in detail previously^{15(b)} and is written as $\Gamma_{kj} = \gamma_{kj}(\Gamma_{kk}\Gamma_{jj})^{1/2}$, where γ_{kj} lies in $[-1, 1]$. Equation (A9) is an n_b by n_b matrix equation of the form $\mathbf{G}(z) = \mathbf{F}(z)^{-1}$, and with Eq. (A10) the matrix $\mathbf{F}$ is

$$\mathbf{F}(z) = \begin{pmatrix} z - E_1 + i\Gamma_{11} & -V_{12} + i\Gamma_{12} & \cdots & -V_{1n_b} + i\Gamma_{1n_b} \\ -V_{21} + i\Gamma_{21} & z - E_2 + i\Gamma_{22} & \cdots & -V_{2n_b} + i\Gamma_{2n_b} \\ \vdots & \vdots & & \vdots \\ -V_{n_b1} + i\Gamma_{n_b1} & -V_{n_b2} + i\Gamma_{n_b2} & \cdots & z - E_n + i\Gamma_{n_b n_b} \end{pmatrix}. \quad (\text{A11})$$

The G_{kj} matrix elements are thus of the form

$$\langle \Phi_k | G(z) | \Phi_j \rangle = \frac{\text{adj}[\mathbf{F}(z)]_{kj}}{\det[\mathbf{F}(z)]}. \quad (\text{A12})$$

$\det(F)$ is a polynomial of degree n_b in z and has n_b complex roots, ω_k , so that Eq. (A8) may be integrated in the complex plane to obtain

$$g_{kj}(t) = \sum_n^{n_b} \frac{\text{adj}[\mathbf{F}(\omega_n)]_{kj}}{\prod_{n' \neq n}^{n_b} (\omega_n - \omega_{n'})} e^{-i\omega_n t/\hbar}. \quad (\text{A13})$$

Introducing Eq. (A12) in Eq. (A6), expressions for the spec-

trum are obtained. While we assume n_c continua, the resulting final expression for the spectrum involves sums over n_c that collapse into the model parameters.

The difficult part is calculation of $\det(F)$, $\text{adj}(F)$ and the ω_n roots. For $n_b \leq 3$ they are obtained analytically; $n_b = 2$ explicit expressions of the spectrum, $\sigma(E)$, and vibrational populations are obtained.^{15(b)} For $n_b > 3$ the required quantities are obtained numerically.

Two discrete representations are considered. In the first one, called the zero-order model, H is factorized as in Eq. (5) and the zero-order bound states are

$$\Phi_k = \chi_v(r) \Phi_{v_n}^J. \quad (\text{A14})$$

The bright state is a particular one with $v = v_i$ and $n = n_i$ so

that the α_i coefficients in Eq. (A4) are all zero except the one corresponding to this state. The parameters needed are the energy positions, E_k , and halfwidths, Γ_{kk} , of the n_b zero-order bound states, plus the $n_b(n_b-1)/2$ coupling terms of the type $-V_{kj} + i\gamma_{kj}(\Gamma_{kk}\Gamma_{jj})^{1/2}$. We first determine an approximate idea of the parameters by fitting only the spectrum. We then vary the parameters to simultaneously describe both the spectrum and relevant time-dependent vibrational probabilities. The resulting parameters are by no means unique, and adding more parameters can improve the quality of the fits. However, our main point is to show that just a few states (and thus parameters) serve to semiquantitatively reproduce both the spectra and time-dependent probabilities. A problem is that the fits are very sensitive to the couplings V_{kj} . As the number of participating discrete states becomes larger than three, the increase in the number of V_{kj} parameters makes the fitting procedure numerically difficult. It is thus convenient to consider a second representation, the first-order model, in which V is diagonal in the discrete subspace. Instead of Eq. (A14), one employs discrete states

$$\Phi_k = \sum_{vn} \alpha_{k,vn} \chi_v \Phi_{vn}^J, \quad (\text{A15})$$

which are assumed to be such that $V_{kj}=0$ for $k \neq j$. The initial state ϕ is then a linear superposition of the first-order states, with $\alpha_k \equiv \alpha_{k,v=v_i, n=n_i}$. The parameters to be adjusted are less sensitive and instead of fitting the $n_b(n_b-1)/2 V_{kj}$ coupling terms only $n_b \alpha_k$ coefficients are needed. While the reduction of parameters facilitates the fitting procedure, only the the bright state and dissociation probabilities can then be obtained.

- ¹J. A. Blazy, B. M. DeKoven, T. D. Russell, and D. H. Levy, *J. Chem. Phys.* **72**, 2439 (1980); K. E. Johnson, W. Sharfin and D. H. Levy, *ibid.* **74**, 163 (1981); D. H. Levy, *Adv. Chem. Phys.* **47**, 323 (1981).
- ²N. Goldstein, T. L. Brack, and G. H. Atkinson, *J. Chem. Phys.* **85**, 2684 (1986).
- ³J. J. Breen, D. M. Willberg, M. Gutmann, and A. H. Zewail, *J. Chem. Phys.* **93**, 9180 (1990).
- ⁴(a) M. L. Burke and W. Klemperer, *J. Chem. Phys.* **98**, 1797 (1993); (b) M. L. Burke and W. Klemperer, *J. Chem. Phys.* **98**, 6642 (1993).
- ⁵Q. Liu, J. K. Wang, and A. H. Zewail, *Nature*, **364**, 427 (1993).
- ⁶Y. Yan, R. M. Whitnell, K. R. Wilson, and A. H. Zewail, *Chem. Phys. Lett.* **193**, 402 (1992).

- ⁷N. F. Scherer, D. M. Jonas, and G. R. Fleming, *J. Chem. Phys.* **99**, 153 (1993).
- ⁸R. Zadoyan, Z. Li, P. Ashjian, C. C. Martens, and V. A. Apkarian, *Chem. Phys. Lett.* **218**, 504 (1994).
- ⁹O. Roncero, N. Halberstadt, and J. A. Beswick, *Chem. Phys. Lett.* **226**, 82 (1994).
- ¹⁰J. A. Beswick and J. Jortner, *Adv. Chem. Phys.* **47**, 363 (1981).
- ¹¹G. E. Ewing, *J. Chem. Phys.* **71**, 3143 (1979).
- ¹²M. Bixon and J. Jortner, *J. Chem. Phys.* **48**, 715 (1968).
- ¹³K. F. Freed and A. Nitzan, *J. Chem. Phys.* **73**, 4765 (1980).
- ¹⁴O. Roncero, J. Campos-Martínez, A. M. Cortina, P. Villarreal, and G. Delgado-Barrio, *Chem. Phys. Lett.* **148**, 62 (1988).
- ¹⁵(a) N. Halberstadt, S. Serna, O. Roncero, and K. C. Janda, *J. Chem. Phys.* **97**, 341 (1992); (b) O. Roncero, P. Villarreal, G. Delgado-Barrio, N. Halberstadt, and K. C. Janda, *ibid.* **99**, 1035 (1993).
- ¹⁶S. K. Gray, *Chem. Phys. Lett.* **197**, 86 (1992).
- ¹⁷S. K. Gray and O. Roncero, *J. Phys. Chem.* **99**, 2512 (1995).
- ¹⁸N. Halberstadt, J. A. Beswick, and K. C. Janda, *J. Chem. Phys.* **87**, 3966 (1987).
- ¹⁹R. T. Pack and J. O. Hirschfelder, *J. Chem. Phys.* **49**, 4009 (1968); R. T. Pack, *ibid.* **60**, 633 (1974); G. C. Schatz and A. Kuppermann, *ibid.* **65**, 4642 (1976); G. G. Balint-Kurti and M. Shapiro, *Chem. Phys.* **61**, 137 (1981).
- ²⁰R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
- ²¹E. J. Heller, *J. Chem. Phys.* **68**, 2066 (1978); E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981); G. G. Balint-Kurti R. N. Dixon, and C. C. Marsten, *J. Chem. Soc. Faraday Trans.* **86**, 1741 (1990).
- ²²B. P. Reid, K. C. Janda, and N. Halberstadt, *J. Phys. Chem.* **92**, 587 (1988).
- ²³L. Fox, *The Numerical Solution of Two-Point Boundary Value Problems in Ordinary Differential Equations* (Oxford U.P., London, 1957); J. W. Cooley, *Math. Comput.* **15**, 363 (1961); L. L. Barnes, N. F. Lane, and C. C. Lin, *Phys. Rev. A* **137**, 388 (1965).
- ²⁴T. J. Park and J. C. Light, *J. Chem. Phys.* **85**, 5870 (1986); C. Leforestier, R. H. Bisseling, C. Cerjan, M. D. Feit, R. Friesner, A. Guldberg, A. Hammerich, G. Jolicard, W. Karrlein, H.-D. Meyer, N. Lipkin, O. Roncero, and R. Kosloff, *J. Comp. Phys.* **94**, 59 (1991).
- ²⁵S. K. Gray, *J. Chem. Phys.* **96**, 6543 (1992).
- ²⁶E. M. Goldfield, O. Roncero, and S. K. Gray (unpublished).
- ²⁷S. S. Huang, C. R. Bieler, K. C. Janda, F.-M. Tao, W. Klemperer, P. Casavecchia, G. G. Volpi, and N. Halberstadt, *J. Chem. Phys.* **102**, 8846 (1995).
- ²⁸U. Peskin, H. Reisler, and W. H. Miller, *J. Chem. Phys.* **101**, 9672 (1994).
- ²⁹See the Appendix by W. H. Miller in T. Uzer, *Phys. Rep.* **199**, 74 (1991).
- ³⁰L. Mower, *Phys. Rev.* **142**, 799 (1966).
- ³¹J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.* **7**, 149 (1969).
- ³²M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).