Time and frequency resolved dynamics of ArBr₂

Jose Cabrera,^{a)} Craig R. Bieler,^{b)} Natalie McKinney,^{b)} Wytze E. van der Veer,
Jordan M. Pio, and Kenneth Janda^{c)}

*Department of Chemistry and Institute of Surface and Interface Science, University of California,
Irvine, California 92697-2025, USA*

Octavio Roncero

Instituto de Matemáticas y Física Fundamental, CSIC, Serrano 123, 28006 Madrid, Spain

(Received 16 November 2006; accepted 12 September 2007; published online 25 October 2007)

We report the first spectroscopic observation of and vibrational predissociation dynamics for ArBr₂. Measurements are reported for the linear and T-shaped isomers with time and frequency resolution near the Fourier limit of a 15 ps pulse. For the T-shaped isomer, the Ar–Br₂ bond energy D_0 for the B state, $\nu' = 19$, is found to be 200 cm⁻¹, yielding a $D_0(X)$ value of 213 cm⁻¹. Product appearance rates are determined for $\nu' = 16$ –25 of the B state of ArBr₂. While the rate generally increases with increasing vibrational quantum number, the trend is not monotonic. Also, obtaining reproducible rates for any given vibrational level requires very careful control of the experimental conditions. The data suggest that ArBr₂ undergoes vibrational predissociation (VP) in the sparse intramolecular vibrational relaxation regime. These observations are consistent with theoretical calculations that show that T-shaped ArBr₂ undergoes VP in the sparse regime, such that lifetimes are strongly dependent on both the vibrational and rotational quantum numbers. As for ArI₂, a linear isomer of ArBr₂ is found to contribute a quasicontinuous background to the excitation spectra. Direct excitation of this continuum results in a very broad product vibrational distribution. © 2007 American Institute of Physics. [DOI: 10.1063/1.2794332]

I. INTRODUCTION

The noble gas–halogen van der Waals molecules offer a unique opportunity to observe how various molecular properties influence intramolecular dynamics, including the transition from direct vibrational predissociation (VP) to the onset of intramolecular vibrational relaxation before vibrational predissociation dynamics with an increasingly high density of states. For this reason, many combinations of a noble gas atom with a halogen molecule have been studied. However, so far no data have been reported for ArBr₂. Here, we report the first combined experimental and theoretical study of ArBr₂ vibrational predissociation dynamics in the electronic state associated with an Ar atom attached to the B electronic state of Br₂. For convenience, we will refer to this as the B electronic state of ArBr₂. Spectra for both the T-shaped and linear isomers of ArBr₂ are observed.

In one sense, we are probably fortunate that data for ArBr₂ have previously proved to be difficult to collect. The results presented here are quite complicated and would have been difficult to interpret without the background of previous studies of ArCl₂ (Refs. 1 and 2) and, especially, ArI₂.^{3–12} The complications arise from the facts that (1) both T-shaped and linear isomers are produced in the supersonic expansion; (2) the linear isomer has a continuous spectrum so that at any frequency the signals are weak; (3) the T-shaped isomer has

discrete bands, but the contribution from the underlying linear isomer continuum is not negligible; (4) the spectra are highly congested so it is difficult to achieve isotopomer separation; and (5) electronic predissociation is almost certainly contributing to the dynamics, but in an unknown quantity. In this first report on the ArBr₂ molecule, we concentrate on the T-shaped isomer which yields discrete bands and more intense experimental signals. Product appearance times are reported for vibrational levels between $\nu' = 16$ and 25. The results are consistent with an intramolecular vibrational relaxation (IVR) mechanism in the sparse regime. These experimental data are compared to accurate wave packet calculations on a potential energy surface adjusted to be qualitatively consistent with the data.

Evidence for IVR in a triatomic van der Waals molecule was first observed for ArCl₂.¹ The experimental evidence for IVR was that the dependence of the product rotational distribution on the initial vibrational level was quite complex and impossible to understand on the basis of a direct dissociation model. The IVR interpretation was later confirmed by a detailed theoretical analysis.² The ArCl₂ dynamics that have been studied to date are all in the sparse regime of IVR. For ArI₂, the conclusions regarding IVR are not as clear. A reasonable interpretation of the experimental data assumes that the vibrational predissociation rate varies monotonically with the I₂ vibrational quantum number,^{3,4} indicating that ArI₂ undergoes IVR in the dense regime. This is consistent with an intuitive hypothesis that, all else being equal, ArI₂ should have a higher density of states than ArCl₂. However, the theoretical analysis to date indicates that ArI₂ should still

^{a)}Current address: Department of Geophysics, Stanford University, Stanford, California, USA.

^{b)}Current address: Department of Chemistry, Albion College, Albion, Michigan, USA.

^{c)}Electronic mail: kjanda@uci.edu

be in the sparse-to-intermediate coupling regime, unless rotational averaging is responsible for washing out the observed resonances.⁵ This apparent contradiction between experiment and theory has led to considerable discussion and also complicates the analysis of electronic predissociation data for ArI_2 . Given that the mass, vibrational frequencies, and rotational constants of Br_2 are intermediate between those of Cl_2 and I_2 , data for ArBr_2 should help with the interpretation of the ArI_2 problem.

ArI_2 is also the molecule for which the experimental evidence for concomitant T-shaped and linear isomers was worked out.^{3–12} This analysis has a long and interesting history. Kubiak *et al.* first observed and analyzed the T-shaped isomer.⁸ Later, Valentini and Cross made the puzzling observation that it was possible to excite ArI_2 to energies well above the I_2 dissociation limit and still obtain I_2 products after dissociation of the Ar atom.⁹ This was called the one-atom cage effect. For several years, it was assumed that this data resulted from the T-shaped isomer, and much theoretical effort was expended trying to explain how an Ar atom attached to the side of an I_2 molecule could provide significant vibrational relaxation of the I_2 . Burke and Klemperer then observed that there was a continuous background spectrum for the molecule due to a linear isomer, and that the linear isomer is responsible for the apparent cage effect.¹⁰ The linear isomer spectrum is quasicontinuous because of its rapid dissociation dynamics. This rapid dynamics is due to a combination of effects. Most obviously, upon exciting the $X \rightarrow B$ transition, the I_2 bond length increases resulting in a direct force between the I and Ar atoms. This effect is enhanced by a short Ar–I bond length in the X state of the linear isomer and a repulsive Ar–I interaction in the Franck-Condon allowed region of the B state potential. In a recent analysis of the problem, Darr *et al.* conclude that excitation of the linear isomer is not so much a one-atom cage effect as it is direct excitation to the van der Waals continuum associated with bound levels of the I_2 molecule.¹¹ However, the work of Roncero *et al.* makes it clear that the quasicontinuum associated with the linear isomer has a complex underlying resonance structure.¹² The data below will be much easier to interpret if the essentials of the ArI_2 analysis are kept in mind. There are discrete bands due to the T-shaped isomer, a quasicontinuous spectrum due to the linear isomer, and an unknown contribution of electronic predissociation dynamics.

Time and frequency resolved pump-probe data are reported for ArBr_2 using an optical parametric oscillator-optical parametric amplifier (OPO-OPA) system having a time resolution of 15 ps. This limits the frequency resolution to about 2 cm^{-1} , often good enough to size select the clusters, the Br_2 isotopomer, and the B state vibrational level, but not the rotational quantum numbers. As will be clear from the data presented below, there is significant spectral congestion, so cluster size and isotopomer selection is not perfect. Also, the excitation spectra reveal both discrete spectral bands attributed to T-shaped ArBr_2 , and diffuse spectra due to the linear isomer. Probe spectra obtained at different pump-probe delays yield information that allows the characterization of product appearance due to the dissociation of

FIG. 1. A schematic for a typical pump-probe experiment to detect $\Delta v = -2$ and -3 dissociation from the T-shaped isomer. The wells on the left side of the figure represent the van der Waals Ar– Br_2 bonds, and the flat part of the curves on the right side of the figure represents the energy of the free Br_2 states as labeled. The vertical arrows represent transitions employed in the experiment. Br_2 double resonance is observed as transition (e) followed by transition (f). Ar– Br_2 double resonance, not observed in this experiment, would have been detected as transition (a) followed by transition (b). Pump-probe signals are represented by transition (a) followed by transition (c) or (d). Also shown are the arrows marked IVR and VP to schematically denote intramolecular vibrational relaxation of ArBr_2 followed by vibrational predissociation. A similar scheme would apply to the linear isomer, except that the B state curves would be shifted to the right, so that Franck-Condon excitation from the X state would reach the repulsive part of the Ar– Br_2 curves.

the initially excited T-shaped or linear ArBr_2 . Finally, time-delay scans yield the product appearance times for the T-shaped ArBr_2 vibrational levels. Assignments of the observed features in the spectra to either the T-shaped or the linear isomer are based on the assumption that the ArBr_2 structure and dynamics are analogous to those previously studied for ArI_2 , as discussed above.

II. EXPERIMENTAL SECTION

As illustrated in Fig. 1 for the T-shaped isomer, the time and frequency resolved pump-probe technique enables three types of experiments to be performed. In each case, the pump laser excites the $\text{Br}_2 X \rightarrow B$ transition, the probe laser excites the $\text{Br}_2 B \rightarrow E$ transition, and fluorescence from the $\text{Br}_2 E$ state is detected. First, excitation spectra are obtained by scanning the pump laser through an $\text{ArBr}_2 X \rightarrow B$ transition, while the probe laser is fixed on a known $\text{Br}_2 B \rightarrow E$ transition. Second, probe spectra to measure the product state distributions for a particular excitation transition are obtained by fixing the pump laser to a particular $X \rightarrow B$ transition of the complex and scanning the probe laser. Finally, the rate for forming a specific product channel is determined by fixing both the pump and probe lasers on appropriate transitions and measuring the signal as a function of the time delay between the pulses. The qualitative description of the linear isomer experiments would be similar, except that the van der Waals potential curves for the excited state would be substantially shifted to the right in Fig. 1. Thus, Franck-Condon

FIG. 2. Four examples of excitation spectra in the region of the $\Delta\nu = -2$ closing. (a) The excitation spectrum obtained by setting the probe laser to detect Br₂ ($B, \nu' = 15$), while the pump is scanned across the ($B, \nu' = 17$) Br₂ region. (b) The excitation spectrum obtained by setting the probe laser to detect Br₂ ($B, \nu' = 16$), while the pump is scanned across the Br₂ ($B, \nu' = 18$) region. (c) The excitation spectrum obtained by setting the probe laser to detect Br₂ ($B, \nu' = 17$), while the pump is scanned across the Br₂ ($B, \nu' = 19$) region. Note that, in this case, no band due to ArBr₂ is observed. (d) The excitation spectrum obtained by setting the probe laser to detect Br₂ ($B, \nu' = 16$), while the pump is scanned across the Br₂ ($B, \nu' = 19$) region. In each case, the ArBr₂ excitation spectrum is represented by a solid line. The dashed line shows the corresponding free Br₂ molecule LIF spectrum so that the blue shifts can be visualized.

excitation from the ground state leaves the Ar–Br separation on the repulsive portion of the van der Waals potential of the B state, resulting in rapid, direct dissociation.

The apparatus and experimental conditions used in these studies are quite similar to those of a recently reported study of the NeBr₂ molecule.¹³ So, only a brief description will be given here. An Ar/He/Br₂ gas mixture is obtained by passing an Ar/He gas mixture over a natural isotopic mixture of bromine held between -15 and -20 °C in a stainless steel trap. This maintains the Br₂ partial pressure at about 20 mbars. The gas mixture is expanded through a 150 μ m diameter pinhole into a vacuum chamber. Two independent OPO-OPA systems^{14,15} synchronously pumped by a mode-locked Nd:YAG (YAG denotes yttrium aluminum garnet) laser are employed to record pump-probe spectra to study the time evolution of the dynamics that proceed on the B electronic surface. The ArBr₂ complex created in a pulsed free jet expansion is excited by the “pump” laser to the desired Br₂ stretching level associated with the B state of Br₂. The “probe” laser then excites the free Br₂, resulting from dissociation of the ArBr₂, to the E state. Fluorescence from the E state is detected as the experimental signal. The variable time delay between the pump and probe pulses is achieved by sending the probe laser pulse through a delay line comprised of a prism mounted on a computer controlled linear translation stage. In order to minimize contributions from Br₂ rotational coherences, measurements were performed with the polarization of the pump laser rotated 54.7°, with respect to

the polarization of the probe laser. The pump laser polarization was adjusted with a mica broadband half-wave plate. The experiments were performed using two sets of gas expansion conditions: (1) a 1% Ar, 99% He gas mixture at 14 bars and (2) a 5% Ar, 95% He gas mixture at 4 bars. The rotational temperatures could not be estimated for either of these expansions from the contour of the vibrational bands in the Br₂ $X \rightarrow B$ spectrum due to the bandwidth of the laser. However, evidence of the warmer expansion with the lower backing pressure could be seen in the enhancement of hot band ($X, \nu'' = 1$) $\rightarrow$ (B, ν') transitions and the lack of continuum onsets due to linear HeBr₂ (Ref. 25) that were easily observed using the higher pressure expansion.

III. EXPERIMENTAL RESULTS

As discussed briefly above, the first step of this study involved recording excitation spectra to identify ArBr₂ $X \rightarrow B$ transitions. Figure 2 shows four examples of such spectra in which the ArBr₂ excitation bands, solid lines, are compared to the laser-induced fluorescence (LIF) spectra (dashed lines) of the analogous free Br₂ band. Excitation to ArBr₂ $B, \nu' = 17$ and 18 can be detected by the $\Delta\nu = -2$ dissociation channel [transition (a) followed by transition (c) of Fig. 1] as shown in panels (a) and (b). Panel (c) shows that there is little or no $\Delta\nu = -2$ signal for ArBr₂ $\nu' = 19$, while panel (d) shows that there is strong $\Delta\nu = -3$ signal [transition (a) followed by transition (d) of Fig. 1] for this level. In each case, the band corresponding to T-shaped ArBr₂ is found to be

FIG. 3. Probe spectra obtained by positioning the pump laser on the $\text{Ar } ^{79}\text{Br}_2$ ($X, \nu''=0 \rightarrow B, \nu'=21$) transition for several pump-probe delays. The peak labels refer to specific Br_2 ($B \rightarrow E$) transitions. See the text for details.

shifted by 13 cm^{-1} to higher energy from the parent Br_2 monomer. This compares to a band shift of 9.5 cm^{-1} for ArCl_2 (Ref. 16) and 13.26 cm^{-1} for ArI_2 .⁶ The T-shaped ArBr_2 bond energy can be determined as first discussed by Blazy *et al.*⁶ Given that the $\Delta\nu=-2$ dissociation channel is clearly open for $\nu'=18$, with $\Delta E=204.1 \text{ cm}^{-1}$, but closed (or nearly so) for $\nu'=19$, with $\Delta E=195.9 \text{ cm}^{-1}$, we assign a value of $200 \pm 4 \text{ cm}^{-1}$ to $D_0(B)$. Adding the ArBr_2 blueshift to $D_0(B)$ yields a value of $213 \pm 4 \text{ cm}^{-1}$ for $D_0(X)$, in good agreement with the value obtained from high-level *ab initio* molecular electronic structure calculations.¹⁷

Figure 3 shows probe spectra for several different pump-probe delay times following excitation of the T-shaped ArBr_2 to the ($B, \nu'=21$) level. For $t=-50 \text{ ps}$ (the $-$ sign indicates that the probe laser crosses the molecular beam before the pump), no transitions are observed, as expected. For $t=0 \text{ ps}$ the two pulses are coincident, and only weak, diffuse spectra are observed. This result is quite different from that of the analogous study of NeBr_2 (Ref. 13) for which both double resonance and product signals could be easily identified in the $t=0 \text{ ps}$ spectra. At $t=50 \text{ ps}$, distinct product probe spectra are evident, and they become more intense for longer delay times. Transitions due to $\Delta\nu=-3$ to -9 are observed, yielding somewhat congested spectra. Most of the bands due to loss of more than three Br_2 stretching quanta are triplets due to the fact that all three Br_2 isotopomers are contributing to the bands, as discussed below.

If only T-shaped ArBr_2 were produced in the supersonic expansion, it would have been quite surprising to see $\Delta\nu=-5$ to -9 products in Fig. 3. For instance, the $\Delta\nu=-5$ channel contributes less than 1% of the products for ArI_2 .^{7,12} The fact that $B \rightarrow E$ transitions due to all three isotopomers contribute to these probe transitions can be seen clearly in the ($B, \nu'=15$) $\rightarrow$ ($E, \nu=1$) and ($B, \nu'=15$) $\rightarrow$ ($E, \nu=2$) bands of Fig. 3. Since spectroscopic isotopomer selection is not possible without discrete transitions in the excitation spectrum, this indicates that a linear isomer with a broad excitation spectrum is being simultaneously excited along with the dis-

FIG. 4. (a) Probe spectrum that reveals the presence of a linear ArBr_2 isomer. The excitation laser is set to $18\,363 \text{ cm}^{-1}$, where no discrete excitation transitions are present, while the probe laser is scanned across the $B \rightarrow E$ spectrum. (b) Probe spectrum of linear ArBr_2 with the excitation laser set to $18\,844 \text{ cm}^{-1}$. Product states ranging from $\nu'=14$ to $\nu'=22$ are observed with significant intensities. Even larger $\Delta\nu$ values are observed with small intensity.

tinct T-shaped ArBr_2 band. The rate of product formation for the linear isomer is consistent with the expected rapid direct dissociation dynamics. By 50 ps , the linear isomer product peaks have already reached their maximum intensity. In contrast, the $^{79}\text{Br}_2(B, \nu'=18)$ product channel due mainly to the dissociation of T-shaped $\text{Ar}^{79}\text{Br}_2(B, \nu'=21)$ is still increasing even after 100 ps .

Recording data such as described here necessarily involves using a mixture of helium and argon as the expansion gas. Increasing the backing pressure increases the ArBr_2 band intensity and decreases the rotational temperature. Increasing the backing pressure, however, also increases the production of HeBr_2 . The expansion conditions used to obtain the data for Fig. 3, $P_0=4 \text{ bars}$, 5% Ar, were carefully chosen to significantly reduce the spectral contamination by HeBr_2 signals.

Figure 4(a) shows a probe spectrum with the excitation laser set at $18\,363 \text{ cm}^{-1}$, about 50 cm^{-1} to the red of the $^{79}\text{Br}_2$ ($X, \nu''=0$) $\rightarrow$ ($B, \nu'=20$) transition. There are no discrete features at this excitation energy. As for Fig. 3, the vibrational product state distribution is broad, and each band is an isotopomer triplet consistent with linear ArBr_2 . The first

TABLE I. Experimental values of the product vibrational state distribution due to dissociation of T-shaped ArBr₂ B , ν' =19, and 25.

Initially Excited ν'	Detected ν'	% (expt.)	% (theory)
19	17	0	8
19	16	77	62
19	15	23	23
19	14	0	6.3
19	13	0	7
21	19	0	0
21	18	62	65.6
21	17	26	23.6
21	16	12	8.5
21	15	0	2
21	14	0	0.3
25	23	0	0
25	22	54	45.5
25	21	24	27.8
25	20	15	16.1
25	19	6	7.0
25	18	0	3
25	17	0	0.7

clearly detected product channel is (B , ν' =16), and significant product is detected for ν' =11, the lowest vibrational level that could be observed in this range of probe energies. After normalizing the probe transitions in Fig. 4(a) (see below for normalization procedure), the peak of the product state distribution is near ν' =13 and 14. To confirm that these detected products are due to an Ar–Br₂ complex, the same probe spectrum was taken with a 100% He gas mixture under identical expansion conditions, and only weak transitions due to Br₂ B , ν' =19, 18, and 17 were observed from the dissociation of linear HeBr₂. Locating an excitation threshold for which a linear ArBr₂ product channel opens as was done for linear ArI₂ (Ref. 11) has proven to be difficult due to the weakness of the first open product channel. Thus, it has not been possible to determine the ground state bond energy of the linear conformer.

Figure 4(b) shows a probe scan for the linear ArBr₂ at an excitation energy of 18 844 cm⁻¹, 33 cm⁻¹ to the red of the ⁷⁹Br₂ (X , ν'' =0) $\rightarrow$ (B , ν' =26) transition. Again, there are no

discrete features at this excitation energy so we are only exciting the linear conformer. The first clearly detected vibrational product state is (B , ν' =22). Probe transitions originating from ν' =23 are labeled in Fig. 4(b), but these features are overlapping with other probe transitions so the presence of this vibrational level cannot be confirmed. The peak of the product state distribution is at ν' =17 and 18, and products all the way down to ν' =11 are detected. Probe transitions originating from ν' =10 are not observed.

Table I gives the vibrational product state distributions for T-shaped Ar⁷⁹Br₂ B , ν' =19, 21, and 25 obtained from probe spectra of these species, along with the theoretical distributions reproduced from Table II. Since the discrete T-shaped isomer band always lies over the linear isomer continuum, the probe spectra for T-shaped species will always be contaminated as in Fig. 3. Since the linear product states appear more quickly than the T-shaped product states, this contamination was removed by subtracting the 50 ps spectrum from the 300 ps spectrum. The remaining peaks then are only due to T-shaped Ar⁷⁹Br₂ (B , ν' =21). These $B \rightarrow E$ transitions are normalized as follows: The (B , ν') $\rightarrow$ (E , ν) transition is recorded in a Br₂ (X , ν'' =0) $\rightarrow$ (B , ν') $\rightarrow$ (E , ν) double resonance, and its integrated signal intensity is divided by the (X , ν'' =0) $\rightarrow$ (B , ν') LIF intensity. Because the radiative lifetimes of Br₂ B state increase with increasing ν' (Ref. 33) and are on the same time scale, ~ 10 μ s, as the time the Br₂ is in the detector region, this step of the normalization can introduce error by overestimating the intensity of (X , ν'' =0) $\rightarrow$ (B , ν') transitions with shorter (B , ν') radiative lifetimes. While this source of error should not be significant for the narrow range of products observed in the T-shaped distributions, it could be problematic for the much wider linear product distributions, so for the linear ArBr₂ probe spectra, we only used this normalization procedure to give us a qualitative picture of the linear isomer's product state distribution. The normalized Br₂ double resonance $B \rightarrow E$ intensity factors are used to obtain normalized intensities and product state distributions for the Ar⁷⁹Br₂ probe scans. $B \rightarrow E$ transitions originating from the same (B , ν') are compared to ensure that they give the same normalized intensities. For ν' =19 and 25, the pure T-shaped probe spectrum was obtained by detuning the excitation laser from the T-shaped transition and recording the probe spectrum for the

TABLE II. Calculated values of the product vibrational state distribution due to dissociation of T-shaped ArBr₂.

Initial ν'	$\Delta\nu=-2$	$\Delta\nu=-3$	$\Delta\nu=-4$	$\Delta\nu=-5$	$\Delta\nu=-6$	$\Delta\nu=-7$	$\Delta\nu=-8$
ν' =14	85.2	12.9	1.7	0.2			
ν' =15	78.6	18.0	2.9	0.4			
ν' =16	66.3	26.7	5.8	1.1	0.1		
ν' =17	65.8	26.1	6.6	1.3	0.1		
ν' =18	71.0	23.0	5.0	1.0	0.1		
ν' =19	8.0	62.0	23.0	6.2	0.7		
ν' =20	0	64.9	26.0	8.0	1.1		
ν' =21	0	65.6	23.6	8.5	2.0	0.3	
ν' =22	0	58.9	25.8	11.3	3.3	0.7	
ν' =23	0	45.0	30.3	16.6	6.6	1.5	
ν' =24	0	41.3	27.8	19.0	8.6	2.9	0.5
ν' =25	0	45.5	27.8	16.1	7.0	3.0	0.7

FIG. 5. Three time-delay scans for $\text{Ar}^{79}\text{Br}_2$ B state $\nu'=16$ and $\nu'=23$. (a) Free Br_2 (B , $\nu'=18$) double resonance delay and laser autocorrelation curve. The width of the autocorrelation curve is 19 ps. (b) Appearance of Br_2 (B , $\nu'=20$) due to vibrational predissociation of ArBr_2 (B , $\nu'=23$) via $\Delta\nu=-3$, along with the best fit curve, $\tau=15 \pm 2$ ps. (c) Appearance of Br_2 (B , $\nu'=14$) due to vibrational predissociation of ArBr_2 (B , $\nu'=16$) via $\Delta\nu=-2$, along with the best fit curve, $\tau=76 \pm 8$ ps.

linear isomer. The linear isomer probe spectrum was subtracted from the probe spectrum taken with the excitation laser on the T-shaped transition to give the pure T-shaped probe spectrum. Unlike using the early time probe scan to remove the linear contribution, this method did not remove any intensity due to the T-shaped isomer, so it gave slightly better signal to noise. However, both methods were equally effective at removing the transitions due to the linear isomer.

Typical time-delay studies for $\text{Ar}^{79}\text{Br}_2$ (B , $\nu'=16$) and $\text{Ar}^{79}\text{Br}_2$ (B , $\nu'=23$) are shown in Fig. 5. Figure 5(a) shows the $^{79}\text{Br}_2$ double resonance signal, which is used to extract both the $t=0$ calibration and a Gaussian fit to the pump-probe autocorrelation width, 19 ps. For Fig. 5(b) the pump laser is set on the maximum of the $\text{Ar}^{79}\text{Br}_2$ $X \rightarrow B$ ($\nu''=0 \rightarrow \nu'=23$) band [transition (a) of Fig. 1], the probe is set to the $^{79}\text{Br}_2$ $B \rightarrow E$, ($\nu'=20 \rightarrow \nu=6$) transition [transition (d) of Fig. 1], while E state fluorescence is collected as a function of pump-probe delay. Figure 5(b) shows the appearance of the Br_2 product from the $\Delta\nu=-3$ vibrational predissociation of $\text{Ar}^{79}\text{Br}_2$ (B , $\nu'=23$) and a fit to the data that yields an $\text{Ar}^{79}\text{Br}_2$ (B , $\nu'=23$) lifetime³⁶ of 15 ± 2 ps. In Fig. 5(c), the pump laser is set on the maximum of the $\text{Ar}^{79}\text{Br}_2$ $X \rightarrow B$ ($\nu''=0 \rightarrow \nu'=16$) band with the probe fixed on the $^{79}\text{Br}_2$ $B \rightarrow E$, ($\nu'=14 \rightarrow \nu=1$) transition. In this case, the product appearance time is determined to be 76 ± 8 ps.

The details for fitting these curves and extracting product appearance times have been discussed previously.¹³ However, in this work we have used more analytical methods for assigning error bars. In short, the trace due to appearance of Br_2 product is fitted to a single exponential increase convoluted with the laser cross correlation, which is assumed to be Gaussian. To obtain error bars, data were simulated by assuming that each data point was sampled from a Gaussian distribution having a mean given by the best fit line and a standard deviation given by the experimental noise. Each

TABLE III. Vibrational predissociation product appearance times for $\text{Ar}^{79}\text{Br}_2$ B state.

Initially Excited ν'	Detected ν'	τ_{exp} (ps)	τ_{theory} (ps)	ω_R^a cm^{-1}
16	14	76 ± 8	99	220
17	15	44 ± 6	41	212
18	16	32 ± 4	118	204
19	16	38 ± 3	220	299
20	17	48 ± 4	34	288
21	18	74 ± 6	36	275
22	19	34 ± 4	17	263
23	20	15 ± 2	16	250
24	21	22 ± 2	16	238
25	22	24 ± 3	11	226

^aEnergy released from the Br_2 stretching vibration for each dissociation channel.

data set generated was then fitted with the same single exponential rise function as the real data, and a distribution of product appearance times was obtained. The distribution was approximately Gaussian. Under the assumption that the distribution was Gaussian, 95% confidence intervals (about 2σ) were used as the error bars.

Data similar to that described above were obtained for $\text{Ar}^{79}\text{Br}_2$, $16 \leq \nu' \leq 25$, and the results are given in Table III. For each initial vibrational level, the product appearance time for the lowest open $\Delta\nu$ channel was monitored in order to favor the T-shaped isomer. Delay scans were also collected with the excitation laser detuned from the T-shaped transition to account for the contribution of the linear isomer. The linear isomer delay scan was then subtracted from the T-shaped delay scan. In most cases, the contribution of the linear isomer was negligible and had little effect on the product appearance time. The final column of Table III gives the energy released from the Br_2 stretching mode for each dissociation process.

For NeBr_2 we were able to report excited state disappearance times in addition to product state appearance times. This is not possible for ArBr_2 since no double resonance transitions were observed. There are two possible contributions to this observation. First, it could be that the double resonance transitions are diffuse due to rapid IVR in the E ion-pair state. Similar phenomena were observed for high vibrational levels of NeBr_2 . Second, it could be that electronic predissociation dynamics in the E state of ArBr_2 eliminates the fluorescence channel that we detect. Also, an attempt was made to extend this study to lower vibrational levels. This attempt was unsuccessful for two reasons. First, excitation to the lower levels involves smaller Franck-Condon factors. This by itself would not be a fatal flaw; however, the ArBr_2 spectra are inherently weak because of the mixture of two isomers and three isotopomers. Finally, we suspect that electronic predissociation is important for the lower vibrational levels and may contribute to the weakness of the spectra.

We have presented convincing evidence for the concomitant existence of both T-shaped and linear isomers of ArBr_2 . Although the integrated intensity of the linear isomer

spectra is probably larger than that of the T-shaped isomer, the T-shaped isomer is easier to study because its spectra consist of discrete bands. We have measured product appearance times for a range of initial vibrational levels of the T-shaped isomer. Although the product appearance times tend to decrease as the bromine stretch is excited to higher levels, the trend is not monotonic. This is indicative of IVR in the sparse regime. In the following section, we provide a theoretical analysis of this data.

IV. WAVE PACKET DESCRIPTION OF THE FRAGMENTATION DYNAMICS

For ArBr₂, several resonances are involved in the fragmentation dynamics, and they will be studied here using an exact wave packet treatment described elsewhere in detail.¹⁸ A brief overview is given here. For describing the dynamics of the T-shaped isomer, the initial ϕ_1 “bright” states correspond to a single Br₂ (B, ν') excited vibrational level, while the van der Waals modes remain in their ground state. These states, denoted by their J, K , and ν quantum numbers, are calculated variationally in basis sets composed of numerical radial functions multiplied by angular functions composed of Wigner rotation matrices and spherical harmonics.¹⁸ The r coordinate is described by a single $\chi_\nu(r)$ vibrational function of free Br₂ (B, ν). Thus, the number of bound states for each ν manifold considered independent is higher than 100. For higher energies, the density of states increases considerably, maximizing at the Ar+Br₂ (B, ν) asymptotic limit, and it becomes difficult to converge the corresponding states. A qualitative description of the density of levels is found in Fig. 1 of Ref. 19.

The dissociation dynamics is followed by expanding the total wave packet as

$$\Psi_t^{J,M,K,\nu} = \sqrt{\frac{2J+1}{8\pi^2}} \sum_{\Omega,\nu'} D_{M\Omega}^{J*}(\phi, \theta, \chi) \chi_\nu(r) \Phi_{\Omega,\nu'}^{J,K,\nu}(R, \gamma; t). \quad (1)$$

For each initial J, K, ν state, 11 vibrational functions, $\nu' = \nu-7, \nu-6, \dots, \nu+3$, are used in the expansion, and all Ω projections are included, but reduced by using parity symmetry adapted combinations of Wigner matrices. The $\Phi_{\Omega,\nu'}^{J,K,\nu}(R, \gamma; t)$ coefficients are described in finite grids formed by 256 equidistant points for R , in the $R \leq R \leq 21$ Å interval, and 60 Gauss-Legendre quadrature points for γ (reduced to 30 in the $[0, \pi/2]$ interval). They are obtained by numerically integrating the corresponding time dependent Schrödinger equation using a Chebishev propagator.²⁰ For each time step, 50 fs, the wave packet is multiplied by an absorbing function, $f(R) = \exp[-\alpha(R-R_{\text{abs}})^2]$, for $R > R_{\text{abs}} = 18$ Å, with $\alpha = 0.025$ Å⁻². The propagation is performed until most of the probability has been absorbed, typically several hundreds of picoseconds for low ν' and less for higher ν' 's for which the dissociation dynamics are faster.

The Ar–Br₂(B) potential used in this work is formed by three pairwise interaction terms. The Br–Br interaction is described by a Rydberg-Klein-Rees potential from Ref. 21.

FIG. 6. Calculated vibrational populations vs time for ArBr₂ ($B, \nu', J=0$), for initial $\nu' = 15$ (top panel) and $\nu' = 24$ (bottom panel). Dissociation probabilities are obtained by summing all open vibrational channels.

Each Ar–Br is described by a Morse function, with $D = 114$ cm⁻¹, $\alpha = 1.8$ Å⁻¹, and $R_e = 4.1$ Å. D was optimized to reproduce the experimental dissociation energy, while α and R_e were estimated based on the corresponding parameters used to describe analogous complexes formed by Ne and Ar atoms with Cl₂, Br₂, and I₂ molecules. The binding energy simulated for the ArBr₂ (B, ν'), varies slightly with ν' . For $\nu' = 18$, the binding energy is 196.8 cm⁻¹, which agrees with the value obtained above within experimental error.

Calculations were performed for initial $\nu' = 16$ to $\nu' = 24$ and zero total angular momentum. Up to $\nu' = 19$, two vibrational quanta are required to fragment the system, higher levels require three quanta. In all cases, the population on the initial ν' oscillates as a function of time, as do all the populations in all closed vibrational channels. Two typical examples are shown in Fig. 6. The reason for the oscillations is that the initial “bright” state interacts with “dark” states in the lower closed vibrational channels. These “dark” states act as doorway states for dissociation, thus driving the outcome of dissociation. The population in the “dark” states can couple to lower and/or to higher vibrational levels, giving rise to the recurrences in the vibrational populations. The nature of the “dark” states can be analyzed by monitoring the evolution of the wave packet. As an example, in Fig. 7(a), snapshot of the wave packet for $t = 15$ ps is shown for initial ArBr₂ ($B, \nu' = 15$), clearly showing that, in the $\nu' - 1$ channel, the wave-packet remains bound, corresponding to a highly excited bending level in the $\nu' - 1$ manifold.

As a consequence of the interaction among zero-order bound states, the oscillator strength is shared and the spectrum becomes broader, yielding several peaks, as shown in Fig. 8. For $\nu' = 15$, an intense peak just below -197.1 cm⁻¹ provides most of the oscillator strength, but two minor peaks at -197.3 and -198.6 cm⁻¹, which are wider and probably have larger components of excited van der Waals levels in the $\nu' - 1$ manifold, provide smaller contributions. In this case the IVR takes place over a few states and can be classified as being in the sparse limit. For $\nu' = 24$, the spectrum is composed of more peaks, each wider than for $\nu' = 15$. This is

FIG. 7. Contour plots of the probability density associated with the wave packet at 15 ps after excitation to ArBr_2 (B , $\nu'=15$). The three panels correspond to $\nu'=15$ (top), $\nu'=14$ (middle), and $\nu'=13$ (bottom).

a consequence of the larger density of bound “dark” states because the $\Delta\nu=-2$ channel is closed. Thus, $\nu'=24$ can be assigned to the sparse-intermediate regime.

The dissociation rate generally increases with ν' , as expected. In order to quantify the dissociation rate, the dissociation probabilities are fitted to exponential decay expressions. Although more than one resonance contributes to each decay, the dissociation probability is rather well described by exponential functions, except for $\nu'=19$. The case for $\nu'=19$ is more complicated because the spectrum is in the region of the $\Delta\nu=-2$ threshold. The average lifetimes are presented in Table III along with the experimental values. The experimental and simulated dissociation lifetimes both generally decrease with ν' although not monotonically. Table II reports the calculated product vibrational state branching ratios for the T-shaped isomer. As with the product appearance times, the trends are not monotonic. For instance, the probability for observing $\Delta\nu=-2$ generally decreases with ν' , but the probability for $\nu'=18$ is higher than that for either $\nu'=16$ or 17 . For the assumed potential, the $\Delta\nu=-2$ channel is still partially open for $\nu'=19$.

FIG. 8. Absorption spectra calculated for $\nu'=15$, $J=0$ (top panel) and $\nu'=24$, $J=0$ (bottom panel). Energies are referenced to the $\nu'=15$ and $\nu'=24$ asymptotic limits, respectively.

The calculated product appearance times for $\nu'=18$ and $\nu'=19$, near the $\Delta\nu=-2$ channel closing, are extremely long. In these two cases, the density of “dark” states effectively coupled to the initial “bright” state is very low. The rates are very sensitive to the energy differences between the “bright” and “dark” states, which vary with ν' . This effect is highly nonlinear and is strongly affected by the details of the potential. Slight changes in the assumed parameters for the potential yield quite different deviations from the overall trends. Also, the lifetimes for these levels depend not only on the potential but also on the total angular momentum. To illustrate this last point, wave packet calculations were carried out for the different rotational sublevels for ArBr_2 (B , $\nu'=19$, $J=5$) and (B , $\nu'=21$, $J=5$). The corresponding initial state probability versus time, shown in Fig. 9, depends strongly on the rotational sublevel. Given that the experiment populated a large number of rotational levels and the calculations reported here are mainly for $J=0$, the overall agreement between the experimental data and the calculated values can be considered to be quite good.

V. DISCUSSION

As discussed above, the data presented here, by itself, would be difficult to interpret. It is only with the insight gained from 20 years of noble gas–halogen studies²² that we can confidently assign the discrete bands to a T-shaped isomer and the continuous spectrum to the linear isomer. The analogy between the results presented here and those previously obtained for ArI_2 are particularly convincing. The difficulties encountered in this study help explain why the ArBr_2 molecule had not been previously observed in spite of the intense interest in this noble gas–halogen species. The data reported here take a first step toward filling this gap. While high resolution spectroscopic measurements are not

FIG. 9. (Color) (a) ArBr₂ (*B*, ν' =21, J =5) and (b) ArBr₂ (*B*, ν' =19, J =5) decay curves for the 11 rotational sublevels.

yet available for the discrete bands, other spectroscopic signatures, such as the blueshifts and the bond dissociation energy, are consistent with the presumed T-shaped structure. The currently accepted values for noble gas–halogen T-shaped isomer ground state bond energies are given in Table IV. The value for ArBr₂, 213 cm^{−1}, lies nearly in the middle of the range between those of ArCl₂, 188 cm^{−1}, and ArI₂, 234 cm^{−1}. It is interesting to note that the bond energies for the Ar-dihalogen species vary over a significantly larger range than those of the He-dihalogen and Ne-dihalogen species. The blueshift of the ArBr₂ electronic transition (13 cm^{−1} for excitation to *B*, ν' =19) is quite similar to

TABLE IV. Currently accepted values for the ground state binding energies for T-shaped isomers of rare gas–dihalogen van der Waals complexes.

Complex	$D_0(X)$ (cm ^{−1})	Reference
HeCl ₂	16.4	27
HeBr ₂	16.6±0.8	25 and 30
HeI ₂	16.6±0.6	6 and 26
NeCl ₂	60±2	24
NeBr ₂	70±1.1	23
NeI ₂	65.3±1.0	6 and 31
ArCl ₂	188±1	16
ArBr ₂	213±4	This work
ArI ₂	234	6 and 32
KrCl ₂	237±2	34
XeCl ₂	286±1	34

that of ArI₂, and slightly larger than that of ArCl₂. The bond energy trends in the electronic excited states are similar to those in the ground states.

Table III lists the measured and calculated product appearance times for T-shaped ArBr₂ vibrational levels $16 \leq \nu' \leq 25$. The experimental data and the calculations are in qualitative agreement in the sense that the product appearance times generally decrease with increasing vibrational excitation, but the deviations from the trend are quite different for experiment and theory. The calculations suggest that there is a particularly low density of IVR doorway states for levels near the closing of the $\Delta\nu=-2$ dissociation channel, resulting in particularly long predicted lifetimes for $\nu'=18$ and 19. In contrast, the measured values for these levels are actually shorter than the product appearance times of adjacent levels. We suspect that some of these differences can be attributed to the fact that only $J=0$ levels are included in the calculations. Also, there has been no attempt to fine tune the assumed potential or to incorporate the effects of electronic predissociation. A thorough comparison between experiment and theory will thus require extensive calculations, well beyond the scope of this work.

For the higher excited levels, the agreement between experiment and theory is quite good, indicating that these levels have settled into the intermediate IVR regime for which the coupling between bright and dark states is not so sensitive to the details of the potential or the rotational level. In this sense, the data for ArBr₂ are more consistent with the calculations than the analogous results for ArI₂. In that case, more fluctuations from the trend were observed in the calculations than in the data. It would be quite useful to measure excited state lifetimes for ArI₂ for a wide range of vibrational levels. So far, only those for $\nu'=18$ and 21 have been measured.²⁸ Determining the total rate would help determine whether variations in the ratio of the vibrational predissociation and electronic predissociation rates are due to variations in the vibrational or electronic predissociation rates. This issue has recently been reviewed by Buchachenko *et al.*²⁹ Overall, for ArBr₂, the calculations are in remarkably good agreement with the data except near the closing of the $\Delta\nu=-2$ channel.

A major problem for comparing experiment and theory is that the lifetimes are dependent on rotational level. For the experiment, we are limited to changing the expansion conditions to change the distribution of rotational levels being excited. Theory is able to examine individual rotational levels, but time constraints limit the number that can be examined. For levels above the $\Delta\nu=-2$ dissociation channel closing at $\nu'=19$, the measured product appearance times are less dependent on expansion conditions. Also, in this region, variations from the trend are smaller, and the agreement between experiment and theory is better. We attribute this to a higher density of doorway states in this region so that the lifetime of any given initial state is not so dependent on a specific resonance. As can be seen in Fig. 9(a), the different sublevels of $\nu'=21$, $J=5$ have lifetimes that fall in the range of 30 ps < τ < 60 ps, compared to 36 ps for $J=0$ (reported in Table III) and experimental values of 78 and 79 ps for the two expansion conditions of the experiment. In contrast, the

lifetimes for the sublevels of $\nu'=19$, $J=5$ vary from 100 to 700 ps, compared to 220 ps for $J=0$ and measured values between 35 and 43 ps. $\nu'=19$ may be a “worst case” comparison since it lies so near the $\Delta\nu=-2$ channel closing and may thus be ultrasensitive to specific resonances. There is a similarly strong disagreement between theory and experiment for $\nu'=18$.

Calculations for ArI_2 are similar to those presented here for ArBr_2 in that the predicted dynamics are in the intermediate IVR regime such that the results are strongly dependent on the initial state quantum numbers. In contrast, experimental results for ArI_2 have been interpreted assuming the dynamics are in the statistical IVR regime.³ One suggestion for reconciling experiment and theory for ArI_2 is that rotational averaging may smooth out the predicted theoretical variations. In this regard, it is interesting to note that for ArBr_2 the data do not vary as much as predicted by theory, but rotational averaging does not result in a monotonically smooth dependence of product appearance time on vibrational level.

In addition to data for the T-shaped ArBr_2 isomer discussed above, we report initial data for the linear isomer. As for ArI_2 , the linear isomer of ArBr_2 contributes a quasicontinuous spectrum. Based on the X state potential energy surface^{17,27} and the expected B state surface, Franck-Condon excitation of the linear isomer is expected to deposit significant energy into the $\text{Ar}-\text{Br}$ mode and lead to rapid dissociation. The data reported here indicate that the lifetime for the linear isomer is, at most, 20 ps. It is not yet clear whether this represents a residual time due to a bound state component contributing to the excited state or some other effect. The product state distributions obtained from the probe spectra in Fig. 4 indicates that much of the energy deposited goes into the product translation and rotation, although, given the linear configuration, the translational degree of freedom likely receives most of the energy. If we estimate the linear ground state bond energy to be near that of the T-shaped isomer, 213 cm^{-1} , then, for the excitation at 18 363 cm^{-1} , the most probable product channel of $\nu'=13$ has almost 500 cm^{-1} of excess translational and rotational energy. Similarly, for the excitation at 18 844 cm^{-1} , the most probable product channel of $\nu'=17$ has about 520 cm^{-1} of excess energy. The lowest vibrational level detected at this excitation energy, $\nu'=11$, has 1200 cm^{-1} of excess energy. This result is consistent with recent work on linear ArI_2 by Darr *et al.*,¹¹ where they observed a continuum signal corresponding to product translational energy extending for over a 1000 cm^{-1} while probing for I_2 (B , $\nu'=28$). Preliminary results for linear ArBr_2 indicate a disagreement between experiment and theory: the measured vibrational distribution is much broader than the calculations. In the future, we hope to provide careful source pressure dependence studies to determine if the experimental results are contaminated by larger clusters.

There is also much still to be done to better characterize the T-shaped isomer. Many unassigned peaks were observed in the excitation spectra. We suspect that some of these peaks may be due to excited van der Waals vibrational modes. If so, it will be very interesting to determine how the lifetimes depend on excitation of the van der Waals modes. If the signal-to-noise ratios can be further improved, it will also be

useful to study both higher and lower vibrational levels for a more complete comparison to theory. Such work would justify an attempt to optimize the assumed potential energy surface and calculate results for other rotational levels. Given that the lifetimes are quite sensitive to the assumed potential, it may be worthwhile to study the other isotopomers. For the lower vibrational levels with longer lifetimes, it would be useful to perform higher frequency resolution studies to determine lifetimes for different angular momentum components of the distribution. Although it is unlikely that complete rotational resolution will be obtained for ArBr_2 , any progress toward that goal would still be useful.

Finally, we wish to comment further on the bond energy trends revealed in Table IV. The data contributed here complete the matrix of possibilities for He, Ne, and Ar bound to Cl_2 , Br_2 , and I_2 . The three $\text{He}-\text{X}_2$ bonds have nearly the same D_0 value for the ground electronic state. The NeBr_2 bond is distinctly stronger than that of NeCl_2 and even slightly stronger than that of NeI_2 . Only for $\text{Ar}-\text{X}_2$ is the expected trend realized: $D_0(\text{ArCl}_2) < D_0(\text{ArBr}_2) < D_0(\text{ArI}_2)$. For Cl_2 , bond energies also have been measured for Kr and Xe.³⁴ The trends in going from HeCl_2 to XeCl_2 are as expected, but the details are still interesting. The NeCl_2 bond is nearly four times as strong as that of HeCl_2 . Half of this difference is due to the mass difference, rather than the potential energy difference. The ArCl_2 is three times as strong as that of NeCl_2 , most of this difference is due to the potential energy. The KrCl_2 and XeCl_2 bonds are only incrementally stronger than that of ArCl_2 . The fact that there is no incipient chemical bonding for XeCl_2 has already been noted,³⁵ it would be interesting to revisit this issue as electronic structure codes continue to improve.

VI. SUMMARY AND CONCLUSIONS

We have presented evidence for the concomitant existence of both a T-shaped and a linear isomer for ArBr_2 . Interpretation of this data is facilitated by similarities to the extensively studied ArI_2 molecule. For the T-shaped isomer, a ground state $\text{Ar}-\text{Br}_2$ bond energy of 213 cm^{-1} is obtained. This is nearly in the middle of the range between the $\text{Ar}-\text{Cl}_2$ and the $\text{Ar}-\text{I}_2$ bond energies. Product appearance times from vibrational predissociation of the T-shaped isomer are reported for a range of Br_2 stretching vibrational levels. Although the product appearance times generally decrease as vibrational excitation increases, there are significant deviations from the trend, indicating that specific IVR resonances are important. This is confirmed by accurate wave packet calculations on a potential energy surface adjusted to give qualitative agreement between experiment and theory. The calculated product vibrational distributions are in excellent agreement for the T-shaped isomer, but agreement is not as good for the linear isomer. Since minimal adjustments were made to the potential in this study, it may be possible to achieve better agreement for the linear isomer by improving the potential. The calculations suggest that the dissociation dynamics changes from the sparse regime for low vibrational levels to the intermediate regime for the higher levels. Agreement between experiment and theory is particularly

good in the intermediate regime. In general, the dissociation dynamics of the T-shaped isomer are dominated by the lowest open $\Delta\nu$ channel except in the region of a channel closing. In contrast, dissociation of the linear isomer results in large translational energy release into the product degrees of freedom. This initial study suggests that ArBr₂ may be a particularly fruitful case for the comparison of theory to experiment. Although obtaining experimental data for this molecule is quite challenging, it will be worth the effort to extend the studies reported here.

ACKNOWLEDGMENTS

This work has been supported by the U.S. National Science Foundation, Award Nos. CHE-0213149 and CHE-0404743. The UC-Mexus-Conacyt program funded visits between Cuernavaca (Professor Hernández) and Irvine to discuss the results presented in this paper. One of us (O.R.) would like to acknowledge the “Ministerio de Educación y Ciencia” for a grant “Salvador de Madariaga” for supporting his sabbatical stay at UCI. We would also like to acknowledge Lee G. Moritz for machining key parts that led to the success of these experiments. Another author (C.R.B.) acknowledges support from the Hewlett-Mellon Faculty Development Fund and the Herbert H. and Grace A. Dow Trustee’s Professorship of Albion College. Another author (N.M.) received additional financial support from the Albion College Foundation for Undergraduate Research, Scholarship and Creative Activity.

- ¹D. D. Evard, C. R. Bieler, J. I. Cline, N. Sivakumar, and K. C. Janda, *J. Chem. Phys.* **89**, 2829 (1988).
- ²N. Halberstadt, J. A. Beswick, O. Roncero, and K. C. Janda, *J. Chem. Phys.* **96**, 2404 (1992).
- ³M. L. Burke and W. Klemperer, *J. Chem. Phys.* **98**, 6642 (1993).
- ⁴A. E. S. Miller, C. C. Chuang, H. C. Fu, K. J. Higgins, and W. Klemperer, *J. Chem. Phys.* **111**, 7844 (1999).
- ⁵O. Roncero and S. K. Gray, *J. Chem. Phys.* **104**, 4999 (1996).
- ⁶J. A. Blazy, B. M. DeKoven, T. D. Russell, and D. H. Levy, *J. Chem. Phys.* **72**, 2439 (1980).
- ⁷K. E. Johnson, W. Sharfin, and D. H. Levy, *J. Chem. Phys.* **74**, 163 (1981).
- ⁸G. Kubiak, P. S. H. Fitch, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **68**, 4477 (1978).
- ⁹J. J. Valentini and J. B. Cross, *J. Chem. Phys.* **77**, 572 (1982).
- ¹⁰M. L. Burke and W. Klemperer, *J. Chem. Phys.* **98**, 1797 (1993).

- ¹¹J. P. Darr, J. J. Glennon, and R. A. Loomis, *J. Chem. Phys.* **122**, 131101 (2005).
- ¹²O. Roncero, B. Lepetit, J. A. Beswick, N. Halberstadt, A. A. Buchachenko, *J. Chem. Phys.* **115**, 6961 (2001).
- ¹³J. A. Cabrera, C. R. Bieler, B. C. Olbricht, W. E. van der Veer, and K. C. Janda, *J. Chem. Phys.* **123**, 054311 (2005).
- ¹⁴W. E. van der Veer, U.S. Patent No. 6,804,044 B2 (12 October 2004).
- ¹⁵W. E. van der Veer, *Laser Focus World* **37**, 141 (2001).
- ¹⁶D. D. Evard, J. I. Cline, and K. C. Janda, *J. Chem. Phys.* **88**, 5433 (1988).
- ¹⁷R. Prosimi, C. Cunha, P. Villareal, and G. Delgado-Barrio, *J. Chem. Phys.* **116**, 9249 (2002).
- ¹⁸O. Roncero, D. Caloto, K. C. Janda, and N. Halberstadt, *J. Chem. Phys.* **107**, 1406 (1997).
- ¹⁹N. Halberstadt, S. Serna, O. Roncero, and K. C. Janda, *J. Chem. Phys.* **97**, 341 (1992).
- ²⁰H. Tal-Ezer and R. Kosloff, *J. Chem. Phys.* **81**, 3967 (1984).
- ²¹R. F. Barrow, T. C. Clark, J. A. Coxon, and K. K. Yee, *J. Mol. Spectrosc.* **51**, 428 (1974).
- ²²A. Rohrbacher, N. Halberstadt, and K. C. Janda, *Annu. Rev. Phys. Chem.* **51**, 405 (2000).
- ²³M. Nejad-Sattari and T. A. Stephenson, *J. Chem. Phys.* **106**, 5454 (1997).
- ²⁴J. I. Cline, N. Sivakumar, D. D. Evard, C. R. Bieler, B. P. Reid, N. Halberstadt, S. R. Hair, and K. C. Janda, *J. Chem. Phys.* **90**, 2605 (1989).
- ²⁵D. S. Boucher, D. B. Strasfeld, and R. A. Loomis, J. M. Herbert, S. E. Ray, and A. B. McCoy, *J. Chem. Phys.* **123**, 104312 (2005).
- ²⁶S. E. Ray and A. B. McCoy, J. J. Glennon, J. P. Darr, E. J. Fesser, J. R. Lancaster, and R. A. Loomis, *J. Chem. Phys.* **125**, 164314 (2006).
- ²⁷L. Beneventi, P. Casavecchia, G. G. Volpi, C. R. Bieler, and K. C. Janda, *J. Chem. Phys.* **98**, 178 (1993).
- ²⁸J. J. Breen, D. M. Willberg, M. Guttmann, and A. H. Zewail, *J. Chem. Phys.* **93**, 9180 (1990).
- ²⁹A. Buchachenko, N. Halberstadt, B. Lepetit, and O. Roncero, *Int. Rev. Phys. Chem.* **22**, 153 (2003).
- ³⁰D. G. Jahn, S. G. Clement, and K. C. Janda, *J. Chem. Phys.* **101**, 283 (1994).
- ³¹A. Burroughs, G. Kerenskaya, and M. C. Heaven, *J. Chem. Phys.* **115**, 784 (2001).
- ³²A. Burroughs and M. C. Heaven, *J. Chem. Phys.* **114**, 7027 (2001).
- ³³M. C. Heaven, *Chem. Soc. Rev.* **15**, 405 (1986).
- ³⁴C. R. Bieler, K. E. Spence, and K. C. Janda, *J. Phys. Chem.* **95**, 5058 (1991).
- ³⁵D. M. Proserpio, R. Hoffman, and K. C. Janda, *J. Am. Chem. Soc.* **113**, 7184 (1991).
- ³⁶As pointed out by the reviewer, we are reporting “product appearance times” for the excitation to a particular level. More precisely, what we refer to as a lifetime is $1/k$ for a single exponential fit to the product appearance. Given the frequency width of our laser and the uncertainty width of the individual rotational levels, it is not possible to directly measure state-to-state dynamics. We therefore follow the traditional practice of referring to the inverse product appearance rate constants as lifetimes.