Dynamics of linear and T-shaped Ar–I₂ dissociation upon \( B \leftrightarrow X \) optical excitation: A dispersed fluorescence study of the linear isomer

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(Received 3 June 1999; accepted 11 August 1999)

We report the dispersed fluorescence spectra of the linear and the previously well-studied T-shaped isomers of Ar–I₂ following \( B \leftrightarrow X \) optical excitation for \( \nu_{\text{pump}} = 16–26 \), below the I₂ dissociation limit. The linear isomer has a continuum excitation spectrum. For excitation at the highest pumping energy (\( \nu_{\text{pump}} = 26 \)), the product vibrational state distribution is nearly identical to that observed for excitation above the I₂(\( B \)) dissociation limit; it shows a broad, nearly Gaussian distribution of I₂(\( B \)) vibrational states, with about 22% of the available excess energy deposited in translation of the Ar+I₂. This gives direct evidence that the ‘‘one-atom cage’’ effect seen above the I₂(\( B \)) dissociation limit is attributable to the linear Ar–I₂ isomer. The product vibrational state distribution becomes increasingly Poisson for decreasing excitation energies, and only about 7% of the excess energy is deposited in translation for \( \nu_{\text{pump}} = 16 \). The bond energy in the linear isomer is determined from the spectra, \( 170(\pm 1.5) < D_0^L(\text{linear Ar–I}_2(X)) < 174(\pm 1.5) \text{ cm}^{-1} \). A bond energy of \( D_0^T(\text{T-shaped Ar–I}_2(X)) = 142\pm 15 \text{ cm}^{-1} \) is estimated based on the linear to T-shaped population ratio observed in the beam, which is about 90 cm⁻¹ smaller than that determined from fluorescence spectra. We suggest that electronic quenching in the T-shaped isomer is nearly 100% for the highest vibrational level produced by vibrational predissociation. © 1999 American Institute of Physics.

I. INTRODUCTION

The binding, structure, and dynamics of van der Waals complexes of rare gases with halogens have been the subjects of long-standing investigation. Studies on Ar–I₂ have been most prominent, due to the readily accessible optical spectrum of I₂ together with the facile, inexpensive production of Ar–I₂. In pioneering research, Blazy, DeKoven, Russell, and Levy established the existence of the T-shaped isomer of Ar–I₂; they observed vibrationally-resolved fluorescence emanating from the B state I₂ following the \( B \leftrightarrow X \) electronic excitation of Ar–I₂.

The 1981 report by Saenger, McClelland, and Herschbach showed that fluorescence of free I₂ could be observed following excitation of Ar–I₂ up to 1400 cm⁻¹ above the dissociation limit of I₂. This result was soon confirmed by Valentini and Cross, who observed the dispersed fluorescence of the free I₂ after excitation of ArI₂ by 488 nm radiation. They suggested that the ‘‘one-atom caging’’ effect is the result of impulsive transfer of the iodine atom vibrational energy to translational energy of the argon atom. This energy transfer was also seen by Philippoz, van den Bergh, and Monot, who reported the vibrational state distributions of I₂ from fluorescence observed following excitation of the I₂ \( B \leftrightarrow X \) transition above the B-state dissociation limit in the complexes Ar–I₂, Ne–I₂, and Kr–I₂. For all cases, the vibrational distributions show broad gaussian distributions, with an average vibrational energy loss for the Ar–I₂ of about 22% of the total excess energy deposited in the B state Ar–I₂. Various dynamical calculations used to model the energy transfer based on the presumed T-shaped geometry gave results in poor agreement with the observed amount of I₂ to Ar energy transfer. Such impulsive energy transfer could readily be the result of a linear isomer of Ar–I₂. However, this isomer was not believed to be present in the adiabatic expansion, since the very low effective temperature generally produces considerable selectivity and it was generally assumed that only one isomer is present with enough population to be detected. In a little noted paper, Brown, Schwenke, and Truhlar reported the calculated potential energy surface of He–I₂; they found comparable minima for linear and T-shaped geometries.

Fluorescence studies of Ar–I₂ were continued by Burke and Klemperer; they collected total fluorescence following excitation of the Ar–I₂ (\( B \leftrightarrow X \)) band. They were able to partially rotationally-resolve the excitation spectrum, thereby determining the rotational constants of the T-shaped Ar–I₂ in the X and B states. More importantly, in addition to the absorption band of the T-shaped isomer, they observed a wavelength-independent fluorescence, which they attributed to the fluorescence from continuum excitation onto a repulsive potential surface of the linear isomer of Ar–I₂. Their data gave the first indication that both linear and T-shaped isomers are present under the identical expansion conditions. Additional experimental indications of the existence of two geometrically distinct isomeric forms has been given by the photoionization studies of Cockett, Beattie, Donovan, and Lawley. Since these works, the dynamics of the Ar–I₂ photodissociation has been re-examined using a linear Ar–I₂ geometry, and other calculations have shown the coexistence of linear and T-shaped Ar–I₂ complexes in the elec-
tronic ground state. For example, recent theoretical work by Kunz, Burghardt, and Hess, using a supermolecular ab initio calculation, has shown the coexistence of linear and T-shaped Ar—I₂, with calculated well depths (Dab) of 192.5 cm⁻¹ and 179.2 cm⁻¹, respectively. Most recently, Burroughs, Van Marter, and Heaven have reported that fluorescence-depletion, i.e., “hole-burning,” experiments demonstrate that fluorescence from free I₂ produced from excitation above the B-state dissociation limit is not depleted with excitation into the T-shaped B—X band of Ar—I₂; they did observe fluorescence depletion from the adjacent continuum which had been assigned to the linear isomer by Burke.

Linear isomers of rare-gas halogen complexes have been confirmed by direct observation of the rotational spectroscopy of Ar—ClF (Ref. 20) and He—ClF. For He—ClF, not only were pure rotational transitions of both the linear and the T-shaped isomer observed, but direct transitions between the linear and the T-shaped isomers establish the linear isomer to be the lower in energy. The experimental data and calculated potential curves indicate both the linear and T-shaped geometries are on the same, ground state potential energy surface of He—ClF.

Independent confirmation of the isomeric forms of Ar—I₂ is made difficult by the extremely small dipole moment of Rg—X₂, such that high resolution microwave spectroscopy on Rg—I₂ is difficult. In an elegant microwave study, Xu, Jäger, Ozier, and Gerry observed only the T-shaped isomer of ArCl₂. Studies on Rg—X₂ systems have been mainly conducted via the B—X electronic excitation of X₂, for example, Ne—Br₂, Ne—Cl₂, and Ar—Cl₂, and only T-shaped structures have been found.

In this paper, we extend the work of Burke by dispersing the laser-induced fluorescence of linear Ar—I₂ in the spectral region of 571 nm (v = 16) to 543 nm (v = 26), to obtain the nascent vibrational populations of I₂(B) produced by dissociation of Ar—I₂ following excitation of the B—X transition in the complex. As indicated by Burke, the B —X fluorescence from excitation of linear Ar—I₂, when integrated over all excitation wavelengths, is 2.1±0.4 times the total integrated fluorescence of the T-shaped isomer. However, the measured fluorescence of the linear isomer at any particular wavelength is approximately 15 times weaker than the peak fluorescence intensity of the T-shaped isomer, as the excitation is split into a continuum. In view of the impossibility of saturating an absorption continuum, the present work exploits the intracavity excitation technique to obtain the relatively weaker dispersed LIF signal for the linear isomer of Ar—I₂. Our methodology and results are strikingly similar to the work of Philippoz et al., where fluorescence was dispersed following excitation above the B state dissociation limit.

II. EXPERIMENT

The Ar—I₂ was formed in a molecular beam apparatus which was designed to fit within the cavity of a cw ring dye laser (Coherent model 899-21); the apparatus is shown schematically in Fig. 1. The molecular beam chamber consists of a 4 in. o.d. “tee” which is mounted inverted and with the tee perpendicular to the laser beam, in the region above the dye jet. The laser beam enters and exits the chamber through Brewster windows glued to 1/2 in. o.d. tubing mounted in Cajon-ultra-Torr fittings. The laser beam is at a 7° angle with respect to horizontal at the intersection with the chamber; the cajons are mounted at a similar angle, and ~0.5 in. below the tubing center line. The chamber, in combination with the Brewster windows settings, fits in the available space within the laser cavity. The chamber is pumped from above by a Roots-type mechanical blower with pumping speed 300/s.

The argon used in the expansion flowed through a bubbler which was filled with I₂ and teflon chips (to increase the surface area) and held at 60°C. The inlet line following the bubbler was held at 70°C to prevent condensation of the I₂. The Ar—I₂ complex was formed by supersonic jet expansion through a slit nozzle (100 μm×8 mm), located 5–6 mm below the laser beam. The backing pressure behind the nozzle was 15–30 psi, resulting in a chamber pressure of 20–60 mTorr. The dye laser was pumped by 6–8 W of light from an argon-ion laser operating in a multiwavelength mode. Two different output couplers were used during these experiments; with a nominally 2% output coupler the dye laser output power was 300 mW, which corresponds to a circulating intracavity power of 15 W. Replacing the coupler with a 1% output coupler resulted in an intracavity power ~4 times higher, or 60 W (the output power was too low to measure directly). The frequency stabilization was 1 MHz for the long periods of integration time needed for acquisition of the data shown here. Fluorescence was collected by a single 2 in. diam f/3 lens located ~12 in. from the interaction region. The image was rotated from nearly horizontal to nearly vertical by two mirrors, and then reimaged at the entrance slit of a 0.5 m (f/6.9) monochromator (Acton Research Corporation SpectraPro-500). Since the entrance slit is vertical, the uniform section of the laser/molecular beam fluorescence image corresponds to sampling across a narrow, uniform region which is parallel to the slit nozzle, i.e., which corresponds to a region of uniform temperature and jet conditions. Moving the nozzle to laser distance made no changes in the observed...
vibrational populations or spectral features. The monochromator was operated with a grating ruled at 300 grooves/mm, which provides adequate resolution of the vibrational bands. Fluorescence was detected with a silicon array detector (Princeton Instruments, RY-512), operating at −20 °C. This experimental configuration gave coverage over 80 nm spectral range in a single data set. Spectra shown are spliced from several sets of overlapping data, obtained by changing the center wavelength of the grating by 50 nm. Each data set was accumulated over 10–30 min integration time.

With our experimental conditions (laser power levels, use of a slit jet, and appropriate heating of the I₂ in the inlet line), the fluorescence following excitation of uncomplexed I₂, T-shaped Ar–I₂, and linear Ar–I₂ in the jet was readily apparent and distinguishable by eye, considerably aiding the optimization of the system. The fluorescence from excitation of the T-shaped Ar–I₂ isomer is distinct from that from excitation of uncomplexed I₂ by the blue-shift in the excitation band; the fluorescence from excitation of the linear isomer is distinct by being noticeably lower intensity, and independent of laser wavelength.

III. RESULTS AND ANALYSIS

The lifetimes of the T-shaped Ar–I₂(B) isomer is estimated to be 70 ps,²⁶ that for the linear isomer is estimated to be 150 fs, as discussed later in this paper. Since the lifetime of the complexes are orders of magnitude shorter than the radiative lifetime of the I₂ (10⁻⁶ s), the observed fluorescence signals originate from the dissociated I₂(B) photofragment emission. The dispersed fluorescence spectra therefore reveal product vibrational state distributions of the I₂(B) photofragment following dissociation of the complexes as has been shown in detail by Levy and co-workers.³,⁴ Figures 2(a), 2(b), and 2(c) show the dispersed fluorescence spectra of I₂ monomer, T-shaped and linear Ar–I₂ isomers upon I₂ B(ν₂ = 24)→X(ν’ = 0) excitation. The locations of excitation frequencies for each isomer and validation for formation of binary Ar–I₂, rather than higher order Arₙ(I₂)ₙ (m >1, n >1), have been extensively discussed by Burke.⁵ The T-shaped Ar–I₂ excitation band is discrete and is blue-shifted by 14 cm⁻¹ with respect to the I₂ B→X band. The excitation spectrum for the corresponding linear isomer is broadly continuous. The dispersed fluorescence spectrum resulting from the continuous linear Ar–I₂ isomer feature, as in Fig. 2(c), is at a maximum when the pump laser frequency is tuned to within ±5 cm⁻¹ from the uncomplexed I₂ B→X band origin. The dispersed fluorescence from the continuous linear Ar–I₂ is approximately a factor of 2 lower in intensity in between the maxima. The relative fluorescence intensity distributions for both isomers show little variation as experimental conditions (i.e., backing pressure and I₂ concentration) are varied. This assures that the excitation is from the Ar–I₂ isomers, rather than higher order clusters, as well as that the I₂ product vibrational distribution is not irreversibly altered by collisions in the jet. The carrier gas density remains high using a slit, rather than pinhole jet, and some collisional relaxation of the nascent I₂ is unavoidable. The remarkable difference shown in the dispersed fluorescence spectrum between Fig. 2(b) and 2(c) demonstrates the coexistence of both linear and T-shaped Ar–I₂ isomers under identical conditions in the jet.

To obtain details of the dissociation dynamics of the Ar–I₂ isomers in the B state, we have recorded the dispersed fluorescence spectra of both the T-shaped and the linear Ar–I₂ isomers following excitation in the spectral region of the I₂ (B(ν₂ = 16–26)→X(ν’ = 0) transitions (corresponding to 571 nm to 543.5 nm in wavelength). To avoid the complexity from high order clusters of Arₙ(I₂), the spectra of the linear isomers were carefully recorded using an excitation within 1 cm⁻¹ of the corresponding free I₂ B→X band origin. Determining the relative population of final product vibrational states from the measured dispersed fluorescence spectra is quite straightforward. The measured dispersed fluorescence intensity as a function of wavelength is determined by the relative population of final product vibrational states and the Franck–Condon factors (FCFs) of I₂ B→X. We calculated the corresponding FCFs based on the well-determined I₂ X and B states RKR potentials.²⁷ using

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**FIG. 2.** Overview of dispersed fluorescence spectrum following B(ν₂ = 24)→X(ν’ = 0) excitation of (a) I₂ monomer (b) T-shaped Ar–I₂ and (c) linear Ar–I₂. The peaks indicated by • are due to laser scattering. A noticeable energy gap (three I₂ vibration quanta) between the pump laser and first fluorescence emission band [I₂ B(ν’ = 21)→X(ν’ = 0)] in (b) clearly indicates that the product vibrational state distribution for the T-shaped complex is dominated by the Δν = 3 channel. For the linear Ar–I₂, the most intense feature in the dispersed fluorescence is peaked at 581.8 nm, or 33.6 nm red-shifted from the excitation wavelength. This peak has its main contribution from I₂ B(ν’ = 17)→X(ν’ = 2) emission. This indicates that for the linear isomer the dissociation process is quite facile, which leads to significant energy transfer from I→I vibration to fragments translation, with the most likely process loss of seven vibrational quanta from I₂(B). The feature labeled by • in (a) is due to the I₂ (B(ν’ = 23)→X(ν’ = 0) emission which is indicative of slight collisional relaxation in the jet.
LeRoy’s LEVEL program. The observed fluorescence intensity is also weighted by \( \nu^{-3} \) to correct for spontaneous emission probability. Our fits were taken from the bluer emission; at redder wavelengths the grating efficiency decreases slightly and the fitted spectrum generally shows a higher intensity than that measured. The vibrational intervals of the \( B \) state have a spacing approximately half that of the \( X \) ground state. This results, at our level of resolution, in overlapping bands. In the spectra only the bluest emission features, \((\nu_p, 0)\) and \((\nu_p - 1, 0)\) are distinct. For lower vibrational levels, such as \( \nu' = 14 \), the Franck–Condon factor for \((14, 0)\) is almost an order of magnitude smaller than the redder features, \((14, 1)\) and \((14, 2)\). The redder features, however, consist of overlapping bands with transitions from smaller \( \nu' \). For this reason we have only labeled the highest frequency feature, \((\nu_p, 0)\) in the figures.

Under our experimental conditions, the \( I_2 (B) \) fragments produced from the photodissociation of \( \text{Ar}–I_2 \) undergo slight collisional relaxation prior to radiative decay to the ground electronic state. The measured product vibrational state distributions must be corrected for this relaxation. It is evident from the \( I_2 \) monomer dispersed fluorescence spectrum as shown in Fig. 2(a), that there is a significant amount of \( I_2 (B) \) at \( \nu' = 23 \); the emission at 550.8 nm as denoted by \( \bullet \), is the \( I_2 (B, \nu' = 23) \rightarrow I_2 (X, \nu'' = 0) \) transition. This shows that \( I_2 (B) \) at \( \nu' = 23 \) is populated due to the collisional relaxation from the initially prepared \( I_2 (B, \nu' = 24) \) state. The population ratio of \([I(\nu' = 23)]/[I(\nu' = 24)]\), with FCFs taken into account, is approximately 0.25. We recorded the \( I_2 \) monomer dispersed fluorescence from \( \nu' = 15 \) to \( \nu' = 26 \) and found that in our jet conditions the corresponding population ratio, \([I(\nu' - 1)]/[I(\nu')]\), is invariant with the initially prepared \( \nu' \) state. This is also consistent with the results previously reported by Levy and co-workers. The ratio of \( \Delta \nu = -2/\Delta \nu = -1 \) may be estimated to be near 1/4 from early collisional relaxation measurements. Thus the \( \Delta \nu = -2 \) collisional relaxation is too small to make a significant contribution to the fitted vibrational distribution, and therefore was assumed to be zero. We thus take the collisional relaxation into account and correct the product vibrational state distribution obtained from the measured dispersed fluorescence spectra. The results are summarized in Table I. Figure 3 represents the corrected product vibrational state distributions of linear \( \text{Ar}–I_2 \) upon \( I_2 (B(\nu_{\text{pump}}) \rightarrow X(\nu' = 0)) \) excitation with \( \nu_{\text{pump}} \) ranging from 16 to 26.

There is no evidence of significant rotational excitation

![Image](https://i.imgur.com/3G75.png)

**FIG. 3.** The relative population of \( I_2 (B) \) product vibrational states resulting from photodissociation of linear \( \text{Ar}–I_2 \) following \( I_2 (B(\nu_{\text{pump}}) \rightarrow X(\nu' = 0)) \) excitation. The distribution for each \( \nu_{\text{pump}} \) state is deduced from the dispersed fluorescence spectra (as shown in Fig. 2(a)) with the corresponding \( I_2 (B \rightarrow X) \) Franck–Condon factors. For consistency, the pump laser frequency used in each excitation is centered about the corresponding \( I_2 (B \rightarrow X) \) band origin (less than \( \pm 1 \) cm\(^{-1}\)). A gradual shift in the \( I_2 \) product vibrational distribution from Gaussian to Poisson is observed as \( \nu_{\text{pump}} \) varies from 26 \( r_{26}(1-1) = 3.35 \) Å to 16 \( r_{16}(1-1) = 3.19 \) Å.
in the I$_2$(B) produced from photodissociation of either the linear or T-shaped Ar–I$_2$. First, higher resolution spectra taken using a 1200 grooves/mm grating, but not shown here, show no difference in the rotational envelope in the fluorescence from the linear or T-shaped Ar–I$_2$ as compared to that of the monomer I$_2$. Some rotational relaxation is evident in the spectra of all three, which is attributed to collisions within the high-pressure jet; an average of two collisions would make an average loss of four rotational quanta. Second, the peak envelopes are not broadened with decreasing vibrational level in the dispersed fluorescence spectra. This demonstrates that the excess energy is partitioned into translational energy, not rotational excitation. Third, the peak positions (frequencies) are as predicted for a fluorescing I$_2$ rotational population at low-J levels. The peak positions also do not show a frequency shift which changes with decreasing vibrational level in the dispersed fluorescence spectra. These results are consistent with little to no rotational excitation of the photodissociated I$_2$, which is as expected if the Ar–I$_2$ dissociates from either an exactly linear or exactly T-shaped geometry.

Each isomer of Ar–I$_2$ yields a photofragment distribution that is distinctive in the resultant I$_2$ fluorescence. In general, the product vibrational distribution of the T-shaped isomer shows a Poisson distribution, with onset of the I$_2$ product vibrational state (ν') appearing at ν' = (ν$_{\text{pump}}$ - 3) for these excitation frequencies. Our results for the T-shaped fluorescence are in excellent agreement with earlier work of Levy and co-workers; our data show no improvement upon the earlier fluorescence data of Levy and co-workers, and are not shown.

The dispersed fluorescence spectra of the linear isomer, an example of which is shown in Fig. 2(c), demonstrate how dramatically the vibrational populations of the resulting free I$_2$ are affected by the transfer of energy from the I$_2$ oscillator to translational energy of Ar–I$_2$. This energy transfer is also a dramatic function of the excitation energy. For the highest vibrational excitation (ν$_{\text{pump}}$ = 26), the I$_2$ transfers an average of about 22% of the I$_2$ vibrational excitation into kinetic energy of the Ar, and the resultant vibrational distributions are broad and Gaussian. The vibrational distribution is similar to those observed by Valentini and Cross, and by Philippoz et al., for excitations above the I$_2$ B-state dissociation limit. Our data, taken for excitation energies where the two isomers are distinguishable, clearly show that the abundant linear isomer of Ar–I$_2$ is responsible for the “one-atom cage effect” observed at excitation energies above the B-state dissociation limit.

For lower vibrational excitations (ν$_{\text{pump}}$ = 16, 18), the I$_2$ transfers much less of the vibrational energy into kinetic energy of the Ar, with the distribution for ν$_{\text{pump}}$ = 16 being nearly identical to that observed for the T-shaped isomer, as shown in Fig. 4. Both isomers show strikingly similar vibrational distributions, but different onsets for the I$_2$ fragment vibrational product states (ν'), with ν' = (ν$_{\text{pump}}$ - 3) for the T-shaped isomer and ν' = (ν$_{\text{pump}}$ - 2) for the linear isomer.

For both the T-shaped and linear Ar–I$_2$ complexes, the onset of the I$_2$ fragment vibrational product state (ν') resulting from the dissociation of the complex reveals information about the ground state binding energy; these energy relationships are shown schematically in the energy level diagram of Fig. 5. As can be seen from the energy cycle of Fig. 5, the photon energy initially deposited into the complex, $h\nu_i$, is equivalent to the sum of the ground state binding energy and total energy of the fragments resulting from the dissociation of the complex; that is,

\[
\Delta G(I_2(B)) = h\nu_i - \Delta G(I_2(\text{g}))/G(I_2(B)/I_2(\text{g})).
\]

![FIG. 4. Dispersed fluorescence spectrum of (a) T-shaped (b) linear Ar–I$_2$ isomers upon I$_2$ B(ν$_{\text{pump}}$ = 16) – X(ν' = 0) excitation. The peaks indicated by ■ are due to laser scattering. The inset diagrams represent the I$_2$ (B) vibrational product state distributions. Both isomers show strikingly similar Poisson distributions but different onsets of the I$_2$ product vibrational states (ν'), with ν' = 14 for the linear Ar–I$_2$ and that of ν' = 13 for the T-shaped isomer. The overlapped simulated spectra show excellent agreement with the experiment. The linewidth used in the simulation is 1.65 nm, which is mainly limited by the resolution (300 groves/mm) of the monochromator (as is evident from the laser scattering peak width). Here and in Fig. 6 only the highest frequency feature is labeled. As discussed in the text the more intense lower frequency features are blends of several overlapping bands.](image)

![FIG. 5. Energy level diagram showing the relationship between the excitation energy ($h\nu_i$) and fluorescence energy ($h\nu_f$), from which Eqs. (1), (2), and (4) are derived. Note that the energy relationships are correct for both the linear and the T-shaped Ar–I$_2$. Energy increases to the top in the figure, but for clarity the spacing between levels is not proportional to energy. The quantity $\Delta G(I_2(B))$ is defined as the vibrational energy difference between the ν' and ν$_{\text{pump}}$ levels in free I$_2$. G(ν', I$_2$(B)) – G(ν$_{\text{pump}}$, I$_2$(B)).](image)
If the Ar–I₂ has internal energy, the energetics of the excitation and fluorescence process are such that

$$E_0 + h
\nu_j = D_0^\trans(X) + h
\nu_f + E_{\text{trans}} + E_{\text{rot}}. \quad (3)$$

The internal energy $E_0$ consists of rotation and vibration of the Ar–I₂. Some picture of the initial excitation $E_0$ is obtained under the assumption of thermal equilibrium in the jet. The jet temperature of 15±5 K is taken from detailed studies of hydrogen fluoride expansions in argon performed under similar expansion conditions.\(^{29}\) The degrees of freedom relevant to the present are most likely internal vibrations, since it is unlikely that rotational energy of the complex may be facely converted into vibrational energy of $B$-state I₂. The high-frequency vibration of the Ar–I₂ complex is essentially that of I₂, namely, 214 cm⁻¹. At 15 K the population of the first excited state is negligible. The vibrational frequencies of the soft intermolecular modes of the two isomeric forms of Ar–I₂ are similar. For the linear isomer the vibrational interval calculated using the Kunz, Burghardt, and Hess\(^{18}\) potential is 22.2 cm⁻¹ for the degenerate bend. At the nominal jet temperature of 15 K this results in 18% population in this level. The stretching vibrational interval is calculated to be 27 cm⁻¹, resulting in a population of 6% in this level. Adding these two excited populations gives a total excited state population of nearly 25%.

Evaluating the contribution of these excited states, in particular the degenerate bending level, to the estimated dissociation energy is slightly complicated. We first combine the two states and assume that the photofragment distribution is similar to that of the ground state. The vibrational distribution of photofragment $B$-state I₂ following excitation of the higher $\nu_{\text{pump}}$ levels, $\nu_{\text{pump}} \geq 22$ shows a Gaussian distribution, thus the highest $\nu^\trans$ level produced could result from transitions from excited vibrational levels of Ar–I₂(X). The consequence of this would be to increase our estimate of the dissociation energy by 22.2 cm⁻¹. We do not believe, however, that this occurs. For the excitation of low $\nu_{\text{pump}}$ levels, in particular, $\nu_{\text{pump}} = 16$, the photofragment I₂ vibrational distribution is peaked at the highest $\nu^\trans$ level ($\nu^\trans = 14$). This high abundance rules out the production of this level from transitions where the Ar–I₂(X) is excited to the state with one bending quantum. Explicitly, the laser pumping is at 17516.5 cm⁻¹ and the highest energy fluorescence is observed at 17315.7 cm⁻¹, setting an upper limit of 201 cm⁻¹ for the dissociation energy of the complex, $D_0^\trans$. We make similar arguments for pumping at $\nu_{\text{pump}} = 22$ and probably $\nu_{\text{pump}} = 24$ since here the highest level produced, $\nu^\trans = 14$, has a relative population of 14% and 10%, respectively. If all of the highest level were produced from hot band excitation this requires a quite peaked vibrational distribution in the resulting photofragment I₂. This would mean that the dissociation of the hot bending state is entirely different than the ground state. Physically it is not obvious that the energy in the bending mode will appear in the vibration of the I₂ photofragment. We therefore believe that the error estimate of $D_0^\trans$ should not be significantly increased from that obtained ignoring the thermal population of the Ar–I₂.
IV. DISCUSSION

In order to carry out a meaningful discussion of the Ar–I$_2$(B) photodissociation dynamics, we need to establish what is known about the potential curves, i.e., dissociation energies and bond lengths, for the T-shaped and linear isomers in both the X and B states. We take as the starting point our accurate determination of the bond strength for the linear isomer, 170(±1.5)<$D_0^b$(linear Ar–I$_2$(X))<174(±1.5) cm$^{-1}$. The fact that the linear and T-shaped isomers are both observed in the jet under identical conditions shows directly that the bond energies for the linear and T-shaped isomers must be similar, under the assumption of isomerization equilibrium. Burke$^5$ has previously estimated that isomeric composition of the jet is $N_{\text{linear}}/N^T=3$. We note that this estimate was based upon a flat excitation profile for the linear isomer. Here we have found a variation of a factor of two in the excitation profile. This produces an uncertainty in the estimate of the relative absorption of the two isomeric forms. The jet temperature is estimated to be $T=15±2$ K. The geometry of the two isomeric forms is known well enough to obtain the ratio of rotational partition functions; at 15 K the rotational partition function of the T-shaped isomer is approximately eight times greater than that of the linear isomer. The contribution of vibration to the partition functions is ignored. Under the assumption of the existence of equilibration between the two forms we calculate that $D_0^b$ of the linear isomer is (3±0.5)kT larger than that of the T-shaped isomer. This is 30±12 cm$^{-1}$, where our error estimate includes a 5K uncertainty in the temperature. We thus calculate that the T-shaped isomer has a bond strength of 142±15 cm$^{-1}$. This bond energy can be contrasted with the T-shaped bond energy found by Levy and co-workers of 234.2<$D_0^b$(T-shaped Ar–I$_2$(X))<240.1 cm$^{-1}$—a dramatic disagreement. Levy and co-workers used an alternate approach to determine the Ar–I$_2$ bond energy, which is also evident from Fig. 5. They used the alternate relationship,

$$D_0^b(\text{Ar}–\text{I}_2(B))=[G(v'_{\text{pump}},I_2(B))−G(v',I_2(B))]−E_{\text{trans}}(\text{Ar}+I_2),$$

thereby determining the bond energy in the excited B-state Ar–I$_2$ from the point at which the fluorescence photon energy is largest, which presumably occurs at the threshold where $E_{\text{trans}}(\text{Ar}+I_2)$ equals zero. They then applied the $B→X$ blue shift of 14 cm$^{-1}$ to determine the ground-state bond energy. Since our vibrational state distribution for the T-shaped isomer fluorescence is in excellent agreement with theirs, we have no reason to question their fluorescence data. This discrepancy between the expected T-shaped bond energy and the one determined by Levy and co-workers is surprising and unexpected. We conclude that the highest vibrational level of photofragment I$_2$ produced following excitation of T-shaped Ar–I$_2$(B) must be essentially 100% quenched. That is, this level shows nearly 100% “electronic predissociation” to the $B'' ^1\Pi_{uu}$ state of Ar–I$_2$, which has a potential curve which is repulsive, i.e., dissociative to I+I and therefore does not fluoresce. Indeed, small intensities at an I$_2$ vibrational state with $v'=2(v'_{\text{pump}}=2)$ are seen in the dispersed fluorescence spectra of Ar–I$_2$ of Levy and co-workers,$^3$ which is consistent with those states being energetically accessible, and all but a small fraction quenched. Small intensities in these states are below our poorer signal to noise limit. We therefore conclude that the bond energy in T-shaped Ar–I$_2$ is weaker by about one quantum of B-state I–I vibration (80 cm$^{-1}$) than that previously reported. We will return to the dynamical implications of the T-shaped quenching later in this paper.

These bond energies can be compared to the results of the most recent ab initio CCSD(T) calculations of Kunz$^e$ et al., who gave calculated well depths, $D_0^b$, of 192.5 cm$^{-1}$ for the linear isomer and 179.2 cm$^{-1}$ for the T-shaped isomer of Ar–I$_2$. If these are corrected for the zero-point energies, estimated to be about 20 cm$^{-1}$ for the linear isomer and slightly less for the T-shaped isomer, their results give $D_0^b$(linear Ar–I$_2$(X))≈173 cm$^{-1}$, and $D_0^b$(T-shaped Ar–I$_2$(X))≈160 cm$^{-1}$. Their calculated energies for the two isomers are thus in close agreement with our determination of the bond energies for the linear and T-shaped isomers in the ground state.

We summarize the known energetics and molecular parameters as follows: The bond energy of the linear isomer is $D_0^b$(linear Ar–I$_2$(X))=172±3.5 cm$^{-1}$ (this work); the bond energy in the linear excited state is unknown. The difference in energy between the linear and T-shaped isomers, based on the equilibrium linear to T-shaped ratio of 3:1 (determined from the fluorescence in the jet by Burke$^5$) is $D_0^b$(linear Ar–I$_2$(X))−$D_0^b$(T-shaped Ar–I$_2$(X))=30±12 cm$^{-1}$, from which we estimate $D_0^b$(T-shaped Ar–I$_2$(X))=142±15 cm$^{-1}$. The blue shift in the $B→X$ excitation frequency (determined by Levy and co-workers$^3$) is 13−14 cm$^{-1}$ (depending on vibrational level) dictates that $D_0^b$(T-shaped Ar–I$_2$(X))=14 cm$^{-1}$, so that $D_0^b$(T-shaped Ar–I$_2$(X))=128±15 cm$^{-1}$. The rotational contours in the $B→X$ fluorescence spectrum were used to estimate the Ar–I$_2$ bond distances, $R_0^b$(T-shaped Ar–I$_2$(X))=4.02 Å and $R_0^b$(T-shaped Ar–I$_2$(X))=4.04 Å (from Burke$^5$). Bond distances in the linear molecule cannot be determined experimentally, because of the continuum excitation spectrum. Finally, we point out that the observation of the distinct fluorescence spectra show that the two isomers of Ar–I$_2$ are noninterconverting, and the photodissociation dynamics for Ar–I$_2$(B) occur separately, as seen in this work and the recent work of Burroughs et al.$^{19}$

Further discussion of the dynamics of the photodissociation of Ar–I$_2$(B) is now possible, given the above energetics. We begin with the energy balance equations for the initial preparation of the Ar–I$_2$(B) state, shown schematically in Fig. 7,

$$h\nu_i=D_0^b(\text{Ar}–\text{I}_2(B))+T_0(I_2(B))+E_{\text{ vib}}(\text{Ar}–\text{I}_2(B))−G(0)(I_2(B))−D_0^b(\text{Ar}–\text{I}_2(B)).$$

In Eq. (5), $h\nu_i$ is the energy of the exciting photon (as in Eq. (1)); $D_0^b(\text{Ar}–\text{I}_2(X))$ is the bond energy between Ar and I$_2$(X), or 172 cm$^{-1}$; $T_0(I_2(B))$ is the excitation energy of the B state in free I$_2$, or 15724.94 cm$^{-1}$; $E_{\text{ vib}}(\text{Ar}–\text{I}_2(B))$ is the total vibrational energy in Ar–I$_2$(B); $G(0)(I_2(B))$ is the
zero point energy of free $I_2(B)$, or 62.54 cm$^{-1}$; and $D_v'(Ar-I_2(B))$ is the bond energy between $Ar$ and $I_2(B)$, which is not known. Note that the rotational energy, $E_{\text{rot}}$, is assumed negligible, and therefore set equal to zero in Eq. (5), as expected for dissociation of an exactly linear $Ar-I_2$, and as observed from our spectra and discussed earlier. The vibrational energy in the $Ar-I_2$ and $I-I$ potentials, with the zero of energy being at the equilibrium bond distances, is found by substitution into Eq. (5).

$$E_{\text{vib}}(Ar-I_2(B)) = h\nu_2 - 15 834 \text{ cm}^{-1} + D_v'(Ar-I_2(B)).$$

(6)

Following dissociation of the complex, the final vibrational energy in free $I_2$, $E_{\text{vib}}(I_2(B))$, which is observable in this experiment, is given by Fig. 7 and Eq. (7).

$$E_{\text{vib}}(I_2(B)) = E_{\text{vib}}(Ar-I_2(B)) - D_v'(Ar-I_2(B)) - E_{\text{trans}}(Ar+I_2).$$

(7)

The final translational energies of $Ar$ and $I_2$ are determined by the initial parameters of energy (given by Eq. (5)), bond lengths, and atomic momenta of $Ar-I_2(B)$ (determined from the excitation energy and the Franck-Condon parameters). The trajectories of the $Ar-I_2(B)$ are then determined by the evolution of the excited state on the potential energy surfaces of $Ar-I_2(B)$.

An additional view of the system is to define the available excess energy (energy in excess of the $Ar+I_2(B)$ dissociation limit) of $Ar-I_2(B)$,

$$E_{\text{avl}} = E_{\text{vib}}(I_2(B)) + E_{\text{trans}}(Ar+I_2),$$

(8)

which from substitution of Eqs. (6) and (7), or by examination of Fig. 7, can be seen to be entirely determined by the excitation photon energy,

$$E_{\text{avl}} = E_{\text{vib}}(Ar-I_2(B)) - D_v'(Ar-I_2(B))$$

$$ = h\nu_2 - 15 834 \text{ cm}^{-1}.$$ 

(9)

This provides a convenient way to express the partitioning of the excess energy between the resulting vibrational energy of $I_2(B)$ and the recoil translational motion of $Ar$ and $I_2(B)$, average % recoil translational energy

$$= 100\% \times (E_{\text{avl}} - (E_{\text{vib}}(I_2(B))) \bigg/ E_{\text{avl}}. $$

(10)

The average $(E_{\text{vib}}(I_2(B)))$ is directly determined experimentally (population fraction in Table I times the $E_{\text{vib}}(I_2(B)))$. The quantities $E_{\text{avl}}$, $(E_{\text{vib}}(I_2(B)))$, and the average percent recoil translational energy are summarized in Table II. A graph of the average percent recoil translation energy is given in Fig. 8. The data points for the $\nu = 16-26$ are from this work; the two points above the $B$-state dissociation energy are calculated by us using the graphical presentation of the vibrational state distributions given by Philippoz et al. Figure 8 shows in a very dramatic fashion the substantial difference in vibrational/translational energy distribution on going from the lower $\nu_{\text{pump}}$ excitations to the higher $\nu_{\text{pump}}$ excitations. It also gives a clear presentation that the average percent recoil translational energy reaches a maximum at $\sim \nu_{\text{pump}} = 26$, and further, the average percent recoil translational energy shows no discontinuity between excitation in the bound states versus excitation above the dissociation limit.

FIG. 7. Energy level diagram showing the total vibrational energy in $B$-state $Ar-I_2$ as a function of excitation energy, from which Eqs. (5)–(9) are derived. Energy increases to the top in the figure, but for clarity the spacing between levels is not proportional to energy. Note that the vibrational energies $E_{\text{avl}}(Ar-I_2(B))$ and $E_{\text{avl}}(I_2(B))$ are defined with respect to zero at the equilibrium bond distances, and the quantity $\{E_{\text{avl}}(I_2(B)) + E_{\text{trans}}(Ar+I_2)\}$ is defined as the “available energy,” $E_{\text{avl}}$, of Eq. (8).

FIG. 8. Average percent recoil translational energy vs total available energy $(E_{\text{avl}})$ graph represents the wavelength dependent photodissociation dynamics of linear $Ar-I_2 (B)$. Data below the $I_2(B)$ state dissociation limit are taken from Fig. 3 and Table II. Data above the dissociation limit are estimated from Philippoz et al. (Fig. 8 in Ref. 8). The percentage of total available energy partitioned into recoil translation shows a sharp increase from $\nu_{\text{pump}} = 16$ (7.7%) to $\nu_{\text{pump}} = 26$ (21.7%) and reaches a plateau (23.2%) above the $I_2(B)$ state dissociation limit.
B-state dissociation limit. This gives very clear evidence that the caging process observed for excitation to energies above the dissociation threshold has identical molecular dynamics to the process below the dissociation threshold. Stated another way, the process above the dissociation limit therefore does not proceed via a “dissociation” followed by a “re-combination” of the \( I_2 \).

We note that Beswick and co-workers\(^\text{30}\) proposed a mechanism for the 1-atom cage effect beginning by initial excitation to the repulsive \( B''\) \( I_1 I_2 \) state (perpendicular transition) then undergoing nonadiabatic crossing to the \( B \) state. This mechanism has been ruled out by Zewail and co-workers.\(^\text{31}\)

Quantum dynamical calculations on the photodissociation of \( Ar–I_2 \) have been reported by several authors, but have only been concerned with the dynamics above the \( B \)-state dissociation limit.\(^\text{11,13,14}\) A relatively detailed treatment is under-way by Halberstadt and Janda;\(^\text{32}\) their preliminary results do show substantially smaller percent recoil translational energy for the lower \( v_{pump} \). It is beyond the scope of our present work to develop quantum dynamics. We find that a limited development of the classical dynamics of the photodissociation of collinear \( Ar–I_2 \) provides us insight into the trajectory and the energy transfer from the \( I–I \) vibrational coordinate into the \( Ar \) translational motion.

The simplest picture of \( Ar–I_2(B) \) after excitation is that it consists of a compressed oscillator, the \( I–I \), prepared with zero momentum and with a bond distance equal to the equilibrium distance of the ground state, 2.667 Å. The \( Ar \) is considered a “freely attached particle,” meaning that the \( Ar–I_2 \) potential is zero for all distances greater than an arbitrary hard-sphere distance, so that in Eqs. (5) and (6), \( D_0'(Ar–I_2(B)) = 0 \). At the hard-sphere distance the potential (and resultant \( Ar–I_2 \) force) becomes infinite. The initially prepared \( Ar–I_2(B) \) has the \( Ar \) to \( I_2 \) distance at the hard-sphere value. The \( Ar \) is accelerated by the expanding \( I–I \) oscillator until it reaches the maximum velocity of the \( Ar–I_2 \) system, which is at the equilibrium bond distance of \( B \)-state \( I_2 \). At this point, the \( Ar \) separates from the \( I_2 \), with no further change in its momentum. The \( I_2(B) \) oscillator reaches the outer turning point for the reduced vibrational energy. For this classical ball and spring system the final total translational energy is given by

\[
E_T = E_{trans}(\text{Ar}+\text{I}_2) = (M_{\text{Ar}}/(M_{\text{Ar}}+M_{\text{I}_2})) E_{\text{vib}}(\text{Ar–I}_2(B)),
\]

in which \( M_{\text{Ar}} \) and \( M_{\text{I}_2} \) are the masses of \( Ar \) and \( I_2 \). This model predicts that the same fraction, 13.6%, of the vibrational energy of \( Ar–I_2(B) \) is transferred to translational energy, independent of \( v_{pump} \). The amount of this energy (i.e., number of vibrational quanta lost) will decrease with decreasing \( E_{\text{vib}}(\text{Ar–I}_2(B)) \). The oversimplification of this most elementary picture may be readily seen from comparison to Fig. 8, in which the average translational energy released as a function of initial excitation is shown; this simple model gives a horizontal line near the average recoil energy.

We chose to model the classical dynamics of \( Ar–I_2(B) \) in somewhat more detail by solving Hamilton’s equations of motion for the \( Ar–I_2 \) system prepared with the energy as given by Eq. (5). The \( Ar–I_2 \) was constrained to linear geometry. We modeled the \( I_2 \) potential curve by using a parameterization of the \( B \)-state RKR potential curve.\(^\text{33}\) Three different potentials for \( Ar–I_2 \) were chosen, namely, a purely repulsive potential modeled by a single exponential,

\[
V(Ar–I_2(B)) = A \exp[-\beta(R_{\text{Ar–I}_2}–R_{\text{I}_2})]
\]

a simple Morse function,

\[
V(Ar–I_2(B)) = D_e [1 – 2 \exp(-\beta(R_{\text{Ar–I}_2}–R_{\text{I}_2}–R_{\text{e}}))] + \exp(-2\beta(R_{\text{Ar–I}_2}–R_{\text{I}_2}–R_{\text{e}}))]
\]

and the pairwise diatomics-in-molecules (“DIM”) potential,

\[
V(Ar–I_2(B)) = D_e [2 – 2 \exp(-\beta(R_{\text{Ar–I}_2}–R_{\text{I}_2}–R_{\text{e}}))] + \exp(-2\beta(R_{\text{Ar–I}_2}–R_{\text{I}_2}–R_{\text{e}}))]
\]

\[
– 2 \exp(-\beta(R_{\text{Ar–I}_2}+R_{\text{I}_2}–R_{\text{e}}))] + \exp(-2\beta(R_{\text{Ar–I}_2}+R_{\text{I}_2}–R_{\text{e}}))]
\]

\[
– Z.
\]

The various parameters \( A, \beta, D_e, R_{\text{e}}, \) and \( Z \) are taken as adjustable parameters. The bond distance \( R_{\text{Ar–I}_2} \) corresponds to the distance between \( Ar \) and the center-of-mass of the \( I_2 \), and \( R_{\text{I}_2} \) is the \( I–I \) distance. The form of Eq. (14) is taken from Gray,\(^\text{34}\) note that \( 2D_e \) is the bond energy in the \( T \)-shaped isomer of the model potential; the bond energy in the model potential for the linear isomer is somewhat less, and so the zero of energy is adjusted with the parameter \( Z \). We chose parameters for the repulsive curve of \( A = 1–3 \times 10^8 \text{ cm}^{-1} \) and \( \beta = 2.4–4.4 \text{ Å}^{-1} \) and parameters for the Morse potential of \( D_e = 100–200 \text{ cm}^{-1} \), \( \beta = 2.4–4.4 \text{ Å}^{-1} \), and \( R_{\text{e}} = 3.82–4.36 \text{ Å} \). For potential of Eq. (14) we used the values \( D_e = 122 \text{ cm}^{-1} \), \( \beta = 1.3228 \text{ Å}^{-1} \), and \( R_{\text{e}} = 4.2003 \text{ Å} \) (all as given by Gray\(^\text{34}\)), with \( Z = 117.9 \text{ cm}^{-1} \).

The purely repulsive potential between \( Ar \) and \( I_2 \), as in Eq. (12), causes the \( Ar \) to be ejected relatively rapidly, with only about 2%–4% recoil translational energy. In effect, the \( Ar \) “does not wait around” to get a push from the expanding \( I_2 \) oscillator. The small vibrational energy transfer seen experimentally in the \( v_{pump} = 16 \) is somewhat more typical of the purely repulsive \( Ar–I_2 \) potential. The model shows little change in the percent recoil translational energy as a function of \( v_{pump} \) from \( v_{pump} = 16–26 \). There are no “obvious,” that is, physical realizable, parameters whereby the energy transfer is increased with this pure repulsive model potential.

Either the simple Morse potential, Eq. (13), or the Morse-type potential of Eq. (14) give similar results for the vibrational to translational energy transfer. In the first 0.08 ps, the \( Ar \) to \( I_2 \) distance decreases, as the \( I_2 \) oscillator expands, thereby “pushing” the \( Ar \) higher on the potential well at the inner turning point of the \( Ar–I_2 \) potential; this “push” is partially responsible for the increased vibrational to translational energy transfer with the Morse-type potentials. The \( I_2 \) continues to “push,” transferring momentum to the \( Ar \), up to the point at which the \( I_2 \) reaches the outer turning point, after \( \sim 0.15 \text{ ps} \). The rate of momentum transfer decreases after this, although the \( Ar \) continues to accelerate
Ar–I 2 bond energy is about the same, but the Ar–I 2 equilibrium distance of ~8 Å. For the parameters as given above, we find about 20%–32% recoil translational energy; the 20% value is for β = 2.4 and 32% for β = 4.4. (The percent is not very sensitive to either D_e or R_e.) Although this predicted energy transfer is comparable to the recoil translational energy seen experimentally for higher v_pump, these models again show no variation in energy transfer as a function of v_pump.

In conclusion, our fluorescence data give no direct determination of the potential surface (or even bond energy) of linear B-state Ar–I 2. Comparison of our model potentials and classical trajectories to the observed fluorescence suggests: (1) There is no inherent reason for the Ar–I 2 potential to be repulsive to explain the continuum excitation of Ar–I 2. First, the repulsive model potential does not yield final vibrational states which adequately match the observed vibrational distribution in the I 2(B) product. Second, the purely repulsive curve would give a much more rapid, direct photodissociation, such that the fluorescence intensity would show no variation as a function of excitation wavelength, whereas a factor of 2 decrease in the intensity between vibrational bands is observed. Third, a lifetime of Ar–I 2 of 0.15 ps, which is reached at the I–I turning point, corresponds to a lifetime broadening of an individual transition of 18 cm^-1. The overall B→X band system will therefore be broadened, even if the Ar–I 2 state is bound. The Ar–I 2 “lifetime” may be shorter than this; the classical modeling shows that the I 2 has lost about one vibrational quantum of energy (i.e., changed its state) in the first 0.05 ps, corresponding to a lifetime broadening of 53 cm^-1. This is remarkably close to the estimate provided by considering a gaussian of full width 57 cm^-1 centered at each I–I vibrational band, which would result in the observed decrease in intensity between the bands of a factor of 2. We cannot rule out the possibility that the Ar–I 2 is excited onto the repulsive wall of the Ar–I 2 potential, above the Ar–I 2 dissociation limit on the inner turning point, where the energy levels are in the continuum.

(2) The vibrational excitations of v_pump = 16–26 correspond to r_z(I–I) = 3.19 Å to 3.35 Å (which can be contrasted with r_z(I–I) = 2.667 Å for I 2(X)). The Ar–I 2 interaction potential energy is likely a strong function of the I–I bond distance as well as the Ar–I distance. This has been completely ignored in all quantum calculations on the potential surface, and consequently in the dynamical calculations using those surfaces. Of the above three potentials, only the pairwise potential of Eq. (14) has some dependence on the I–I bond distance—the Ar–I 2 bond energy is about the same, but the Ar–I 2 equilibrium bond length somewhat longer (by 0.18 Å) for longer I–I bond lengths. However, we might surmise that it is somewhat more likely that the Ar–I 2 bonding is weaker for smaller I–I distances (lower v_pump), as evidenced by the fact that a dissociative potential more closely mimics the small recoil translational energies for lower v_pump, and a bound-state potential more closely mimics the larger recoil energies seen for higher v_pump.

Theoretical investigations of Ar–I 2 photodissociation dynamics have been carried out by Martens et al. using time-dependent wave packet quantum mechanics and quasiclassical trajectory calculations, based on the Ar–I pair potential obtained from the ZEKE experiments of Neumark and co-workers. They, in reasonable agreement with the experiments above B state dissociation limit by Philippoz et al., have shown that the final vibrational state distributions of I 2(B) following the photodissociation of the linear Ar–I 2 complex is strongly dependent on the weak Ar–I intermolecular interaction potentials. It is also pointed out by these authors that calculations using an inappropriate Ar–I interaction potential, even based on the collinear Ar–I 2 geometry, shows an I 2 product vibrational state distribution significantly different from the experimental ones. For the photodissociation of the linear Ar–I 2, the final I 2(B) vibrational state distribution directly reflects the initial radial distribution of the complex in the ground electronic state with the reflection mediated by the upper B state potential (reflection principle). An unrealistic ground state potential energy surface would not be able to give a true initial radial distribution in the ground state; the electronic excitation of the complex would then vertically propagate the ground-state nuclear wave functions (geometry distributions) onto the B-state wave functions. This would make the predicted initial parameters of the B state very far from the correct ones, and consequently give rise to incorrect product state distributions. Excited state potential energy surfaces are notoriously inaccurate. Indeed, the dynamical calculations have largely relied on model potentials (e.g., diatomics-in-molecules), which would then cause errors in the Ar–I 2 B-state dynamics, amplifying the inaccuracies. It is imperative to obtain high quality ground state and B-state potential energy surfaces for Ar–I 2 as a starting point for dynamics occurring in the B state. The high rigidity of the ground state, together with the very direct dissociation in the B state make it unlikely that large angular excursions can be involved unless the B-state potential is very unstable in the linear geometry. Our observation that high rotational levels of I 2 are not populated in the photofragment I 2 lends experimental evidence that such angular excursions play little, if any, role in the photodissociation dynamics. Our work on the linear Ar–I 2, explored much below the I 2 B-state dissociation limit, has shown a product vibrational state distribution which is quite a strong function of the excitation energy, which will serve as a stringent test of the accuracy of the Ar–I 2 potential surfaces and dynamical calculations, particularly for the lower excitation energies.

The observation of I 2 B→X fluorescence following excitation of the spectrally isolated Ar–I 2 isomers takes place by an initial optical excitation; the excitation is followed by the Ar–I 2 undergoing direct photodissociation, vibrational predissociation, or electronic quenching. The linear Ar–I 2(B) is believed to undergo fast (150 fs), adiabatic ejection of the Ar and suffers no quenching of the B state; vibrational predissociation is also not competitive on this time scale.

The dynamics of the T-shaped isomer are extremely complicated; an abbreviated schematic of the processes involved is shown in Fig. 9. The quenching process is broadly
understood in terms of the interaction of $B^3\Pi_{0^+u}$ with the repulsive $B^\nu\Pi_{1\nu}$. The overall process of excitation of the T-shaped isomer from the ground state to the $B$ state, with subsequent dissociation either into $B$-state $I_2(\nu') + Ar$ or into the $B^\nu\Pi_{1\nu}$ (which dissociates to $I^2P_{3/2} + I^2P_{3/2} + Ar$) may be a complicated admixture of coupled electronic and nuclear motions. As noted by Beswick and co-workers, the $B^\nu\Pi_{1\nu}$ is optically connected to the ground state, albeit with lower oscillator strength than the $B-X$ system. Since in $I_2$ the polarizations of the $B-X$ and $B^\nu-X$ transitions are perpendicular to one another, the excitation spectrum of Ar–$I_2$ to the $B^3\Pi_{0^+u}$ state is probably not mixed coherently with the $B^\nu\Pi_{1\nu}$.

Assuming that the T-shaped Ar–$I_2(B)$ has been prepared, vibrational predissociation is observed to be on the same time scale, and therefore competitive with the quenching of the $B$ state. These two processes are conventionally treated as independent channels. We suggest the highest energetically accessible vibrational level of $B$-state $I_2(\nu') + Ar$ or into the $B^\nu\Pi_{1\nu}$ produced in excitation of T-shaped Ar–$I_2$, is nearly 100% quenched by the Ar. The vibrational predissociation ($V.P.$) and quenching are shown in Fig. 9. This hypothesis is necessary to account for the discord between the T-shaped bond energies determined from the onset of the vibrational fluorescence (of Levy and co-workers) as compared to that estimated in this work by comparison to the linear bond energy. This implies that only states in which the I–I bond stretching vibrational energy has been reduced by at least one quantum can the vibrational predissociation to $I_2(B)(\nu') + Ar$ be competitive with electronic quenching. This further implies that the vibrational predissociation and electronic quenching channels cannot be treated as independent channels.

Since the vibrational predissociation of T-shaped Ar–$I_2(B)$ is slow, on the time scale of 70 ps ($I_2$ vibrations) it has been argued that an intermolecular vibrational redistribution picture is applicable, in which energy leaks out of the hard $I_2$ valence oscillation sequentially into the set of soft mode states. A rough picture of the soft mode states is known. The T-shaped isomer has $C_{2\nu}$ symmetry. The molecule has three vibrational modes, consisting of the stretching of the I–I bond, which is perpendicular to the $C_2$ axis and of $a_1$ symmetry; the symmetric stretch of the Ar–$I_2$, which is parallel to the $C_2$ axis and of $a_1$ symmetry; and the angle bending of the Ar–I–I bond, which is perpendicular to the $C_2$ axis and of $b_1$ symmetry. The weak Ar–I–I stretching frequency is approximately twice the angle bending frequency. Two frequencies 30 and 24 cm$^{-1}$ have been observed; their specific assignment to $v_{\text{stretch}}$ and $v_{\text{bend}}$ is uncertain. We may speculate upon which of the two soft mode motions are effective for electronic quenching and which for the vibrational predissociation. The inner wall of the $B^\nu\Pi_{1\nu}$ potential curve lies close to the inner wall of the $B^3\Pi_{0^+u}$ state. The symmetry of the $B^3\Pi_{1\nu}$ and the $B^\nu\Pi_{1\nu}$ states is such that a perpendicular orientation of the perturber (Ar), as occurs in the T-shaped geometry, is required to effect the Ar-induced transition from the fluorescing $B^3\Pi_{0^+u}$ to the repulsive $B^\nu\Pi_{1\nu}$. This occurs at the inner turning point of $I_2$ and is favored by a short Ar–I–I distance. Thus the electronic quenching should be selected by the soft modes involving the $a_1$ Ar–I–I stretching motion and the $a_1$ I–I stretch. The vibrational relaxation proceeds through the anharmonic mixing of the $a_1$ I–I stretch with even quanta of the $b_1$ bend. Since the bend and I–I stretch are both perpendicular to the $C_2$ axis, it would appear reasonable to expect them to be coupled. The vibrational predissociation likely depends upon cross terms in the interaction potential between the $I_2$ valence coordinate and the Ar–I–I coordinates. Probably these terms are quite anisotropic and therefore can be favored by excitation of the bending motion. The highest free $I_2(B)$ vibrational level produced will have the least translational energy. It will have the slowest rate of separation of the Ar from the $I_2$, and therefore a longer period of time for the Ar to quench the $I_2(B)$ which has just been created by vibrational predissociation. Thus, we can create a plausible (or consistent) scenario for the observation of near 100% quenching of the highest vibrational state of the nascent $I_2(B)$.

Perhaps even more than for the dynamics of the linear Ar–$I_2$, there is very little reason to accept the potentials used for calculations of the predissociation. For example, it has been pointed out by Kunz et al. that the diatomics-in-molecules potential for the $X$ state of Ar–$I_2$ does not even show the existence of the two potential minima. The adequacy of the diatomics-in-molecules potential for the $B$ state therefore cannot be regarded as seriously established. In the event that the dynamics are highly coupled to the vibrational modes, it is interesting to point out that no calculations of the Ar–I–I potential surface have been done in which the I–I bond is allowed to vary. We are aware of only one case, the early calculation by Brown et al. on He–I–I, in which the I–I bond distance was varied.

Finally, the role of weak interactions in altering photodynamics is far from obvious. In the broadest view, two diametrically opposite behaviors may be reasonably predicted. The first states that since the interaction is weak, there can be little coupling to the photoexcited chromophore and there-
before little effect on the dynamics. The second possibility is
that all processes essentially proceed through an energy-
sharing complex, in which the weakest bond breaks first,
thereby producing a substantial change in the dynamical
path. It appears that Ar–I$_2$ follows both extremes. The pre-
dissociation time for the T-shaped Ar–I$_2$(B) is $\sim 10^{-7}$ s,
which is three orders of magnitude longer that the dissociation
time of I$_2$(B). The T-shaped isomer, if excited above the
B-state dissociation limit, therefore proceeds along the I$_2$
dissociation pathway, with little effect from the Ar atom, i.e.,
T-shaped Ar–I$_2$(B) follows the first choice of little effect
from the weak interaction. The linear isomer exhibits weak
potential coupling; it has essentially the same bond energy as
the T-shaped isomer. In this case, the kinetic coupling is
maximal, leading to the second type of dynamical behaviour
in which the Ar so dramatically influences the path that the
I$_2$(B) does not fragment into I+I. The one atom produces a
complete cage. The difference in isomeric behavior is essen-
tially geometric, since the coupling is kinetic. It would ap-
pear that this is likely to be general since the potential cou-
pling is by definition weak.

We point out that the long-standing puzzle of the origin
of the one-atom cage effect in Ar–I$_2$ is in large measure a
consequence of extreme difficulties in predicting the nuclear
dynamics of excited electronic states of polyatomic mol-
ecules. It is indeed the nuclear dynamics of the T-shaped B
state isomer which, in our opinion, presents the greatest the-
etorical challenge; the complete dynamics of excitation and
dissociation appears to be an extremely difficult problem in-
volving curve hopping as well as vibrational predissociation.

We return briefly to the question of isomeric forms for
the Ne–I$_2$, Kr–I$_2$, and Xe–I$_2$ complexes, for which we did
not conduct experiments. Fluorescence from the continuum
excitation has been observed by Burke$^5$ in the corresponding
B$\rightarrow$X region of Kr–I$_2$. Philippoz et al.$^8$ observed the fluo-
rescence from the high energy excitation of Ne–I$_2$, Kr–I$_2$,
and Xe–I$_2$. We attribute this fluorescence to the linear iso-
mers of Ne–I$_2$, Kr–I$_2$, and Xe–I$_2$. The fluorescence data
show an increase in energy transfer with increasing mass of
the rare gas binding partner. The observed changes, however,
are somewhat less than predicted from the extremely simple
classical ball-and-spring model of Eq. (11), which depends
essentially only upon mass and ignores the variation of
Rg–I$_2$ interaction potential. We made no attempt to model
the other Rg–I$_2$ dynamics with classical models similar to
Eqs. (12)–(14).

The complexes with krypton and xenon show no struc-
tured fluorescence excitation spectrum from a T-shaped iso-
mer. The lack of observation of T-shaped isomers of the
heavier rare gases with I$_2$ can originate from several different
effects, the most likely of these is the electronic quenching of
the I$_2$ B state.$^{38}$ As has been noted in a collisional quenching
study of I$_2$(B), heavier rare gases are more effective colli-
sional quenchers.$^{39}$

V. CONCLUSIONS

We have used the dispersed intracavity laser induced
fluorescence technique to obtain the I$_2$(B) vibrational pro-
duct state distribution of linear and T-shaped Ar–I$_2$ following
B$\rightarrow$X excitation of the complexes. The coexistence of both
the linear and the T-shaped isomers of Ar–I$_2$ under identical
conditions is now conclusively established.

Each isomer of Ar–I$_2$ is distinctive both in the excitation
spectrum and the resultant I$_2$ fluorescence. The T-shaped iso-
mer has well-resolved excitation transitions, and the I$_2$ fluo-
rescence is sharply peaked at the next highest vibrational
level accessible within the energetic constraints of the Ar–I$_2$
bond dissociation. Our experimental results for the T-shaped
fluorescence are in excellent agreement with earlier work of
Levy and co-workers.$^{3,4}$ The linear isomer has a continuum
excitation, and the vibrational populations of the resulting
free I$_2$ are affected by the loss of the Ar. For the highest
vibrational excitation ($\nu_{\text{pump}}=26$), the I$_2$ transfers an aver-
age of about 22% of the I$_2$ vibrational excitation into kinetic
energy of the Ar+I$_2$. The product I$_2$(B) vibrational state
distribution is similar to those observed by Valentini and
Cross,$^7$ and by Philippoz et al.$^8$ for excitation above the I$_2$
B-state dissociation limit. Our data clearly show that the lin-
ear isomer of Ar–I$_2$ is responsible for the "one-atom cage
effect." For lower vibrational excitations ($\nu_{\text{pump}}=16$), the
I$_2$ transfers much less of the vibrational energy into ki-
etic energy of the Ar+I$_2$.

Our classical modeling of the Ar–I$_2$ dynamics of the
linear system shows that the linear Ar–I$_2$(B) lives a fraction
of an I$_2$ vibrational period, with most of the momentum
transfer occurring by the time the I$_2$ has reached the outer
turning point of the vibration. The lifetime of linear
Ar–I$_2$(B) of less than 0.15 ps can be contrasted to the 70 ps
predissociation lifetime$^{5,6}$ of T-shaped Ar–I$_2$(B).

The origin of the continuum absorption of linear Ar–I$_2$ is
not completely determined by this study. We interpret the
data, and our classical dynamics calculations, to suggest that
all excitation lines are lifetime broadened so that the result-
ing band appears as a continuum. The continuum structure
may be due to a large bond length increase in Ar–I$_2$(B) from
that in Ar–I$_2$(X), so that the Franck–Condon allowed transi-
sions are to the repulsive wall at the inner turning point of
the potential curve, above the Ar–I$_2$(B) dissociation limit.

The analysis of the excitation and fluorescent photon ener-
gy puts tight limits on the Ar–I$_2$(X) bond energy; we find
this limit to be $170(1.5)$ cm$^{-1}$ $\leq D^0_0$(linear Ar–I$_2$(X))
$\leq 174(1.5)$ cm$^{-1}$. Relative populations of the linear and
T-shaped Ar–I$_2$ in the jet lead us to conclude that
$D^0_0$(T-shaped Ar–I$_2$(X)) $\approx 142\pm 15$ cm$^{-1}$. This can be
contrasted to the T-shaped bond energy found by Levy and
co-workers, 234 cm$^{-1} \leq D^0_0(\text{T-shaped Ar–I}_2(B)) \leq 240$ cm$^{-1}$. We conclude that in
T-shaped Ar–I$_2$(B) fluorescence quenching is most likely an
integral part of the dynamics producing vibrational predissoci-
ation. Our hypothesis to explain the apparent discord in
isomerization energy of Ar–I$_2$(X) is a strong channel com-
petition in the T-shaped Ar–I$_2$(B), in which the highest
vibrational level of I$_2$(B) that could energetically be produced
from the photodissociation must be essentially 100% quenched by the Ar.

We would greatly enjoy theoretical support for this in-
terpretation. This dramatic, new interpretation of the well-
established fluorescence data raises the concern for systems
where the fluorescence yield is less than unity that reliable
thermodynamic and dynamical information may not be as
directly evident from the fluorescence spectra as has been
previously assumed.

ACKNOWLEDGMENTS

We thank Professor K. C. Janda, and Dr. M. L. Burke
for helpful discussions, and Dr. D. D. Nelson, Jr. for his
assistance in using the SpectraPro-500 Spectrometer. Cour-
teous loan of the SpectraPro-500 Spectrometer from Aero-
dyne Research is gratefully acknowledged. We thank Profes-
sor R. J. LeRoy of the University of Waterloo for use of
his LEVEL and RKR computer programs. A.E.S.M. thanks
the Bunting Institute of Radcliffe College for an ONR Sci-
College Research Program for support. This research was
supported by the National Science Foundation.

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\( A_5 = -128.298.49 \); \( A_6 = 12.616 465 \); \( A_7 = -703.476 41 \); and \( A_8
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