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A combined experimental-theoretical study of the vibrational predissociation and product rotational distributions for high vibrational levels of $\text{He}^{79}\text{Br}_2$

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Pump-probe spectra of HeBr_2 in vibrational states $v' = 10$ and 39 through 48 of the B electronic state are reported and the fragment rotational distributions from vibrational predissociation of the cluster are extracted from the measured $E(0_g^+) \leftarrow B(^3\Pi_{0u}^+)$ spectra of Br_2 . The experimental results are compared to theoretical calculations on the $B \leftarrow X$ spectra using atom-atom model potentials and performing a thermal average over transitions that contribute to the net excitation. Very good agreement between experiment and theory is obtained, except in the region of $v' = 44$, where the $\Delta v = -1$ channel closes, and in the region of $v' = 48$ where the $\Delta v = -2$ channel closes. For $v' = 43$, and $v' = 44$, the agreement is less satisfactory because the dynamics are extremely sensitive to details of the potential energy surface due to threshold effects associated with the $\Delta v = -1$ channel closing. Similar sensitivity to the potential due to the $\Delta v = -2$ channel closing impairs the agreement between experiment and theory for $v' = 48$. Below $v' = 43$, the rotational distributions for $\Delta v = -1$ and $\Delta v = -2$ are quite similar. Above $v' = 43$ the peaks of the rotational distributions for $\Delta v = -2$ move to higher values of j . These results are compatible with the theoretical conclusion that dissociation shifts from a direct mechanism to one involving intramolecular vibrational distribution in the region of the closing of the $\Delta v = -1$ channel. Although the simple additive potential model used in this work succeeds in reproducing most of the experimental data for this system, further improvements in the potential energy surface will be required to achieve precise agreement between experiment and theory for large Br-Br separations. © 1999 American Institute of Physics. [S0021-9606(99)03801-5]

I. INTRODUCTION

Rare gas-halogen van der Waals (vdW) molecules are prototype systems for the study of vibrational predissociation (VP), intramolecular vibrational redistribution (IVR) and intermolecular forces. Progress in this field has been a consequence of a fruitful interplay between high resolution experiments and accurate theory and calculations.¹ In particular, two issues have received considerable attention over the past several years. First, the ground state potential energy surfaces have been found to be much more “interesting” than previously assumed, with separate wells for linear and perpendicular (or T-shaped) isomers.² Second, the effects of the intermediate state IVR coupling in the dissociation dynamics has proved to be more difficult to understand than might have been expected for a seemingly simple triatomic molecule.^{3–11}

In this paper we focus our attention on the latter issue; whether IVR plays an important role in the dissociation dy-

namics of high vibrational levels of the HeBr_2 molecule. HeBr_2 was first observed by van de Burgt *et al.*¹² who recorded laser induced fluorescence spectra at high resolution. The authors were also able to determine vibrational predissociation lifetimes from linewidth measurements. A more detailed investigation of the dynamics of HeBr_2 was undertaken by Jahn *et al.*¹³ in 1994. Using the pump-probe spectroscopy technique, B state vibrational levels v' (quantum number for the Br_2 stretching vibration within the complex) of 34 to 48 were examined: blue shift trends were presented and VP linewidth data were analyzed in terms of “momentum gap”¹⁴ and “energy gap”¹⁵ models. They found that the $\Delta v = -1$ channel for VP (transfer of one Br_2 vibrational quantum to the vdW modes and breakup of the complex) is closed for levels $v' = 44$ and higher. From these data the HeBr_2 binding energies in both X and B states could be determined. One particularly interesting result is that the van der Waals bond energy decreases with increasing v' until $v' = 40$, but then the trend reverses. This indicates a qualitative change in the nature of the interaction between the He and the Br_2 as the Br_2 subunit approaches dissociation. Data

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(blue shifts, average geometries and linewidths) for lower levels ($v' = 8, 10, 12, 16, 20$) were obtained by the same group a year later using high resolution spectroscopy.¹⁶ Sivakumar *et al.*¹⁷ reported unresolved distributions which were sufficient to determine the partitioning of energy between rotational and translational degrees of freedom. They found that the dissociation is mainly a $V \rightarrow T$ process with little excitation of the rotational motion of the Br_2 product fragment. The present work extends previous studies by reporting detailed product rotational distributions for the vibrational predissociation of $\text{He}^{79}\text{Br}_2(B, v' = 10, 39-48)$. These data are quite sensitive to the details of the potential and of the fragmentation dynamics.

Given the difficulty of calculating accurate *ab initio* potential energy surfaces (PES) for these many-electron clusters near the dissociation limit, quantum dynamics calculations are very useful for testing empirical or semiempirical PES against experimental data. In the HeBr_2 case, Jahn *et al.*¹⁶ tested two different anisotropic potentials for the ground electronic state and proposed an atom-atom form for the B state. They obtained good agreement with measured blue shifts and predissociation lifetimes for $v' = 8, 10, 12, 16, 20$. The main band of the excitation spectra is accurately reproduced, but the simple B state potential does not give a completely satisfactory fit to a secondary band involving excitation to an excited bending state. Recently, González-Lezana *et al.*¹⁸ used simple atom-atom Morse potentials (for both electronic states) in accurate quantum mechanical calculations which gave excellent agreement with most of the data^{12,13,16} for $v' = 8-38$. Krause and Clary¹⁹ used the same PES in a wave packet study on the vibrational predissociation for $v' = 8, 10$, and 12 and obtained good agreement with earlier time-independent and experimental results. In addition, Buchachenko *et al.* showed that the pairwise PES provides good agreement with the experimental data on the vibrational energy transfer in the $\text{He} + \text{Br}_2$ collisions.²⁰ Vibrational levels higher than 38 were also studied by González-Lezana *et al.*^{18,21} One of the main results for this regime is that the closing of the $\Delta v = -1$ channel at $v' = 44$ and the binding energy were in perfect agreement with experiment. The predicted linewidths and blueshifts for $v' > 38$, however, showed less agreement with experiment. For these high v' levels the calculated linewidths and blueshifts show complicated oscillatory patterns, but the experimental observation of decreasing spectral shifts for $v' > 40$ is not found in the simulations. Thus the B state PES for large interhalogen distances requires further refinement. The authors of the experimental work¹³ suggested that for these large Br-Br distances, the HeBr_2 potential should gradually convert to a sum over the He-Br atom-atom potentials. The diatomics-in-molecules (DIM) theory applied to the rare gas-halogen systems should be very useful in this context.²²⁻²⁴ In the present work, however, we continue to use the PES of Ref. 18 in the dynamics calculations in order to test its performance for predicting product rotational distributions. The present analysis will help to isolate effects due to the potential from the details of the dynamics.

Another of the main goals here is to test the conclusion of González-Lezana *et al.*^{18,21} that IVR is important in the

HeBr_2 fragmentation process for levels near the closing of the $\Delta v = -1$ channel. In particular, the predicted product state distributions will be compared to the data. In the IVR mechanism, the initially prepared state couples with an intermediate state (vibrationally excited in the vdW modes) which then couples with the dissociative continuum. That IVR can occur for such small complexes was first shown by Evard *et al.*³ in their experiments on ArCl_2 . The authors obtained highly structured rotational distributions in the $\Delta v = -2$ regime (where at least a two quantum transfer is needed to break up the complex), which were strongly dependent on the initially excited vibrational level. They attributed the result to the influence of intermediate (doorway) states in a sequential fragmentation dynamics. The model was refined in subsequent works,⁴⁻⁸ where calculations have demonstrated that the $\Delta v = -2$ regime of ArCl_2 corresponds to a sparse limit of IVR ($\rho V \leq 1$, where ρ is the density of states and V is the coupling). IVR in ArI_2 (where more complications arise due to competition with electronic predissociation) has also been studied in detail.⁹⁻¹¹ Another manifestation of a sparse IVR is an erratic dependence of lifetimes and spectral shifts on v' due to the different interactions between the initially prepared state and the intermediate(s) state(s) as v varies.²⁵⁻²⁷ In HeBr_2 , calculated spectral shifts and resonance widths for $v' = 40-46$ showed such behavior. Also, for $v' > 40$ the cross section line shapes are not Lorentzian and, as v' increases, several peaks appear in the simulated cross sections.¹⁸ Later, González-Lezana *et al.*²¹ showed that the HeBr_2 states near the dissociation limit are so strongly coupled that the quantum number, v' (for the Br_2 bond stretching) is no longer a good quantum number. They also found¹⁸ that the $\Delta v = -2$ rotational distributions, which are smooth for low v' levels, become more structured for $v' > 40$. The product rotational distribution predicted for HeBr_2 are not as highly structured as those of ArCl_2 . This is probably due to the fact that the intermediate states in HeBr_2 involve less bending excitation than those of ArCl_2 . Also, departure of the lighter He atom yields less rotational excitation than it does for Ar. It is therefore interesting to compare the manifestation of IVR in these two vdW systems.

Vibrational predissociation of $\text{HeBr}_2(B, v' > 8)$ is fast enough that the linewidths of adjacent rotational transitions in the excitation spectra overlap. Thus, as noted previously,¹⁸ for a realistic comparison between experiment and theory it is necessary to compute cross sections for different state selected transitions and thermally average them. This is done in the present work and, indeed, it is found that the thermally averaged rotational distributions compare much better with the measured ones than those corresponding to any one particular transition.

This paper is organized as follows: Sec. II describes the experimental setup and the pump-probe scheme. Section III presents a brief account of the theory used in the calculations. Results are reported in Sec. IV, which are discussed in Sec. V. Finally, Sec. VI concludes the paper with a summary and suggestions for future work.

FIG. 1. Laser pump-probe scheme for preparation of quasibound levels of HeBr₂(*B*, *v'*, *J'*) and measurement of the vibrational and rotational state distributions of the Br₂(*B*, *v'_f'* - *n*, *j'_f'*) vibrational predissociation fragment.

II. EXPERIMENTAL AND DATA ANALYSIS

The pump-probe scheme used in this study was previously discussed in detail¹³ and is summarized in Fig. 1. Briefly, the pump laser excites the HeBr₂ molecule from the X state (*v''* = 0) to the B state (*v'* = 10, 39–48). Next the Br₂ stretching vibration couples with the van der Waals modes which leads to dissociation of the cluster (vibrational predissociation). Below *v'* = 44 the dissociation can occur by transferring one or more vibrational quanta from the strong bond to the van der Waals modes. The $\Delta v = -1$ channel is closed for *v'* ≥ 44. For these vibrational levels, two (or more) vibrational quanta have to be transferred to dissociate the van der Waals bond. The state distribution for the dissociation product Br₂ (*B* state, *v_f'* = *v' - 1* or *v' - 2*) is measured with the probe laser by recording further excitation to the E state, from where fluorescence is detected. (Note that we use *v''*, *v'* and *v_f'* to indicate the Br-Br stretching quantum number in the HeBr₂ X state, B state, and the product Br₂ B state, respectively. Also, *J''* and *J'* will be reserved for the total angular momentum of HeBr₂, while *j_f'* is used for the rotational angular momentum of the Br₂ products.)

Figure 2 shows the experimental set-up. The HeBr₂ van der Waals molecules were produced in a free jet chamber

FIG. 2. Schematic diagram of the experimental apparatus.

FIG. 3. Probe spectrum obtained by tuning the pump laser to the peak of the HeBr₂ *B*(*v'* = 39) ← *X*(*v''* = 0), transition and scanning the probe laser across the Br₂ *E*(*v_f'*) ← *B*(*v_f'*) transition.

equipped with a pulsed solenoid nozzle (nozzle diameter 200 μm). High purity helium (350 psi pressure) was passed over liquid bromine in a stainless steel trap. The gas mixture was expanded into the vacuum chamber pumped by a 10000 ℓ/s diffusion pump backed by a roots blower and mechanical pump. These conditions result in a rotational temperature of about 1.5 K. Two excimer pumped dye lasers were used: one (the pump laser) was operated with Coumarin 503 laser dye to obtain 510 nm radiation, with a bandwidth of about 0.4 cm⁻¹, to excite the HeBr₂ *B*(*v'*) ← *X*(*v''*) transitions. The second dye laser (the probe laser) was pumped by the same excimer laser as the pump laser, after an optical delay of about 10 ns. Kiton Red was chosen as laser dye to obtain radiation near 620 nm. This light was frequency doubled, using a phase-matched KDP crystal, to excite the Br₂ *E*(*v_f'*) ← *B*(*v_f'*) transitions. An UV filter (Schott UG-5) was used to reject the undoubled probe-laser light. An angle tuned intracavity étalon in the probe laser narrowed the probe-laser bandwidth to 0.04 cm⁻¹. The two laser beams were combined with a dichroic mirror and focused into the molecular jet. Fluorescence from the E state was collected by a photomultiplier tube (EMI 9659) equipped with a quartz lens and a Corning 7-54 filter to reject scattered light and B state fluorescence. The spectra were recorded and stored by sampling the output of the photomultiplier tube with a gated boxcar integrator interfaced with a personal computer.

The probe laser spectrum was converted to rotational distributions by fitting the spectrum with the rotational constants for the B (Ref. 28) and E (Ref. 29) electronic states and taking populations of the lower state and the Doppler linewidth as parameters. A more detailed description of the fitting process is given elsewhere.³⁰ The calculation of the line intensities included the appropriate Hönl-London factors³¹ and a statistical weight factor of 5/3 to account for the nuclear spin of ⁷⁹Br (*I* = 3/2). The intensities of the even and odd *j_f'* rotational lines were normalized separately to 100%. An example of such a fit is shown in Fig. 3. Due to small rotational constants, the spectrum is still congested even though an intracavity étalon was employed. As illus-

trated in Fig. 3, the P branch forms an unresolved bandhead, but the R branch is mostly resolved and allows for a reliable extraction of product populations. Incomplete resolution is one of two main sources of uncertainty in the analysis. The other source of uncertainty is due to variations in the states being excited due to overlapping excitation transitions. To estimate the error bars due to these two effects, each spectrum was recorded and analyzed between 3 and 6 times. Subsequent figures showing the distributions include error bars that indicate the standard deviations of the mean for the several measurements.

III. QUANTUM-MECHANICAL CALCULATIONS

In this section, the basic equations for the three dimensional quantum-mechanical calculations are reviewed. More details on this theory are given elsewhere.^{18,32} The aim is the calculation of partial cross sections for

$$\text{HeBr}_2(X, v''=0) \xrightarrow{t} \text{He} + \text{Br}_2(B, v_f'', j_f''),$$

where t stands for the radiatively allowed $\text{HeBr}_2 B(v') \leftarrow X(v'')$ transitions. In the following, t_i and t_f will be used to denote the initial and final states, respectively, of the excitation transitions and v_f'' and j_f'' are the vibrational and rotational quantum numbers of the diatomic fragment. The partial cross section is given by

$$\sigma_{v_f'' j_f''}^t(\omega) \propto \omega |\langle \Psi_E^{t_f}(B) | \boldsymbol{\mu} \cdot \mathbf{e} | \Psi^{t_i}(X) \rangle|^2, \quad (3.1)$$

where ω and $\mathbf{e}$ are the angular frequency and the polarization vector of the incident photon, $\boldsymbol{\mu}$ is the transition dipole moment for the electronic transition being considered, $\Psi^{t_i}(X)$ and $\Psi_E^{t_f}(B)$ are bound and dissociative nuclear wave functions with energies E_{t_i} and E , respectively, and $E = E_{t_i} + \hbar\omega$. The wave functions are eigenstates of the Hamiltonian [for ground ($\epsilon = X$) and excited ($\epsilon = B$) electronic states, respectively]:

$$H^\epsilon = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{\mathbf{l}^2}{2mR^2} + \frac{\mathbf{j}^2}{2\mu r^2} + V_{\text{Br}_2}^\epsilon(r) + W_{\text{HeBr}_2}^\epsilon(r, \theta), \quad (3.2)$$

written in Jacobi coordinates: $\mathbf{r}$ is the vector joining the two Br nuclei, $\mathbf{R}$ is the vector from the center of mass of Br_2 to the helium nucleus, and θ is the angle between $\mathbf{r}$ and $\mathbf{R}$. The reduced masses of Br_2 and HeBr_2 are μ and m , while $\mathbf{l}$ and $\mathbf{j}$ are angular momenta associated with the vectors $\mathbf{R}$ and $\mathbf{r}$, respectively. Finally, $V_{\text{Br}_2}^\epsilon$ and $W_{\text{HeBr}_2}^\epsilon$ are the intramolecular and vdW intermolecular interaction potentials. In a previous publication,¹⁸ a PES constructed as a sum of pairwise Br-Br and He-Br interactions was proposed and tested against a wealth of experimental measurements. In this work, we use the same PES where all the atom-atom interactions are given by Morse functions, except for Br-Br interaction in the excited electronic state which is described by a RKR potential from Ref. 28. Potential parameters are presented in Table I.

The initial and final wave functions are expanded as follows:

TABLE I. Morse parameters of the HeBr_2 X and B state potential energy surfaces, built as a sum of atom-atom interactions.

		$D(\text{cm}^{-1})$	$\alpha(\text{\AA}^{-1})$	$\rho_e(\text{\AA})$
Br-Br	X	24557.674	1.588	2.281
	B	RKR potential (Ref. 28)		
He-Br	X	19.62	1.55	3.81
	B	17.00	1.55	3.92

$$\begin{aligned} \Psi^{t_i}(X) &\equiv \Psi_i^{J''M''p_i''p_j''}(\mathbf{R}, \mathbf{r}; X) \\ &= \sum_{v''j''\Omega''} \phi_{v''j''\Omega''}^i(R) \chi_{v''}^X(r) \Theta_{j''\Omega''}^{J''M''p_i''p_j''}(\hat{\mathbf{r}}, \hat{\mathbf{R}}), \end{aligned} \quad (3.3)$$

$$\begin{aligned} \Psi_E^{t_f}(B) &\equiv \Psi_{v_f''j_f''\Omega_f''E}^{J'M'p_i'p_j'}(\mathbf{R}, \mathbf{r}; B) \\ &= \sum_{v'j'\Omega'} \phi_{v'j'\Omega'}^{v_f''j_f''\Omega_f''E}(R) \chi_{v'}^B(r) \Theta_{j'\Omega'}^{J'M'p_i'p_j'}(\hat{\mathbf{r}}, \hat{\mathbf{R}}), \end{aligned} \quad (3.4)$$

where χ 's are eigenfunctions of the effective Hamiltonian $-(\hbar^2/2\mu)(\partial^2/\partial r^2) + V_{\text{Br}_2}^\epsilon(r)$. On the other hand, $\{\Theta_{j\Omega}^{JM p_i p_j}\}$ is a free rotor basis set,^{18,32} where J is the total angular momentum, M and Ω its projections onto the space and body fixed z axes, respectively, p_i is the parity under inversion of the nuclear coordinates, and p_j is the parity under bromine nuclei exchange ($p_j = +1$ or -1 when the rotational quantum number j is even or odd, respectively).

Several considerations are made in the cross section calculations. First, the electric field is defined to lie along the space-fixed z axis and a random distribution of molecular orientations is assumed. In addition, the transition dipole moment lies along the Br_2 axis and it is assumed that its magnitude is independent of the internuclear distance, r . In this way, the partial cross section is written as^{30,32}

$$\begin{aligned} \sigma_{v_f'' j_f''}^t(\omega) &\propto \omega (2J' + 1)(2J'' + 1) \\ &\times \sum_{\Omega_f''} \left| \sum_{v''j''\Omega''} \sum_{v'j'\Omega'} \langle \phi_{v'j'\Omega'}^{v_f''j_f''\Omega_f''E} | \phi_{v''j''\Omega''}^i \rangle \langle \chi_{v'}^B | \chi_{v''}^X \rangle \right. \\ &\times (2j' + 1)^{1/2} (2j'' + 1)^{1/2} (1 + |\delta_{\Omega'0} - \delta_{\Omega''0}|)^{1/2} \\ &\times \begin{pmatrix} j' & 1 & j'' \\ 0 & 0 & 0 \end{pmatrix} \sum_s \begin{pmatrix} j' & 1 & j'' \\ -\Omega' & s & \Omega'' \end{pmatrix} \\ &\times \left. \begin{pmatrix} J' & 1 & J'' \\ -\Omega' & s & \Omega'' \end{pmatrix} \right|^2. \end{aligned} \quad (3.5)$$

Note that, in obtaining Eq. (3.5), we have carried out a sum over transitions between all M'' and M' states, as well as over the quantum number Ω_f'' (the projection of the fragment angular momentum onto the body fixed z axis). On the other hand, the selection rules for the transitions studied here are: $\Delta p_i = -1$, $\Delta p_j = -1$ and $\Delta J = 0, \pm 1$ (with $J'' = 0 \rightarrow J' = 0$ forbidden).

FIG. 4. Br_2 rotational product distributions for HeBr_2 vibrational predissociation via the $\Delta v = -1$ channel for initial (HeBr_2) Br_2 stretching vibrational quantum numbers $v' = 10, 39-43$. Experimental distributions are given by open squares connected by solid lines. The error bars are the standard deviation of the mean for several (3–6) measurements. Theoretical distributions are given by full circles joined by dotted lines. The even and odd j_f'' populations are normalized separately to 100%. See text for more details.

The line shape for producing fragments in vibrational state v_f'' is

$$\sigma_{v_f''}^t(\omega) = \sum_{j_f''} \sigma_{v_f'' j_f''}^t(\omega), \quad (3.6)$$

and the product rotational distribution within vibrational manifold v_f''

$$\mathcal{P}_{j_f'' v_f''}^t(\omega) = \frac{\sigma_{v_f'' j_f''}^t(\omega)}{\sigma_{v_f''}^t(\omega)}. \quad (3.7)$$

The above expressions are suitable for comparison with experiments where the laser and/or natural linewidth is smaller than the separation between transition peaks. When this is not the case, a given photon frequency ω may produce several excited states by means of different transitions, and the calculation of an “initial-state averaged” cross section becomes necessary.^{33,34} Considering that the population of the $\text{HeBr}_2(X, v''=0)$ rotational states is governed by a Boltzmann distribution, the thermally averaged line shape can be written as

$$\sigma_{v_f''}(\omega) = \sum_t \sigma_{v_f''}^t(\omega) g_{t_i} e^{-E_{t_i}/kT}, \quad (3.8)$$

where T is the rotational temperature of the molecular beam, k is the Boltzmann constant, E_{t_i} is the $\text{HeBr}_2(X, v''=0)$ energy level referred to the ground rotational state (i.e., $E_{t_i} = 0$ for $J''=0$) and g_{t_i} is a statistical weight factor accounting for the nuclear spin of ^{79}Br ($I=3/2$): $g_{t_i} = 5/8$ or $3/8$ for $p_j'' = -1$ or $+1$, respectively. Analogously, the thermally averaged rotational product distribution is given by:

$$\mathcal{P}_{j_f'' v_f''}(\omega) = \frac{1}{\sigma_{v_f''}(\omega)} \sum_t \sigma_{v_f'' j_f''}^t(\omega) g_{t_i} e^{-E_{t_i}/kT}. \quad (3.9)$$

The calculation of the bound and dissociative wave functions has been carried out using methods detailed in Ref. 18. The vibrational and rotational channels included in Eqs. (3.3) and (3.4) and the rest of the computational parameters, which were selected after a careful convergence analysis, are those reported in Ref. 18.

IV. RESULTS

Figure 3 shows the probe spectrum of the $\text{Br}_2 E(v_f' = 13) \leftarrow B(v_f'' = 38)$ transition, which was obtained by setting the pump laser to the maximum of the $\text{HeBr}_2 B(v' = 39) \leftarrow X(v'' = 0)$ transition. The dotted line is the fitted spectrum calculated as described above. For high vibrational levels, the spectrum of Br_2 becomes quite congested due to the three isotopomers of the molecule. The band shown in Fig. 3 is in a relatively “clean” portion of the spectrum. However, some structured signal can be observed to the red side of the band head. Similar congestion precluded the extraction of product state distributions for $v' = 46$ and 47 . The rotational state distributions obtained from the fits are shown in Figs. 4 and 5 using open square symbols.

As mentioned above, rotational congestion and significant homogeneous broadening requires that the calculated rotational distributions be thermally averaged over a rather large set of excitation transitions since the distributions from individual states can be quite different from each other. The procedure of the averaging is as follows. First, a set of transitions for the averaging was selected with the aid of a rigid rotor model. Taking the HeBr_2 to be a T-shaped rigid mol-

FIG. 5. Br_2 rotational product distributions for HeBr_2 vibrational predissociation via the $\Delta v = -2$ channel for initial (HeBr_2) Br_2 stretching vibrational quantum numbers $v' = 40$ – 46 and 48 . The symbols are defined as in Fig. 4.

ecule, transition frequencies and line strengths for asymmetric top transitions were computed for a given rotational temperature, using a Boltzmann distribution for the population of the initial states. All transitions above a threshold intensity in the simulated spectrum are included in the average. For $v' = 10$, there is remarkable agreement between the line positions and intensities of the rigid-rotor model and those obtained by rigorous cross section calculations. For the $v' \geq 38$ region, where the line shapes of each transition exhibit complicated structures, the rigid rotor model obviously fails. Still, we have found that the model qualitatively predicts the relative intensities. Table II gives the selected transitions $t = J''_{p''_i} \rightarrow J'_{p'_i}$. Using these transitions, the $\Delta v = -1$, and -2 thermally averaged cross sections [Eq. (3.8)] were computed for different photon frequencies and the product rotational distributions [Eq. (3.9)] were calculated at the frequency ω for which a maximum is found in the simulated excitation spectrum. The results presented here are for a temperature of 1.6 K. Although 1.6 K gave the best agreement between theory and experiment, temperatures as low as 0.6 K also yield satisfactory agreement. The theoretical result is more sensitive to the frequency at which the cross sections are computed. However, variations are again reasonably small. To compare with measured distributions, the $j''_f = \text{even}$ and odd distributions were normalized separately.

Figure 4 shows the experimental and theoretical vibrational predissociation product distributions for the $\Delta v = -1$ channel and for initial HeBr_2 vibrational levels of $v' = 10, 39$ – 43 . The measurements are represented by open squares connected by full lines, while the filled circles connected by dashed lines correspond to the calculations. The $v' = 10$ distributions given in Fig. 4(a) show that the use of the atom-atom Morse potential yields results in remarkable agreement with experiment for the lower vibrational levels.

TABLE II. Transitions involved in the calculations.

t	$J''_{p''_i} (X)$	$J'_{p'_i} (B)$	t	$J''_{p''_i} (X)$	$J'_{p'_i} (B)$
1	0^+	1^-	13	2^-	3^+
2	1^-	1^+	14	2^-	2^+
3	1^+	2^-	15	3^+	2^-
4	1^-	1^+	16	3^-	4^+
5	1^+	2^+	17	3^+	2^+
6	1^-	0^+	18	3^-	4^-
7	1^-	2^+	19	3^-	2^+
8	2^+	1^-	20	3^-	4^+
9	2^+	3^-	21	4^+	5^-
10	2^+	2^-	22	4^+	3^-
11	2^+	3^-	23	4^+	5^-
12	2^-	1^-	24	4^-	5^-

The small probability for $j_f'' \geq 10$, confirms that the fragmentation is mainly a $V \rightarrow T$ process.¹⁷ Little rotational excitation is expected for a light collision partner like He. The rotational distributions extend to nearly the same j_f'' values as for as HeCl_2 .³⁰

The $v' = 10$ result for HeBr_2 shows no evidence for the bimodal j_f'' pattern observed for HeCl_2 (Ref. 30) and NeCl_2 .³⁴ This bimodal pattern was attributed to a quantum interference effect.³⁵ Many of the individual state selected product distributions for HeBr_2 show the bimodal pattern^{18,19} (although less pronounced than for HeCl_2), but this effect is smeared out in the thermal averaging. It is reasonable to expect that the interference effect is weaker when the diatomic molecule is heavier. In fact, the effect has not been observed in NeBr_2 either.³⁶

The experimental $\Delta v = -1$ rotational distributions for $v' = 39\text{--}43$ [Figs. 4(b)–4(f)] are all similar to those for $v' = 10$. They peak at $j_f'' = 2$ and 3 and become quite small by $j_f'' = 11$ and 12. The nearly constant rotational distributions for increasing values of v' , even though the total product kinetic energy is decreasing with v' , is a common result in the vibrational predissociation of rare gas-dihalogen systems.^{30,34} This result is compatible for a fragmentation process proceeding by direct coupling from an initial quasibound van der Waals state which does not strongly depend on v' to continuum states of the $v' - 1$ manifold. In addition, recent quasiclassical trajectory calculations for NeBr_2 (Ref. 36) have shown that, when the available energy is not too large ($< 100 \text{ cm}^{-1}$) the extent of rotational excitation is independent of the available energy. Although the widths of the rotational distributions change only slightly with v' , the distributions of the higher vibrational levels are broader than the $v' = 10$ distribution. The calculation reproduces this effect very well, so that good agreement is obtained for $v' = 41$ and 42, as well as for $v' = 10$. Again, this gives us confidence that the potential employed to calculate the B state dynamics is reasonably accurate.

The good agreement between experiment and theory breaks down at $v' = 43$ [Fig. 4(f)]. The $v' = 43$ level is the last before the $\Delta v = -1$ channel closes due to the anharmonicity of the Br-Br stretching vibration. The dynamics in this energy region are very sensitive to the potential because the exact energy at which the $\Delta v = -1$ channel closes will control which product states are accessible. Also, the states right at threshold can be expected to undergo more complicated dynamics that are very sensitive to small errors in the potential. The potential used here leads to the following predictions. At the frequency for which the $v' = 43$, $\Delta v = -1$ dissociation was computed, the channel $j_f'' = 8$ is open for all the state selected transitions of Table II. For rotational channels j_f'' ranging between 9 and 12, j_f'' is open for only some the excitation transitions. Finally, $j_f'' = 13$ is closed for all excitation transitions. For $v' = 44$, $\Delta v = -1$ can occur only for excitation on the blue edge of the excitation band, in nice accordance with experiment.¹³ For $v' = 45$, the $\Delta v = -1$ channel is completely closed, also in agreement with experiment.¹³ Thus the dynamics in this energy region provides an extremely sensitive test of the PES. The theoretical distribution for $v' = 43$, $\Delta v = -1$ [Fig. 4(f)] dies out at

smaller values of the rotational quantum number than the experimental one, indicating that some rotational channels which should be open are closed in the theoretical simulation. Thus the true potential probably has a slightly shallower effective van der Waals attraction of He to Br_2 in $v' = 43$. There could be a contradiction between this conclusion and the fact that the theory gives larger spectral shifts than experiment in that v' range. This apparent “paradox” is indeed an interesting problem that should be solved in further investigations.

In the theoretical distribution of Fig. 4(f) it can be seen that the rotational population decreases quite rapidly, but not abruptly, in the region of $j_f'' = 5$ and 6. Above $j_f'' = 7$ the calculated populations are very small even though product channels remain open (at least for some transitions) up to $j_f'' = 12$. Thus rotational excitation to the highest open channels appears to be an unlikely process. A centrifugal barrier higher than the relative kinetic energy of He and $\text{Br}_2(j_f'')$ fragments (which is, in fact, quite small for these channels) could explain the low probability of dissociating to high j_f'' states. The experimental rotational distribution, on the other hand, extends up to $j_f'' = 11$ with a non-negligible probability and besides is quite similar in shape to the $v' = 41$ and 42 ones. The theoretical distribution would have been closer to the experiment if it were computed at a higher excitation energy, for which more rotational channels are open. This again suggests that the PES used in this study is slightly too deep.

The rotational product distributions for the $\Delta v = -2$ channel are presented in Fig. 5 for initially excited levels $v' = 40\text{--}48$. Note that for $v' = 46$ and 47 the product Br_2 spectra were overlapped with unassigned transitions, possibly from another isotope of bromine, which precluded the determination of product distributions. First, we discuss the experimental results. It is clear from Fig. 5 that the rotational distributions change when the $\Delta v = -1$ channel closes. Up to $v' < 44$, where the $\Delta v = -1$ channel is still open, all the $\Delta v = -2$ rotational distributions are quite similar, and are also similar to those for $\Delta v = -1$. They peak around $j_f'' = 2$ and extend up to $j_f'' = 12$. These similar distributions are characteristic of dissociation that proceeds by direct coupling from the quasibound state of level v' to the dissociation continuum states correlating with the $v' - 1$ and $v' - 2$ levels.^{34,36} For $v' \geq 44$, where the $\Delta v = -1$ is closed, the $\Delta v = -2$ distributions become broader and peaked at a higher rotational state ($j_f'' = 4, 5$). The calculated distributions are very similar to the measured ones for initial levels $v' = 41, 42$, and 45; that is to say, before and after the closing of the $\Delta v = -1$ channel. The comparison is less good for the $v' = 43$ and 44 levels and becomes worse for $v' = 48$. It is interesting that the theory and experiment disagree for $v' = 43$ and 44 for $\Delta v = -2$ dissociation, in addition to the $\Delta v = -1$ dissociation, because this helps separate how the inaccuracies in the potential lead to disagreement with the experiment. The problem of obtaining precise energy values for closing of the $\Delta v = -1$ channel, discussed in the preceding paragraph, is not an issue for the $\Delta v = -2$ channel. Thus we conclude that the disagreement in the $\Delta v = -2$ distributions is more strongly due to more complicated dynamics

that occur near threshold rather than to the specific channels that are open. This is discussed further below.

The origin of the disagreement for the $v'=48$, $\Delta v = -2$ rotational distribution [Fig. 5(h)] is, on the other hand, very similar to that for the $v'=43$, $\Delta v = -1$ distribution. With the PES used in this work, $v'=48$ is the last level where the $\Delta v = -2$ channel is open. For $v'=49$ the $\Delta v = -2$ channel is closed at the frequency where a maximum peak is found for the $\Delta v < -2$ partial cross sections, and the channel opens on the blue edge of the excitation band. This feature is analogous to the closing of the $\Delta v = -1$ channel at $v'=44$ discussed above. For $v'=48$, the channel $j_f''=10$ is the highest open channel for all the calculated transitions but, as discussed above for the $v'=43$, $\Delta v = -1$ distribution, the small product kinetic energy corresponding to the highest open channels seemingly makes rotational excitation an unlikely process. The experimental rotational distribution extends to higher rotational channels suggesting that the $v'=48$ vdW level is shallower than in the calculations, so that available energy is larger. Therefore the $v'=48$ distribution provides another significant test of the potential.

In summary, we find that theory and experiment are in remarkable agreement concerning $\Delta v = -1$ and -2 product rotational distributions except in the region where the $\Delta v = -1$ and -2 channels close. This indicates that the PES for HeBr₂ is quite accurate. The origin of the disagreement for the $\Delta v = -2$ distribution in the region of the $\Delta v = -1$ channel closing is discussed in the next section.

V. DISCUSSION

Over the past several years, the product rotational distributions for many of the noble gas-halogen van der Waals molecules have been measured with the pump-probe method. The list of molecules studied includes He, Ne and Ar bonded to Cl₂,^{3,30,34} He and Ne bonded to Br₂,^{36,37} and He and Ne bonded to ICl.³⁸ Of all these examples, the present one, HeBr₂, is the first that appears to show a distinct change in the coupling regime as a function of the initially excited vibrational level. He or Ne bonded to Cl₂ or ICl have only been observed in the direct coupling regime, while no $\Delta v = -2$ dissociation could be observed for ArCl₂ below the IVR regime. Prior to this study, ArCl₂ was the simplest molecule for which definitive IVR dynamics has been observed.³ One of the many interesting aspects of IVR dynamics is that it makes the product rotational distributions very sensitive to the PES. Even for a molecule as simple as ArCl₂ the dynamics are so sensitive to the PES that it has not yet been possible to extract a surface that is even qualitatively in agreement with the measured rotational distributions. More recently, the possibility of IVR contributions to the NeBr₂ $\Delta v = -2$ dynamics was discussed.³⁶ He or Ne bonded to Br₂ may prove to be more amenable to a detailed determination of the PES if the onset of IVR does not complicate the distributions quite so much as for ArCl₂. In addition, HeBr₂ is especially interesting because the available data allows us to study the PES in the region where the Br-Br separation is as large as 5 Å.

Since theory and experiment for HeBr₂ are in close

FIG. 6. Full line, thermally averaged $\Delta v = -2$ cross section for initial excitation to HeBr₂ ($B, v'=45$), as a function of the photon frequency (measured with respect to the Br₂ ($B, v'=45$) $\leftarrow$ ($X, v''=0$) transition). Dashed and dotted lines, cross sections for some individual transitions defined in Table II, multiplied by 5 for clarity.

agreement, except right at the closing of the $\Delta v = -1$ and -2 dissociation channels, it is interesting to investigate the details of the theoretically predicted dynamics that underlie the averaged results presented above. Also, it is interesting to investigate the sensitivity of the observed results to the details of the PES. Finally, we will discuss which experimental data might be best suited to extracting a more detailed potential for HeBr₂.

First, we analyze some of the individual state selected cross sections that went into the thermal averages reported above. Figure 6 shows how the thermally averaged partial cross section for the $v'=45$, $\Delta v = -2$ channel is constructed from state-to-state partial cross sections. (For clarity, only a few of the state-to-state partial cross sections of Table II are shown, and they are multiplied by 5.) All the individual cross sections exhibit two or three peaks, in some cases of equal height. The multiple peaks are due to IVR coupling of one or two intermediate states from the $v'-1$ doorway manifold with the $v'=45$ bright state. This interpretation of the $J'=0$ IVR dynamics has been investigated in detail in Ref. 21. Figure 6 shows that the $J'>0$ results are analogous to those for $J'=0$. Since the band shape is different for each transition, the details of IVR coupling are clearly very sensitive to the total angular momentum and parity block in the v' level. This is consistent with IVR in the sparse limit. The averaging of the state selected cross sections leads to a rather unstructured excitation spectrum, blurring the IVR signature.

Figure 7 shows the calculated excitation cross sections for the $\Delta v = -1$ and -2 channels as a function of excitation energy for $v'=41-46$. This result nicely illustrates the gradual closing of the $\Delta v = -1$ channel. At $v'=41$ the intensity of the $\Delta v = -1$ channel is more than twice the $\Delta v = -2$ intensity; at $v'=43$ the two channels become equally important; and above $v'=44$ the $\Delta v = -1$ channel is closed. The cross sections for $v'=44$ are particularly interesting. At $\omega=4$ cm⁻¹, the $\Delta v = -1$ channel closes right where the $\Delta v = -2$ channel reaches a maximum.

In general, calculated excitation spectra are in good

FIG. 7. Thermally averaged (1.6 K) cross sections for excitation to $v' = 41$ –46 levels, $\Delta v = -1$ and $\Delta v = -2$ partial cross sections are shown as open squares joined by full lines and open circles joined by dashed lines, respectively. The frequency in the abscissa of each plot is measured with respect to the corresponding $\text{Br}_2(B, v') \leftarrow (X, v''=0)$ transition.

agreement with the experiment.¹⁸ A previous analysis of the spectra in this regime, for which only the $0_+^+ \leftarrow 1_-$ transition was studied,¹⁸ showed considerably more variation of the blueshift with v' than is observed in the experiments. The present results show that thermal averaging tends to decrease these variations, but experimental and theoretical spectral shifts are still rather different. In the experimental data, the blueshifts gradually increase until $v' = 40$ and then start to decrease. The theoretical trend is more monotonic. On the other hand, linewidths obtained from the thermally averaged cross sections fall in the range of the experimental estimation for $v' = 40$ –46 (0.8 cm^{-1}), while values obtained from the study of just the $0_+^+ \leftarrow 1_-$ transition were much smaller.¹⁸ A particularly interesting result of the previous study of the $0_+^+ \leftarrow 1_-$ cross sections is that they exhibited several peaks, even for $v' > 41$. This suggests that IVR starts to become important even below the $\Delta v = -1$ channel closing. Similar observations were made for ArCl_2 .⁷ Unfortunately, the present study shows that this effect in the excitation cross section is substantially masked by thermal averaging.

The ability of the calculations presented here to reproduce the change in the experimental rotational distributions for $\Delta v = -2$ from $v' = 42$ and below to $v' = 45$ is quite remarkable, and confirms that the PES used in the calculations

FIG. 8. Product rotational distributions for $\Delta v = -2$ dissociation resulting from several typical state-to-state transitions, t , (defined in Table II) for vibrational levels $v' = 41, 44$ and 45 . All the distributions correspond to transitions leading to $j_f'' = \text{even}$. The relative contributions of each state selected excitation to the averaged rotational distribution are indicated in parentheses.

is quite close to the true surface. For $v' = 43, 44$ and 48 , the results are more sensitive to the details of the surface because of threshold effects associated with the $\Delta v = -1$ and $\Delta v = -2$ channel closing. However, the effect of thermal averaging complicates the refinement of the PES based on the present experimental results. If better state-to-state data can be obtained, either by optical state selection or by decreasing the temperature of the sample, rotational product distributions of the individual transitions will be very useful in determining an improved PES. Figure 8 shows several examples of the state dependence of the rotational distributions that underlie the thermally averaged data in Fig. 5. It is evident from Fig. 8 that the thermal averaging has been crucial to achieving a good agreement with experiments, since the individual transitions yield quite different distributions. Also, Fig. 8 makes it clear that the onset of IVR is associated with a much more sensitive dependence of the product distribu-

tion on the individual state. In the direct coupling regime, $v'=41$, the distributions are rather smooth and peaked at $j_f''=2$ or 4.

An interesting detail regarding the $v'=41$ distributions is that each state resolved distribution peaks at $j_f''=J'$. (The most probably product j state is the J state of the complex before dissociation.) The result of the thermal averaging is a distribution with large populations for j_f'' between 1 and 5 and a slightly populated tail to higher j_f'' values. This effect may be due to the fact that the product translational energy, and thus orbital angular momentum is small, so that, usually, rotational angular momentum is conserved. The situation changes drastically for $v'=44$ and 45, where the individual distributions extend to higher j_f'' and also become much more structured. Most of the distributions display two peaks, one at $j_f''=2$ or 4 and the other at $j_f''=6$ or 8. This distinct behavior of the rotational distributions is due to the IVR dynamics of the intermediate state, which is excited in the bending mode.²¹ This bending excitation plays an important role determining the product rotational distribution. The variation of the product distribution with initial state is particularly great for $v'=44$, and this explains why it is harder for the theory to fit the experiment in this case.

The results presented in this paper show good agreement between experiment and theory in the region of vibrational dynamics that is most strongly affected by IVR type multi-state coupling. Although the experimental signature for IVR is not clear for HeBr₂ as it was for ArCl₂, the comparison between experiment and theory is quite persuasive. Unfortunately, we have also shown that thermal averaging masks many of the details in the excitation line shapes and product state distributions. If the effects of thermal averaging could be overcome, HeBr₂ would provide one of the best possible cases for the determination of a full three dimensional PES that extends to large separations of the strongly bonded component of a van der Waals molecule. One route to more detailed information might be to perform experiments in the time domain.³⁹ Another way to enhance the IVR structure would be to achieve a better initial state selection, either by optical techniques or by lowering the initial rotational temperature of the beam. Considerably lower temperatures could probably be obtained by using a mixture of ³He and ⁴He in the expansion. For $T=0.1$ K the IVR effects would be dramatic. Figure 9(a) shows the theoretical thermally averaged $\Delta v=-2$ partial cross sections for $v'=45$ at 0.1 K. The product rotational distributions corresponding to the two frequencies indicated in Fig. 9(a) are presented in Fig. 9(b). The result of lowering the temperature is a structured line shape and rotational distribution. If such data could be obtained, the PES of the B state of HeBr₂ could be obtained with much more detail than for any other member of the rare gas halogen series of van der Waals molecules. Such data would provide a significant benchmark for future *ab initio* work.

From the results presented in this work as well as previous comparisons with experiment, it is clear that the simple pairwise atom-atom potential used to model the B state PES successfully reproduces most of the experimental data. In the direct coupling regime, $v'<41$, agreement between theory and experiment is almost complete,^{12,13,16} including rota-

FIG. 9. (a) The theoretical $\Delta v = -2$ excitation spectrum for $v'=45$ assuming a rotational temperature of 0.1 K is shown. The photon frequency is measured with respect to the Br₂ ($B, v'=45$) $\leftarrow$ ($X, v''=0$) transition. (b) ($v'=45$, $\Delta v=-2$) rotational product distributions at the frequencies indicated by arrows in (a): open squares connected by full lines correspond to the excitation peak at 3.5 cm⁻¹ while the open circles connected by dashed lines correspond to the excitation peak at 4.7 cm⁻¹.

tional structure, blueshifts, linewidths and product rotational distributions. One experimental result in this regime that theory does not reproduce with the present potential is the van der Waals bending excitation band. Even for most of the data in the IVR regime, the PES used here is in remarkable agreement with the data. The two exceptions to this agreement are the precise details at the closing of the $\Delta v = -1$ and $\Delta v = -2$ channels, and the change in the trend of the blue shift dependence on v' above $v'=40$. The good agreement with the data means that both the anisotropy and R dependence of the PES are reasonably close to those of the true surface. The main error in the present surface is in how the well depth varies with the Br-Br bond length. While it may be possible to construct a purely empirical surface that corrects the remaining disagreements between theory and data, a DIM (diatomics-in-molecule) approach, that explicitly extends to the proper He-Br potential for large Br-Br separations may offer more insight. Previous experience^{22-24,40} indicates that, switching to a DIM-based PES one can expect the qualitative confirmation of the present results and, hopefully, their quantitative improvement. Work in this direction is now in progress.

VI. CONCLUSIONS

Product rotational distributions for the vibrational predissociation of the B state of HeBr₂ are reported and com-

pared to theoretical calculations on the most recently determined potential energy surface. The agreement between the data and results is remarkably good. A key step in obtaining this agreement was to thermally average the calculated data over the thermal distribution of the experimental sample. The thermal averaging also improved the comparison of the theoretical results to previously published data for HeBr₂. This confirms that IVR plays an important role in the HeBr₂ dynamics for $v' \geq 41$. Thus HeBr₂ is the second triatomic rare gas-halogen van der Waals molecule for which IVR dynamics has been shown to be important. In addition, it is perhaps the first system where the transition between a direct to an IVR regime in the vibrational predissociation is traced out in detail.

Although the agreement between theory and experiment is quite good in most respects, there remain several details to be worked out. In particular, the dynamics in the energy region near the $\Delta v = -1$ and $\Delta v = -2$ channel closing is very sensitive to the potential, and will provide a key test for further improvements of the PES. It would be especially useful if data with a better initial state resolution could be obtained, since this would enhance the dependence of the data on the potential. Suggestions for future work along these lines was suggested. In this regard, HeBr₂ possibly provides the most favorable case for an eventual determination of a complete three dimensional potential energy surface.

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