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Wave Packet Studies of the Vibrational Predissociation of Three and Four-Atom Van der Waals Complexes

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Abstract

Vibrational predissociation of XI_2 and X_2I_2 van der Waals complexes, with $X = \text{He}$ and Ne , is studied with wave packets. Three-dimensional calculations are carried out on the three-atom systems. Suitable $X \cdots I$ potential interactions are determined, and product distributions are predicted. Reduced dimension models of $X_2I_2(v') \rightarrow 2X + I_2(v < v')$ are investigated. Comparison is made with available experimental results. Mechanistic issues, including the role of intramolecular vibrational relaxation resonances, are addressed.

1. Introduction

The experiments Levy and co-workers,^{1,2} and theoretical work of Beswick and Jortner³ established van der Waals (vdW) vibrational predissociation as a fascinating dynamical phenomenon. While atypical of chemical reactions because of the small bonding energies involved, basic energy transfer processes can often be understood in detail. Three and four-atom systems are particularly interesting, since unlike larger complexes, there is the possibility of building accurate theoretical models. This paper discusses

with $n = 1, 2$, and $X = \text{He}, \text{Ne}$, which were among the first rare gas/halogen systems studied.^{1,2} Real-time experiments on these systems have recently been performed by Gutmann, Willberg, and Zewail,^{4,5} which complement and improve upon the earlier results.

Despite its place as one of the best known vdW complexes, quantum dynamics work on HeI_2 has been limited to reduced dimension studies,^{2,6} and approximate three-dimensional quantum scattering work.⁷ Classical trajectory calculations on X_2I_2 and much larger clusters have been performed,⁸ but quantum work on such systems has been limited to certain, Golden Rule and perturbative treatments.⁹

$X_n\text{Cl}_2$ systems have been studied experimentally and theoretically by Janda, Halberstadt, and co-workers,^{10,11} and XICl systems have been studied by Lester and co-workers.¹² Three-dimensional wave packet studies on XCl_2 and XICl were performed by Gray and Wozny,¹³ and reduced dimension models of the $X_2\text{Cl}_2$ systems were studied by Le Quéré and Gray.¹⁴ These calculations show how a time-dependent quantum picture provides insights into vibrational predissociation. This paper applies such methods and ideas to the corresponding iodine systems. Mechanistic issues, including the role of intramolecular vibrational relaxation (IVR) intermediates, are also addressed.

2. Theoretical and Computational Details

2.1. Three-atom Wave Packet Calculations

The Schrödinger equation for XI_2 (total angular momentum $J = 0$) is

$$i\hbar \frac{\partial}{\partial t} \psi(R, r, \gamma, t) = \hat{H} \psi(R, r, \gamma, t). \quad (2)$$

R is the distance from X to the I_2 center, r is the I_2 internuclear distance, and γ is the angle between X , the I_2 center, and one I atom. The Hamiltonian is¹³

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2} \left(\frac{1}{\mu R^2} + \frac{1}{mr^2} \right) + V_{\text{II}}(r) + W(R, r, \gamma), \quad (3)$$

where $\mu = 2m_X m_I / (m_X + 2m_I)$, $m = m_I / 2$, and $\hat{j}^2$ is a differential operator in γ . V_{II} is the isolated I_2 potential function, and W is the interaction potential. The potential is taken to be a sum of Morse atom-atom potentials, $V_{AB}(R_{AB}) = D_{AB} [Z^2 - 2Z]$, $Z = \exp[-\alpha_{AB}(R_{AB} - \bar{R}_{AB})]$. Thus, $W = V_{\text{XI}}(R_{X1}) + V_{\text{XI}}(R_{X2})$, with R_{Xk} being the distance of X to the k 'th I atom. This empirical form works reasonably well in the corresponding Cl_2 systems.¹⁰ Table 1 lists potential parameters. (See also Sec. 3.)

The wave packet is written¹³

$$\psi(R, r, \gamma, t) = \sum_{v,j} C_{v,j}(R, t) \chi_v(r) \phi_j(\gamma), \quad (4)$$

where $\chi_v(r)$ are Morse eigenfunctions¹⁷ for V_{II} , and $\phi_j(\gamma)$ are eigenfunctions of $\hat{j}^2$ with eigenvalues $j(j+1)\hbar^2$, $j = 0, 1, 2, \dots$. For I_2 , the $j = \text{even}$ and $j = \text{odd}$ states are uncoupled, and the case $j = \text{even}$ will be studied. Eqn. (2) leads to a set of coupled equations for the $C_{v,j}(R, t)$:¹³

$$i\hbar \frac{d}{dt} \mathbf{C}(R, t) = \mathbf{H} \cdot \mathbf{C}(R, t). \quad (5)$$

The solution is $\mathbf{C}(R, t + \tau) = \exp(-i\mathbf{H}\tau/\hbar) \cdot \mathbf{C}(R, t)$, and a short iterative Lanczos method^{18,19} is used to evaluate the exponential operator's effect over each time step τ . R

is represented on a discrete grid, i.e., $R_k = R_0 + (k-1)\Delta R$, $k = 1, 2, \dots, N_R$. Fast Fourier transforms²⁰ are used to evaluate the $-d^2/dR^2$ terms in (2). Dissociative wave packet amplitude, corresponding to $X + I_2$, is removed periodically by multiplying $C(R, t)$ by $\exp[-C_a(R-R_a)^2]$ for $R > R_a$, for some suitably large R_a value. (See refs. 13-15 for additional details.)

The initial condition $C(R, t=0)$ is a metastable state approximating the quasibound part of a vdW resonance.¹³ Low level stabilization calculations provide reasonable metastable state estimates.²¹ This corresponds to diagonalizing the vibrationally adiabatic effective Hamiltonian $\hat{H}_{\text{eff}}(v') = \langle v' | \hat{H} | v' \rangle$ in a basis set of $F_n(R)\phi_j(\gamma)$ functions, where $F_n(R)$ denotes zero-order vdW stretch functions.¹³ For given v' , the state of interest is the ground vdW stretch and bend state, i.e., the lowest energy state of $\hat{H}_{\text{eff}}(v')$. It then suffices to carry out small diagonalizations of, e.g., 100×100 matrices.

Energy resolved $I_2(v, j)$ product distributions are obtained with the method of Balint-Kurti, Dixon, and Marston.²² This involves carrying out a time Fourier transform (at some energy E of interest) of the various $C_{v,j}(R^*, t)$ coefficients, where R^* is some suitably large value. In principle, resonance energies and decay widths are obtained by Fourier transforming the wave packet autocorrelation function $\langle \psi(0) | \psi(t) \rangle$ at a series of energies, and constructing a spectrum. Peaks in the spectrum correspond to the resonance energies, and the full widths at half maximum are the decay constants. It is more efficient to use Prony's method,²³ which has also been shown to work well for determining resonances in HCO.²⁴ This approach yields accurate estimates of resonance parameters using relatively short time propagations, i.e., propagations such that there is still appreciable wave packet amplitude in the interaction region. It uses the fact that the correlation function, if dominated by one or a few resonances, is simply a sum of a few complex exponential terms $\exp(-i E_s t / \hbar) \exp(-\Gamma_s t / 2 \hbar)$, where E_s is a resonance energy and Γ_s is the decay constant (lifetime = $\hbar / \Gamma_s$). It is a special kind of least squares fit of the correlation function data over a given time period to such a model. (The identity,²⁵

$\langle \psi(0) | \psi(2t) \rangle = \langle \psi^*(t) | \psi(t) \rangle$ can be used to extend the correlation function data to $2t$ if one has propagated a wave packet to time t .)

The grid for HeI_2 is given by $R_0 = 3$ a.u., $\Delta R = 0.25$ a.u., $N_R = 128$. Three vibrational states, $v = v', v'-1$, and $v'-2$, and 25 rotational states, $j = 0, 2, 4, \dots, 48$ are used in eqn. (4). For NeI_2 , $R_0 = 4$ a.u., $\Delta R = 0.2$ a.u., $N_R = 128$, three vibrational states, $v = v', v'-1$, and $v'-2$, and 30 rotational states, $j = 0, 2, 4, \dots, 58$ are used. Propagations are carried out to times between 6 and 10 ps, which is more than sufficient for converging the desired observable quantities using the methods discussed here. [A typical metastable state propagation, on a moderate (≈ 15 megaflop) workstation requires ≈ 1.5 hrs CPU time.]

2.2. Four-Atom Wave Packet Calculations

Quantum dynamics studies of four-atom vdW and hydrogen bonded systems, e.g., H_2HF ,²⁶ and $(\text{HF})_2$,²⁷ are emerging that include all or almost all degrees of freedom. Such studies are facilitated by the presence of two or more light atoms, *and* by the fact that relatively simple fragmentation occurs. X_2I_2 fragmentation is not as easily treated, not only because of the heavier masses involved, but because the sequential process $\text{X}_2\text{I}_2(v') \rightarrow \text{X} + \text{XI}_2(v'' < v') \rightarrow 2\text{X} + \text{I}_2(v < v'')$ is important. This is similar to the "double continuum" problem,^{9a} in collision induced dissociation.²⁸ Both $\text{X} + \text{XI}_2$ and $2\text{X} + \text{I}_2$ continua, and decay from $\text{X} + \text{XI}_2$ to $2\text{X} + \text{I}_2$, must be included.

Le Quéré and Gray's¹⁴ model, used to study X_2Cl_2 , is a reduced dimension model involving R_1 and R_2 , the distances of each X atom to the center of I_2 , and r , the I_2 internuclear distance. The X atoms are in a plane perpendicular to and bisecting I_2 , and execute stretching vibrations against I_2 but do not bend. The equilibrium geometry of X_2I_2 is most likely a distorted tetrahedron, and is one configuration of this model. The angle θ between one X, the I_2 center, and the other X is assumed to be constant at 50° , which is close to the potential minimum in both $\text{X} = \text{He}$ and Ne . While a gross simplification, the

model has several merits, including the fact that both sequential and direct fragmentation processes (simultaneous departure of both X atoms) are included. The Hamiltonian is

$$\hat{H} = \frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_1^2} + \frac{\partial^2}{\partial R_2^2} \right) - \frac{\hbar^2 \cos \theta}{2m_I} \frac{\partial^2}{\partial R_1 \partial R_2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V_{II}(r) + W(R_1, R_2, r; \theta), \quad (6)$$

where μ and m are the same as in Sec. 2.1. The Schrödinger equation is similar to (2), but

$$\psi(R_1, R_2, r, t) = \sum_v C_v(R_1, R_2, t) \chi_v(r) \quad (7)$$

The calculations tend to be more difficult than those of Sec. 2.1. Therefore an embellishment of the Lanczos method, that reduces computational effort by two, is employed to solve the Schrödinger equation.^{24a} Wave packet amplitude is periodically removed from the edges of the (two-dimensional) grid in a manner analogous to Sec. 2.1. Because vibrational products with $v = v'-2$ and $v'-3$ can be important in these systems, four vibrational states, $v = v', v'-1, v'-1, v'-3$, are used. The R_1 and R_2 grids consist of 128 grid points each, with spacings and ranges identical to those described in Sec. 2.1. Propagation times for the He_2I_2 calculations are comparable to the three-atom runs. The Ne_2I_2 calculations require longer times ranging from 15 ps to as much as 30 ps in order to properly converge the quantities of interest. [The calculations can require up to ≈ 5 -10 times more computational effort than the three-atom calculations of Sec. 2.1.]

Resonance energies and lifetimes are inferred by analyzing correlation functions, as outlined in Sec. 2.1. Product distributions are trickier to estimate. Imagine the R_1, R_2 grid broken down into three regions: an interaction region I that corresponds to X_2I_2 metastable complexes, two symmetry related $\text{X} + \text{XI}_2$ regions C ($R_1 = \text{large}, R_2 = \text{small}$, and vice versa), and a $2\text{X} + \text{I}_2$ product region P (R_1 and R_2 large). For convenience, region I can be the rectangle $R_0 \leq R_1, R_2 \leq R_a$, with regions C and P representing the outer parts of the grid where absorption occurs. (See Fig. 1 of ref. 14.) A wave packet is

initiated in I, and portions of it eventually move out into regions C and P. Absorption removes exiting wave packet in regions C and P. Amplitude that reaches C, if allowed to move on in time and space, will eventually decay into some appropriately extended form of region P, because the triatomic complexes are not stable. The portion of this amplitude also associated $XI_2(v'')$ quasibound complexes will decay into various possible $X + I_2(v)$ states, with the first open vibrational predissociation channel (usually $v=v''-1$) being dominant. The probability of forming $I_2(v)$ is given by the total amount of probability that is absorbed in region P *plus* the corresponding amounts absorbed in region C that *would* decay to v if allowed to move on. Further technical details are in ref. 14.

3. Three-Atom Results

In both HeI_2 and NeI_2 , the $X \cdots I$ Morse parameters D_{XI} and α_{XI} are taken to be adjustable parameters, and wave packet calculations are performed to obtain optimal values. $\bar{R}_{XI}$ in both cases is held fixed at $4 \text{ \AA}$ (7.5589 a.u.). This is consistent with expectations based on corresponding (experimentally deduced) values for the XCl_2 systems¹⁰ when the larger iodine atomic radius is taken into account. However, rotational spectra^{1b} for HeI_2 are consistent with an $\bar{R}_{XI}$ value that is 20% larger. However, the dissociation dynamics is not extremely sensitive to $\bar{R}_{XI}$.

A set of possible D_{XI} and α_{XI} values is determined by considering only those D_{XI} and α_{XI} values that lead to a vdW bond energy D_0 consistent with experimental estimates of Blazy *et al.*^{1d} D_0 , if an energy scale such that $X + I_2(v')$ has zero energy is employed, is the negative of the lowest metastable state energy determined as described in Sec. 2.1. There is only a slight dependence of D_0 on the vibrational state v' ; the calculations correspond to $v' = 20$. Fig. 1 displays $D_{HeI}(\alpha_{HeI})$ such that $D_0 \approx 14 \text{ cm}^{-1}$, consistent with the experimental D_0 .^{1d} (A range of $13.6 - 14.8 \text{ cm}^{-1}$ was reported.^{1d}) $D_{HeI}(\alpha_{HeI})$ appears linear over the relevant range. $D_{NeI}(\alpha_{NeI})$ such that $D_0 \approx 66 \text{ cm}^{-1}$, the corresponding experimental mean value,^{1d} is similar, and need not be displayed. Wave

packet calculations were carried out for a variety of parameter choices from the curves, and parameters leading to decay constants $\Gamma(v')$ in reasonable accord with available experimental data were selected. These values (Table 1) are different from those used in previous model studies. For example, the typical choices^{2,6,7} $D_{\text{HeI}} = 18 \text{ cm}^{-1}$, and $\alpha_{\text{HeI}} = 0.6033 \text{ a.u.}$ are different by 15-20 %, and also yield a bond energy of $\approx 20 \text{ cm}^{-1}$, 35 % larger than experiment.

Figs. 2 and 3 display $\Gamma(v')$ for HeI_2 and NeI_2 determined as outlined above. Fig. 2 results from fitting the HeI_2 spectroscopic results of Johnson, Wharton, and Levy,^{1c} and Fig. 3 is a fit to NeI_2 real-time results of Gutmann, Willberg, and Zewail.⁴ Gutmann *et al.* also looked at HeI_2 , and determined smaller $\Gamma(v')$ values by $\approx 20\text{-}25 \%$, which are probably better estimates. These results are consistent with some inhomogeneous broadening in the spectral linewidths. Table 1 lists, in parentheses, the slightly smaller D_{HeI} and α_{HeI} values that result if the real-time experiments are fit. The He_2I_2 results discussed below were calculated with the spectroscopic based potential values.

Since $E_{v'} - E_{v'-1} > D_0$ in all cases, the dominant vibrational product by more than 90% is always $v = v'-1$. For given final v state, the corresponding I_2 rotational distributions are simple. Typical rotational distributions are depicted in Fig. 4. Zhang and Zhang,^{7c} using the approximate but reasonable time-dependent Golden Rule method, and a different potential parameterization, also inferred a similar distribution for HeI_2 . (Their calculated decay constants, however, showed quantitative differences with experiment.) No bi-modal rotational distributions are ever observed, in contrast to the Cl_2 cases¹⁰ where, especially for HeCl_2 , secondary maxima occurred in the higher j limit. As shown in ref. 13b, the likelihood of a bi-modal distribution depends on the form of the wave packet after a relatively short time period. This short time form, in turn, depends on the product of the initial metastable state density and the potential coupling in the small R region. In order to achieve a bi-modal distribution, the short time wave packet density, in the $v = v'-1$ channel, must exhibit two lobes in the interaction region: a primary lobe

associated with X motion in a T-shaped configuration, and a secondary lobe associated with X motion to one side of the I₂ molecule. The secondary lobe leads to a high j tail, and the potential for bi-modality. Analysis of the wave packets does show the existence of secondary lobes, but they are not as intense as the Cl₂ cases, and simply contribute to the high j tails evident in Fig. 3. No experimental I₂ rotational distributions are available.

4. Four-Atom Results

4.1. He₂I₂

Calculations were performed for initial metastable complexes He₂I₂(v') with $12 \leq v' \leq 20$. $\Gamma(v')$ increases with v' in an almost linear fashion, with $\Gamma(v'=12) = 0.13 \text{ cm}^{-1}$, and $\Gamma(v'=20) = 0.34 \text{ cm}^{-1}$, i.e., lifetimes between 41 ps and 16 ps. There are no experimental lifetime results for comparison. Levy and co-workers^{3a} did estimate vibrational product distributions for v' = 20. From ref. 3a one infers $P_{v=v'-1} = 0.02$, $P_{v=v'-2} = 0.94$, and $P_{v=v'-3} = 0.04$. The theoretical product distribution is $P_{v=v'-1} = 0.01$, $P_{v=v'-2} = 0.92$, and $P_{v=v'-3} = 0.07$, in reasonable accord. Experimental errors are probably on the order of ± 0.01 , so that the main conclusion is that both theory and experiment yield the v'-2 product channel as dominant. Similar theoretical product distributions are observed for all the other metastable complexes.

The results are consistent with a sequential fragmentation mechanism, i.e., $\text{He}_2\text{I}_2(v') \rightarrow \text{He} + \text{HeI}_2(v'-1) \rightarrow 2\text{He} + \text{I}_2(v'-2)$, being dominant throughout the $12 \leq v' \leq 20$ range. Note that the vdW bond energy of He₂I₂(v') is $\approx 42 \text{ cm}^{-1}$, and the energy available from a $v' \rightarrow v'-1$ transition is $\approx 100 \text{ cm}^{-1}$, i.e., there is sufficient energy for both He atoms to fly off if I₂ loses just one quantum. However, the He...He interaction energy (Table 1) is small, so there is little energy exchange between He atoms. This sequential mechanism is evident when the wave packet is pictured. Fig. 5 displays the reduced probability density $|C_{v'-1}(R_1, R_2, t)|^2$ at $t \approx 5 \text{ ps}$ from the $v' = 20$ propagation. Simultaneous departure of the two He atoms would correspond to density emanating from

the interaction region along the $R_1 = R_2$ line. This does not occur. Instead, density tends to the $R_1 = \text{small}$, $R_2 = \text{large}$, and vice versa channels, i.e., channels corresponding to $\text{He} + \text{HeI}_2$. As emphasized in Sec. 2.2, this density, if allowed to continue further in time and space, eventually decays into the $2\text{He} + \text{I}_2(v'-2)$ region. Density associated with $v = v'$ (not shown) remains similar in form to the initial condition, i.e., a two-dimensional Gaussian centered on the equilibrium geometry, and exhibits gradual decay in intensity with time. Similar behaviour occurs in He_2Cl_2 .^{11,14} Despite the inherent floppiness of such systems, the weak $\text{He}\cdots\text{He}$ interaction results in a sequential fragmentation with no appreciable correlations between departures of the two He atoms. This is further confirmed by carrying out reduced dimension T-shaped HeI_2 wave packet calculations, and inferring the corresponding decay constants. (Methods as described in Sec. 2.1 are used, except γ is held fixed at 90° .) For $v' = 12$ and 20 , the T-shaped three-atom decay constants are 0.056 and 0.15 cm^{-1} , respectively, i.e., the four-atom decay constants are $\approx$ twice the three-atom results, as would be expected.^{11,14}

The T-shaped HeI_2 decay constants are about twice as big as the three dimensional HeI_2 results (Fig. 2). Thus, the reduced dimension four-atom decay constants may also be too big by ≈ 2 .

4.2. Ne_2I_2

Calculations were performed for complexes with $12 \leq v' \leq 20$. Consider the lower v' region $12 \leq v' \leq 14$. As with He_2I_2 , a simple sequential fragmentation mechanism is operative and $\geq 90\%$ of I_2 products are $v = v'-2$. Plots of the wave packet density are similar to Fig. 5, although more structure is evident in the $\text{Ne} + \text{NeI}_2$ channels. It is less surprising that a sequential mechanism is operative since the vdW bond energy is $\approx 170 \text{ cm}^{-1}$, and thus the $\approx 100 \text{ cm}^{-1}$ of available energy from a $v' \rightarrow v'-1$ I_2 transition is insufficient to break both vdW bonds. No experimental data on the product distributions in this regime are available. As with He_2I_2 , a single resonance dominates the wave packet

dynamics. The corresponding decay constants increase monotonically with v' : for $v' = 12, 13$, and 14 one has $\Gamma = 0.05, 0.07$, and 0.09 cm^{-1} , respectively. These decay constants are expected to be too big by a factor of two in comparison with experiment. (As with the He systems, T-shaped NeI_2 calculations resulted in decay constants that were twice as large as full dimensional NeI_2 results, and twice as small as the reduced dimension four-atom results.) An experimental lifetime for $v' = 12$ of $99 \pm 33 \text{ ps}$ was reported in ref. 2b, corresponding to Γ between 0.04 and 0.08 cm^{-1} . $\Gamma \approx 0.025 \text{ cm}^{-1}$ would have been expected on the basis of the present results. It is possible that inhomogeneous broadening effects are complicating the experimental result. A smaller experimental $\Gamma(v'=12)$ is suggested by real-time experiments on $\text{Ne}_2\text{I}_2(v')$ ^{5c} in the $17 \leq v' \leq 23$ range. The real-time effective decay constant for $v' = 17$ is 0.025 cm^{-1} , suggesting that the $v' = 12$ result, if measured, will be smaller than that implied by the present study. More experimental information in the smaller v' regime is needed.

The $15 \leq v' \leq 20$ regime is interesting because the model yields non-monotonic variation in the dominant resonance $\Gamma(v')$. The correlation functions also show significant (anywhere from 2 to 20%) contributions from a secondary resonance that is $1 - 3 \text{ cm}^{-1}$ away from the main resonance and decays one or two orders of magnitude faster. For $v' = 17, \dots, 20$, one finds dominant resonance decay widths $\Gamma = 0.003, 0.07, 0.03$, and 0.01 cm^{-1} . This is at odds with the real-time experiments of Gutmann *et al.*⁵ which over the $v' = 17, \dots, 20$ range, led to effective decay constants increasing monotonically between 0.025 and 0.047 cm^{-1} (when the $v'-2$ product channel is monitored). Of course, as also implied by the discussion and analysis of Gutmann *et al.*, these real-time experiments are probably not sampling the dynamics of an isolated resonance, particularly in the higher v' regime. The theoretical secondary resonance decay constants do increase monotonically with v' (from 0.3 to 0.45 cm^{-1} over the $17 \leq v' \leq 20$ range), so it is conceivable that appropriate superpositions of primary and secondary resonances might yield dynamics consistent with experiment. It is also possible that the discrepancies here are due to certain limitations in

the theoretical model. Increased dimensionality models will yield more closely spaced resonances that may overlap. There is also a mechanism change when one goes into this higher vibrational excitation regime in that the $v'-3$ product channel becomes significant. With the exception of the $v' = 15$ calculation where $v'-3$ products are just starting to become important (10%), they account for $\approx 70\%$ of the I_2 products for the $v' > 15$ cases, with the $v = v'-2$ product channel taking on the major remaining probability. This latter result is qualitatively in accord with the experiments of Levy and co-workers,^{2b} wherein for $v' \approx 20$ about 40% of the products were in $v'-3$, i.e., a result counter to the simplest sequential mechanism that would suggest much greater dominance of the $v'-2$ channel.

Inspection of the wave packet density shows that a configurational sequential mechanism $Ne_2I_2 \rightarrow Ne + NeI_2 \rightarrow 2Ne + I_2$ *still* occurs, but most density entering the $Ne + NeI_2$ channels corresponds to triatomic complexes with $v = v'-2$, which is inconsistent with the simplest sequential mechanism. Assuming additivity of bond energies, the first step, the departure of one Ne atom, requires not only that one $Ne \cdots I_2$ vdW bond energy be overcome, but that the $Ne \cdots Ne$ bond be broken as well. Table 1 shows that the $Ne \cdots Ne$ binding energy is $\approx 30 \text{ cm}^{-1}$. (In the He calculations, this energy is much smaller and less relevant.) The NeI_2 bonding energy is $\approx 70 \text{ cm}^{-1}$. Thus, for the first step of the sequential process to occur, $\approx 100 \text{ cm}^{-1}$ must be supplied. The $v' \rightarrow v'-1$ transition energy in I_2 decreases with v' , and is $< 100 \text{ cm}^{-1}$ for $v' \geq 15$, where a two quantum change in I_2 is then necessary to overcome the combined NeI_2 and $Ne \cdots Ne$ bonding energies. An appropriate sequential mechanism is: $Ne_2I_2(v') \rightarrow Ne + NeI_2(v'-2) \rightarrow 2Ne + I_2(v'-3)$. The first step, however, is not a direct two-quantum transition, but involves IVR intermediates, which have also been shown to lead to non-monotonic variations in decay constants.^{15,29} Such a mechanism was, in fact, suggested by Gutmann *et al.* to explain their experimental results.⁵ Because a single quantum $v' \rightarrow v'-1$ transition cannot remove a single Ne atom, due to the presence of the other Ne atom, it is possible for zero-order vdW metastable states associated with $Ne_2I_2(v'-1)$ to play intermediate roles: $Ne_2I_2(v')$

$\rightarrow \text{Ne}_2\text{I}_2(v'-1) \rightarrow \text{Ne} + \text{NeI}_2(v'-2)$. The relevant $\text{Ne}_2\text{I}_2(v'-1)$ states must involve appreciable amounts of Ne stretching excitations. The fact that the correlation function analysis of the wave packets, in the higher v' regime, yields two resonances, one slow decaying and the other fast decaying, is consistent with this type of mechanism, which has been worked out in detail (for a triatomic case) by Halberstadt and co-workers.²⁹ The two resonances present in the correlation function analysis may be approximated as $|1\rangle \approx a |n_1=n_2=0\rangle|v'\rangle + b |n_1,n_2>0\rangle|v'-1\rangle$ and $|2\rangle \approx b |n_1=n_2=0\rangle|v'\rangle - a |n_1,n_2>0\rangle|v'-1\rangle$, where $|a| > |b|$, and n_1, n_2 represent stretching quantum numbers associated with R_1 and R_2 . The initial condition is a pure $|n_1=n_2=0\rangle|v'\rangle$ state, and so one would expect contributions to the wave packet from both $|1\rangle$ and $|2\rangle$. An idea of the resonance wavefunction forms is obtained by carrying out time Fourier transforms of the wave packet at the specific resonance energies: $\psi_s = \int dt \exp(iE_s t) \psi(t)$. For the $v' = 17$ metastable state propagation, for example, the major resonance is indeed dominated (95%) by $|n_1=n_2=0\rangle|v'\rangle$, and plots of this resonance are consistent with zero-point motion in the vdW stretches. The secondary resonance is dominated (90%) by the $v = v'-1$ channel, and inspection of the corresponding density reveals nodal structures consistent with significant Ne stretching excitations. It is a little difficult to identify unambiguous n_1 and n_2 zero-order quantum numbers for the secondary resonance, but it is consistent with a (symmetric) superposition of local mode type excitations³⁰ in the $\text{Ne} + \text{NeI}_2$ channels, $|n_1 \approx 4, n_2 = 0\rangle + |n_1 = 0, n_2 \approx 4\rangle$, i.e., classically the secondary resonance corresponds to an $\text{Ne} \cdots \text{NeI}_2$ type excitation with one Ne being significantly extended in relation to the other.

5. Concluding Remarks

A variety of full dimensional three-atom, and reduced dimensional four-atom wave packet calculations on X_nI_2 vibrational predissociation have been discussed.

The three-atom calculations of Sec. 3 allowed determination of suitable vdW Morse interactions. It was possible to determine potential parameters such that both the vdW bond energies and the observed variation in decay constants over a wide range of v' excitations could be reproduced. The theoretical rotational product distributions did not exhibit any bi-modal features, as observed in the corresponding Cl_2 and ICl systems.^{10,12,14} Of course, a sum of Morse atom-atom interactions, while plausible, is a restrictive form. Ideally, one should fit a more general potential to detailed spectroscopic data (e.g., rotational spectra), and one would wish to include more correct long-range interactions.³¹

All the reduced dimension $He_2I_2(v')$ calculations, and the $v' < 15$ $Ne_2I_2(v')$ calculations in Sec. 4 were dominated by a simple sequential mechanism of the sort $X_2I_2(v') \rightarrow X + XI_2(v'-1) \rightarrow 2X + I_2(v'-2)$. It is expected that the calculated theoretical decay constants should be twice as big as experimental or full dimensional theoretical results. For $v' \geq 15$, a more complex mechanism begins in the Ne_2I_2 model results, described by a sequential type breakup of the form $Ne_2I_2(v') \rightarrow Ne + NeI_2(v'-2) \rightarrow 2Ne + I_2(v'-3)$, but where the first step itself involves IVR resonances similar in spirit to those seen in $ArCl_2$ and ArI_2 .^{15,29} The present calculations did not include $Ne \cdots Ne$ stretching motion explicitly, and if included the corresponding zero-point energy would effectively decrease the $Ne \cdots Ne$ bonding energy. This in turn, according to the arguments of the last paragraph of Sec. 4.2, would increase the v' value where the complex sequential mechanism sets in to roughly the $v' \approx 20$ region. Thus, experimental product distributions for a wide range of v' , would be very helpful in both elucidating the nature of such resonances, and in refining the theoretical models. It would also be interesting to see if such behaviour can occur in Ne_2Cl_2 . The experiments of Janda and co-workers^{11b}

focused on $v' \leq 13$, but similar arguments to those above for Ne_2I_2 suggest tht $v' \geq 16$ would be the regime for the IVR onset in Ne_2Cl_2 . Higher dimension model studies are also called for. Unfortunately, the heavy masses and complex reaction mechanisms make this a very challenging task.

To conclude, wave packet calculations can provide both quantitative and qualitative insights into the vibrational predissociation of vdW complexes. Such insights can be achieved only through careful consideration of available experimental data. However, the theoretical work involves more than fitting this data. Analysis of the wave packet allows mechanistic features to be deduced, and suggests additional experiments to verify and explore such issues.

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Table 1 Morse potential parameters used in the wave packet studies.

AB	D_{AB} / cm^{-1}	$\alpha_{AB} / \text{a.u.}$	$\bar{R}_{AB} / \text{a.u.}$
I_2 (a)	4600.2	0.9583	5.6955
HeI (b)	15.4 (15.0)	0.695 (0.665)	7.5589
$\text{NeI}^{(c)}$	42.5	0.81	7.5589
$\text{HeHe}^{(d)}$	7.61	1.125	5.5993
$\text{NeNe}^{(e)}$	29.36	1.1049	5.8412

(a) Inferred¹⁵ by fitting a Morse oscillator to RKR data.¹⁶

(b) Fit to experimental results of Johnson, Wharton and Levy.^{1c} Values in parentheses result when the real-time experiments⁴ are fit.

(c) Determined by fitting wave packet results to the real-time results of Gutmann, Willberg, and Zewail.⁴

(d) Ref. 8(a).

(e) Ref. 8(b).

Figure Captions

Fig. 1 Morse parameters D_{HeI} and α_{HeI} such that the calculated vdW bond energy for HeI_2 is $D_0 \approx 14 \text{ cm}^{-1}$.

Fig. 2 Decay constants $\Gamma(v')$ for $\text{HeI}_2(v') \rightarrow \text{He} + \text{I}_2(v < v')$. Filled circles are the experimental results of Johnson, Wharton, and Levy,^{1c} and the vertical lines passing through the circles represent experimental uncertainties. The solid curve corresponds to the theoretical results at each v' connected by lines.

Fig. 3 The same as Fig. 2, except for the $\text{NeI}_2(v') \rightarrow \text{Ne} + \text{I}_2(v < v')$ reaction. Filled circles correspond the real-time results of Gutmann, Willberg, and Zewail.⁴

Fig. 4 Theoretical I_2 rotational product distributions for the dominant $v = v' - 1$ reaction channels for HeI_2 (open circles) and NeI_2 (filled circles) vibrational predissociation. (These distributions are energy resolved with E taken to be the mean wave packet energy, which turns out to be within 1 cm^{-1} of the resonance energy.)

Fig. 5 Wave packet density in the $v = v' - 1$ channel at a time $t \approx 5 \text{ ps}$ shows a large lobe in the interaction region, due to transitions from the $v' (= 20)$ channel, and tails of reactivity extending out into the $\text{He} + \text{HeI}_2$ channels. (Only a portion of the grid is displayed. The actual grid extends out to about 35 a.u.)

F_{ig}

Fig 2

Fig 3

Fig 4

Fig 5

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