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ArI₂(X)→Ar+I₂(B) photodissociation: Comparison between linear and T-shaped isomers dynamics

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Quantum dynamical calculations on ArI₂ photodissociation have been performed using *ab initio* and semi-empirical potential energy surfaces, which support both linear and T-shaped isomers in the ground electronic state. Whereas the photon absorption spectra for the T-shaped isomer consist of narrow and intense bands, those for the linear isomer result from the superposition of a continuous background and peaks due to linear quasi-bound states. Vibrational distributions for the linear isomer are broader than those originating from the T-shaped one. Rotational distributions for the linear isomer are smooth and characteristic of a fast dissociation dynamics, whereas those for the T-shaped isomer are highly oscillatory. Implications of these results on the interpretation of experimental data are discussed. © 2001 American Institute of Physics.

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I. INTRODUCTION

One of the current goals in the field of chemical physics is to understand the role of weak intermolecular forces (solvation bonds) in chemical reactivity and relaxation. In this context, the iodine molecule has been extensively studied under a wide variety of experimental conditions in gases, liquids and matrices.^{1–12} The van der Waals (vdW) clusters in which several atoms or molecules are bound to a chromophore provide ideal model systems to investigate photo-fragmentation and relaxation processes affected by these weak intermolecular interactions,^{13–19} bridging the gap between gas-phase isolated molecules and molecules solvated in liquids and cryogenic matrices. These complexes can be studied with the use of supersonic beams, and a large number of experimental and theoretical studies have been devoted to the study of the excitation and decay of vdW complexes involving I₂.^{13,20–24}

The M–I₂ complexes (M being a rare-gas atom), in particular ArI₂, have been extensively studied in the excitation region of the bound levels of the excited *B* state, both experimentally^{13,20–22,25,26} and theoretically.^{14,27} These studies have provided a wealth of crucial information, not only on the structure of the complexes but also on the dynamics of vibrational and electronic predissociation.

When the vdW molecule M–I₂ is excited in the spectral region of the I₂(*B*←*X*) transition, the fluorescence excitation

spectrum shows broadened features which are attributed to quasibound levels associated to M–I₂(*B*,*v*). These resonances decay by two competing intramolecular relaxation processes:^{13,14,22} vibrational predissociation (VP)

and complex-induced electronic predissociation (EP)

Since channel (1) produces electronically excited I₂ fragments which can fluoresce while channel (2) is dark, measurements of the I₂ fluorescence quantum yield in conjunction with M–I₂ absorption spectra can provide the relative importance of vibrational predissociation as compared to electronic predissociation.²²

The dissociation dynamics of these complexes when excited above the dissociation threshold of the dihalogen molecule constitutes a nice prototype for caging phenomena. For ArI₂ excited above the dissociation threshold of I₂(*B*), some fluorescence was detected from bound vibrational levels of I₂(*B*).^{28–31} Valentini and Cross²⁹ proposed an impulsive energy transfer from I₂ to Ar in the *B* electronic state. However, quasiclassical trajectory calculations^{32,33} showed that the energy transfer is very unlikely if the complex has T-shaped geometry, as confirmed by recent fluorescence depletion measurements.³⁴ An alternative mechanism was proposed by Beswick and co-workers³⁵ involving a nonadiabatic transition between the repulsive *B*''(¹Π_{1u}) and the bound *B* elec-

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tronic states of I_2 . Later, Klemperer and co-workers^{26,36} assumed the existence of a second linear isomer in the X electronic state in order to explain the measured fluorescence of $I_2(B)$ fragments detected between the discrete $ArI_2 B \leftarrow X$ bands below the $I_2(B)$ threshold. The existence of such linear isomers was confirmed by accurate *ab initio* calculations³⁷ and has also been found in other complexes of Cl_2 .^{38–41} Recent calculations^{42,43} show that the linear isomer can account for the impulsive energy transfer used to explain the recombination of $I_2(B)$ observed in the excitation of ArI_2 above the dissociation threshold. In addition, the measured polarization anisotropy⁴⁴ also supports the idea that the caging dynamics occurs in the B state, excluding the nonadiabatic transition model.³⁵

Below the $I_2(B)$ dissociation threshold, vibrational and electronic predissociation has been extensively studied in ArI_2 ,^{13,22,45–48} especially in the $12 < v < 26$ interval where EP and VP compete with each other. The vibrational predissociation efficiency, measured by Burke and Klemperer²² presents oscillations as a function of the vibrational state from $v = 15$ – 26 . These oscillations were attributed to EP, while the VP rate was assumed to vary monotonically with the initial population.²² Based on this model, the oscillations were reproduced by a simple golden rule treatment of the EP in a single dissociative electronic state yielding $I+I+Ar$ products.⁴⁹ In this interval, VP takes place by the transfer of three vibrational quanta and is mediated by Intramolecular Vibrational Redistribution (IVR).^{45–48} Therefore, the monotonous increase of the VP rate with vibrational excitation assumed by Burke and Klemperer²² can only be explained assuming the IVR statistical limit. However, quantum calculations revealed that only a few zero-order quasibound states participate in the IVR,^{50–53} and it is the VP rate itself which presents strong oscillations with the initial vibrational excitation.

A new controversy has recently appeared that not only complicates the picture about the ArI_2 dynamics, but also introduces doubts about the vdW binding energies on the X and B electronic states. Recent experiments by Miller *et al.*³⁶ on the photofragmentation from linear isomers revealed that the binding energy of linear $ArI_2(X)$ is about 172 cm^{-1} . Assuming the separation of absorbances from linear and T-shaped isomers, their population ratio in the beam was estimated as 1:3.²⁶ Under Boltzmann equilibrium conditions, the value of the bond energy of T-shaped $ArI_2(X)$ becomes about $142 \pm 15\text{ cm}^{-1}$.³⁶ This energy is 90 cm^{-1} lower than that found by Levy and co-workers.⁴⁵ In the latter case the bond energy in the B state was inferred from the closing of the $\Delta v = -3$ channel from the analysis of the fluorescence spectra of $I_2(B)$ fragments. To explain why the $\Delta v = -2$ was not observed by Levy and co-workers, Miller *et al.*³⁶ proposed that, for that channel, the EP process becomes dominant because of the very low available kinetic energy. Recent work by Burroughs and Heaven⁵⁴ found that the rotational distributions of the $I_2(B, v)$ fragments appear to extend to the energy limit and establish an upper bound for the dissociation energies of 220 and 234 cm^{-1} for the $ArI_2(B, X)$ T-shape complexes, respectively. These results cast some doubts on the interpretation of Miller *et al.*³⁶

In order to clarify the interactions and dynamics in the ArI_2 complex it is, therefore, important to check to what extent the experimental findings can be simulated by models that use the two sets of dissociation energies. In this work, we shall compare the photodissociation dynamics of the two isomers, linear and T-shaped, without including the EP process. The present work is organized as follows. In Sec. II, we briefly recall the basic equations used in our model and give some computational details. We describe in Sec. III the different electronic potential energy surfaces used in our work. In Sec. IV, we show the photon absorption cross sections and product state distributions which result from our calculations and interpret them. Finally, in Sec. V, we confront our results with available experimental data.

II. METHOD

In the framework of the first-order perturbation theory for electric dipole transitions, the cross section for photon excitation from an initial bound state $|\Psi_i\rangle$ to a final continuum state $|\Psi_{fE}\rangle$, is defined by:⁵⁵

$$\sigma_{fE \leftarrow i} \propto |\langle \Psi_{fE} | \mathbf{d} \cdot \mathbf{e} | \Psi_i \rangle|^2, \quad (3)$$

where $\mathbf{d}$ is the transition dipole moment and $\mathbf{e}$ is the polarization vector of the incident photon.

The molecular system is parametrized with Jacobi coordinates $(\mathbf{R}, \mathbf{r})$, $\mathbf{R}$ being the vector joining the I_2 center-of-mass to the Ar atom and $\mathbf{r}$ the I_2 internuclear vector. The vector $\mathbf{R}$ forms an angle θ with $\mathbf{r}$. In this coordinate system, the Hamiltonian reads:

$$H = -\frac{\hbar^2}{2\mu_{Ar, I_2}} \frac{\partial^2}{\partial R^2} + \frac{l^2}{2\mu_{Ar, I_2} R^2} - \frac{\hbar^2}{2\mu_{I_2}} \frac{\partial^2}{\partial r^2} + \frac{j^2}{2\mu_{I_2} r^2} + V(r, R, \theta), \quad (4)$$

where μ_{Ar, I_2} and μ_{I_2} are reduced masses, l and j are angular momenta associated to $\mathbf{R}$ and $\mathbf{r}$, and $V(r, R, \theta)$ is the electronic potential. Potentials associated to the X and B electronic states are used for the computation of the initial bound $|\Psi_i\rangle$ and final continuum $|\Psi_{fE}\rangle$ state, respectively.

For a given total angular momentum J , projection M on a space-fixed axis, parity π , the bound or continuum wave function is expanded on a basis of free rotor $\Theta_{j'\Omega'}^{JM\pi}(\hat{r}, \hat{R})$ and I_2 vibrational functions $\varphi_{v'}(r)$:

$$\Psi^{JM\pi v j \Omega}(\mathbf{R}, \mathbf{r}) = \sum_{v' j' \Omega'} \Phi_{v' j' \Omega'}^{JM\pi v j \Omega}(R) \varphi_{v'}(r) \Theta_{j' \Omega'}^{JM\pi}(\hat{r}, \hat{R}). \quad (5)$$

The ground X potential energy surface has two minima in the (R, θ) plane corresponding to the linear and perpendicular isomers. In the calculation of the initial bound state $|\Psi_i\rangle$, we use a primitive nonorthogonal basis resulting from the superposition of the $\theta=0$ and $\theta=\pi/2$ vibrational 1D functions in R . The Schmidt orthogonalized basis deduced from this primitive basis is used in the expansion of the $\Phi_{v' j' \Omega'}^{JM\pi v j \Omega}(R)$ functions.

The absorption spectra have been calculated for the transition: $ArI_2(B, J=0, p=\text{even}, \pi=\text{even}) \leftarrow ArI_2(X, J=1, p=\text{odd}, \pi=\text{odd})$ (p defines the symmetry with respect to

FIG. 1. Energy diagram of I₂ and ArI₂ systems (all in cm⁻¹). The ArI₂(X) energies for linear and T-shaped isomers include zero-point energy.

iodine nuclei permutation and π is the total parity) using a time-independent close coupling method^{56–58} in the energy interval [1800,2800] wave numbers, which covers the I₂(B, v) levels from $v=15$ (1755 cm⁻¹) to $v=27$ (2816 cm⁻¹). Although results have been obtained for the 15 lower ArI₂(X, $J=1, p=odd, \pi=odd$) vibrational eigenstates, spectra will be shown only for the two states representing the ground levels of the linear and T-shaped isomers, which are supposed to be the only states which can be populated significantly in the low-temperature experimental conditions. The energy origin is taken to be the minimum of the I₂(B) and in Fig. 1, an energy diagram is shown for clarity. The spectra were calculated every 1 cm⁻¹ except in the vicinity of narrow resonances where the calculations were done in a more detailed energy grid to characterize the resonances. With a vibrational basis set composed of 13 I₂(B, v) states (dependent on the total energy), the convergence has been checked to be better than 0.1% for the absorption spectra. To converge product vibrational state distributions, larger vibrational basis sets were used, especially for the linear isomers in which the vibration-translation energy transfer is very efficient. Thus about 5–6 closed channels were included. Convergence of these calculations has also been checked by comparison with time-dependent wave-packet propagations showing an excellent agreement. Most of the results shown in the following come from close coupling

calculations, but occasionally, wave-packet results will be presented. In this last case, explicit mention will be given.

The time-dependent wave-packet method used has been described elsewhere.^{59,60} The wave packet is expanded in terms of free rotor functions, $\Theta_{j'\Omega}^{JM\pi}(\hat{r}, \hat{R})$, with well-defined parity. The initial wave packet is the projection of $\mathbf{d} \cdot \mathbf{e} |\Psi_i\rangle$ on a particular J, M rotational state. Moreover, in order to reduce the energy spreading of the wave packet, the initial wave packet is also projected on a reduced vibrational basis of the B electronic state,⁶⁰ with $10 \leq v \leq 30$. The wave packet is represented in grids of R, r , and is propagated using a Chebyshev method⁶¹ up to 10 and 150 ps for linear and T-shaped isomers, respectively. The total absorption spectrum in Eq. (3) is obtained by Fourier transform of the autocorrelation function.

III. POTENTIAL ENERGY SURFACES AND BOUND STATES

A. Potential energy surfaces

The potential energy surfaces (PES's) for this system are described as

$$V(r, R, \theta) = V_{I_2}^\alpha + W^\alpha(r, R, \theta), \quad (6)$$

where $V_{I_2}^\alpha$ are the RKR potentials of the I₂ molecule in the $\alpha=X, B$ electronic states,^{62,63} whereas $W^\alpha(r, R, \theta)$ is the intermolecular interaction. Figure 1 gives a global view on the energetics of the system if the first-order diatomics-in-molecule perturbation theory (DIM PT1) is used to describe both X and B states.⁶⁴ This approach can be considered as an improvement to the earlier intermolecular DIM PT1 model⁶⁵ achieved by the use of refined adiabatic wave functions of I₂ molecule defined by solving the inverse atoms-in-molecule problem as discussed in Ref. 66 for the predissociation of isolated I₂(B) molecule. This improvement does not affect the B PES because the B state is the unique one of the I₂ molecule having 0_u^+ symmetry. According to Fig. 2 (upper panel), $W^B(r, R, \theta)$ has a single minimum at the T-shaped geometry ($D_e=249$ cm⁻¹). In the linear geometry, the potential is bound along the R distance, but its minimum is unstable with respect to deformation angle. The X PES changes significantly and, in contrast to earlier one,⁶⁵ has two minima in T-shaped ($D_e=233$ cm⁻¹) and linear ($D_e=189$ cm⁻¹) geometries (see Ref. 64 and lower panel of Fig. 2). The minimum in the T-shaped geometry is very similar to that in the B state. These values agree with the DIM PES obtained by Naumkin.⁶⁷

Complementary results have been obtained with an *ab initio* X potential from Kunz *et al.*,³⁷ who calculated *ab initio* points on the ArI₂(X) PES using fourth-order Møller Plesset perturbation theory (MP4). They found two isomers with the well depth $D_e=187$ cm⁻¹ (T-shaped) and $D_e=206$ cm⁻¹ (linear). Since no B *ab initio* potential is available, the same DIM PT1 B potential has been used in this case.

Both DIM PT1 and *ab initio* MP4 X potentials have similar global features, in particular, they both have minima in linear and perpendicular geometries. Differences between both potentials are more pronounced for T-shaped geometry

FIG. 2. Contour plots of the ArI_2 DIM PT1 interaction potentials for the X (bottom panel) and B (top panel) electronic states. The contours are separated by 40 cm^{-1} , starting at -200 and -240 for the X and B electronic states, respectively. The I–I internuclear distance lies on the x -axis and its norm has been fixed to the r_{eq} value. The axes of the figure correspond to $x = R \cos \theta$ and $y = R \sin \theta$.

than for linear one: For instance, the *ab initio* perpendicular minimum is 46 cm^{-1} shallower than the DIM PT1 one, but only 17 cm^{-1} deeper for the linear geometry.

None of these potentials are, however, free from uncertainties. The possible sources of error in the DIM PT1 potentials are as follows: First, the reduction of the DIM basis set by the valence state subspace. The effect of the ion-pair states and of the states correlating with excited atomic limits in the iodine molecule are not yet reliably estimated.^{68,69} Second, the DIM PT1 model is subjected to inaccuracies by the uncertainties in the input data, i.e., Ar–I and I_2 potential energy curves. For the Ar–I curve, the empirical potentials determined from ZEKE spectroscopy of ArI^- anion were used.⁷⁰ They provide excellent characterization of the bottom of vdW well, being less certain at long and, especially, short ranges. As far as I_2 potential energy curves used for inverse solution of atoms-in-molecule problem for I_2 adiabatic wave functions are concerned, preliminary analysis⁶⁴ indicated that their different parameterizations may lead to the uncertainty at least 3 and 13 cm^{-1} for the well depths of T-shaped and linear isomers. Here, we implemented the TP2 parameterization^{64,66} which combines known empirical potentials and the *ab initio* data by Teichteil and Pelissier.⁷¹ The third source of inaccuracy is the perturbative treatment which ignores the effect of Ar on the electronic structure of I_2 fragment. It should be most pronounced at the short Ar– I_2 distances.⁶⁵

On the other hand, it is not clear to what extent the *ab initio* calculations are converged. For instance, Naumkin and McCourt⁷² carried out *ab initio* calculations on the $\text{ArI}_2(\text{X})$

PES using a Coupled Cluster technique including Single, Double excitations plus noniterative correction to the triple excitations [CCSD(T)] also used by Kunz *et al.*³⁷ Naumkin and McCourt^{69,72} implemented a less complete basis set and got 143 and 152 cm^{-1} for D_e 's of T-shaped and linear isomers, respectively, i.e., $40\text{--}50 \text{ cm}^{-1}$ lower than the values obtained by Kunz *et al.* At the same time, they found that their method led to a great underestimation of the Ar–I binding energies (100 or 50 cm^{-1} , depending on the electronic state). Unfortunately, Ref. 37 does not give explicit results for ArI , but the lowering of ArI_2 energies with respect to Ref. 72 still does not cover the disagreement in Ar–I *ab initio* and ZEKE potentials.

Since this work was completed a new detailed *ab initio* study by Naumkin has been published.⁷³ Implementing the most extended basis sets and effective relativistic core potential for I within the CCSD(T) method, he arrived to the best *ab initio* estimation of the bond energies of T-shaped and linear isomers, 203.1 and 224.4 cm^{-1} , respectively. The scaling procedure accounting for the difference in *ab initio* and experimental results for Ar–I predicted that converged non-relativistic *ab initio* values of dissociation energies should lie in the 242 ± 11 and $250 \pm 8 \text{ cm}^{-1}$ intervals for T-shaped and linear isomers, respectively. It was noted that the former prediction agrees well with the Levy's experimental result.

B. Bound states

Figure 3 shows the amplitude density associated to the first eigenstates of $\text{ArI}_2(\text{X}, J=0)$ on the X DIM PT1 potential. The sixth state is the ground vibrational state of the linear isomer. Up to -145 cm^{-1} , all the states can be assigned either to the linear or T-shaped isomers, above this energy, the states are delocalized as regards the angular coordinate. Vibrational zero point energies (see Table I, difference between D_0 and D_e) are 23 and 24 cm^{-1} for linear and T-shaped isomers, respectively. For the MP4 potential, the situation is different: The ground state corresponds to the linear isomer, but the first excited vibrational state is already the T-shaped isomer, the excitation energy being 11 cm^{-1} . Zero-point energies are now 27 and 19 cm^{-1} for linear and T-shaped isomers.

Rovibrational levels have been calculated for $J=0, 1$ and 2. Eigenvalues corresponding to linear states were fitted to the expression

$$E_{L,v,n_s,n_b}^{J\Omega} = E_v^L + \hbar \omega_b^L(n_b + 1) - \hbar \omega_b \chi_b^L(n_b + 1)^2 + \hbar \omega_s^L(n_s + 1/2) + B[J(J+1) - \Omega^2], \quad (7)$$

where $n_s = 0, 1, \dots$; $n_b = \Omega, \Omega+2, \dots$. In contrast, the eigenvalues for T-shaped ones were fitted to the expression

$$E_{T,v,n_s,n_b}^{JK} = E_v^T + \hbar \omega_b^T(n_b + 1/2) + \hbar \omega_s^T(n_s + 1/2) + E_{JK}, \quad (8)$$

with $n_s, n_b = 0, 1, \dots$ and E_{JK} are the asymmetric top eigenvalues obtained after diagonalization of the rotational Hamiltonian depending on the A, B, C rotational constants.⁷⁴

FIG. 3. Contour plots of the amplitude density of the first bound states for ArI₂(X, $J=0$) and for the equilibrium I–I distance of r_{eq} (top panels) and ArI₂(B, $J=0, v=21, p=\text{even}$) (bottom panels). The energies are referred to the Ar+I₂(X, $v=0$) asymptotic state and to I₂(B, $v=21$) vibrational energy (which is 2316.34 cm⁻¹), respectively.

In the two equations above, ω_b and ω_s are the frequencies associated to bending and stretching vibrations, respectively, while the term $E_v^{T,L}$ is the vibrational energy of I₂ in its ground electronic state plus the binding energy of each of the two complexes.

Based on these results, the eigenvalues can be obtained for large rotational angular momentum and the T-shaped to linear isomers population ratio can be obtained by computing the Boltzmann partition functions for both DIM PT1 and MP4 potentials at $T=15$ K jet temperature. This population ratio is found to be 109 and 1.6 for DIM PT1 and MP4 potentials, respectively. Both results are far from the experimental value of 1:3 obtained by Burke and Klempner.²⁶ This discrepancy may be due to inaccuracies in the potentials or in the experimental population ratio or to the inadequacy of the Boltzmann equilibrium hypothesis. We discuss this issue in more detail in Sec. V of this paper.

IV. DYNAMICAL RESULTS AND INTERPRETATION

A. Absorption spectra

Figures 4 and 5 show the absorption spectra for the ground T-shaped (top panel) and linear (bottom panel) initial states on the DIM PT1 and *ab initio* MP4 potentials, respectively. T-shaped isomer spectra show narrow intense peaks and little continuous background. By contrast, linear isomer spectra result from the superposition of a large background increasing with energy and broader and less intense peaks. The increase in energy of the background occurs by steps correlated to vibrational thresholds, as in ArCl₂.⁷⁵ Change of the X potential does not significantly modify the linear spectrum. For the T-shaped isomer, some of the peaks appear on both spectra with similar energies and same widths; however, peaks are more numerous for the MP4 PES than for the DIM PT1 one.

FIG. 4. ArI_2 absorption spectra for $(B, J=0, \pi=\text{even}, p=\text{even}) \leftarrow (X, J=1, \pi=\text{odd}, p=\text{odd})$ transitions, for the ground T-shaped (upper panel) and linear (lower panel) isomers. The DIM PT1 potential is used for the initial ground state. In order to present the details of the spectra, the maximum of the peaks have been cut, especially for the T-shaped isomer for which the peaks are very narrow and intense.

The peaks which appear on the T-shaped spectra have been interpreted by zero-order bound states on the B potential coupled to dissociative continua. The bound states are eigenfunctions of an effective Hamiltonian obtained by averaging the Hamiltonian in Eq. (4) over the I_2 vibrational state $\varphi_v(r)$.

Figure 3 shows the eigenvalues and amplitude density associated to the first 15 eigenstates with $v=21, J=0$ and with even symmetry with respect to the iodine nuclei interchange. Eigenstates up to $E_{14}(-123 \text{ cm}^{-1})$ are localized near T-shaped geometries. The energies of these states can be correlated with the positions of the peaks on the T-shaped spectra. The shape of the DIM PT1 X potential is very similar to the B one in the T-shaped configuration. As a result, the Franck–Condon factors between the ground X vibrational state and these T-shaped B eigenstates decrease quickly with vdW excitation. Thus, intensities of the peaks on the spectra obtained using DIM PT1 PES's rapidly fall down with energy. By contrast, MP4 PES has more differences with the DIM PT1 B potential, and excited vdW modes appear with larger intensities on the spectra. More peaks thus appear on the T-shaped spectra corresponding to the MP4 potential. However, in the experimental spectra only the bands associated to the ground and first two vdW excitations on the B

FIG. 5. Same as the previous figure, but for the *ab initio* MP4 initial potential. These calculations were performed using a wave-packet method.

electronic state are observed.²² Moreover, regarding the absolute transition frequencies, the use of DIM PT1 PES's yields a 13 cm^{-1} redshift relative to the uncomplexed I_2 transitions, while the use of MP4 X PES increases it up to 54 cm^{-1} . The measured shift is blue and amounts to 13 cm^{-1} .

This relatively large error in the theoretical spectral shift has the origin in that the DIM-based models formulated so far⁶⁴ underestimate the binding energy in the X state relative to that of the B state. This error in the DIM PT1 model, being clearly smaller than that obtained using the MP4 PES for $\text{ArI}_2(X)$, does not have important effects in the dissociation dynamics from linear and T-shaped isomers. It could be easily corrected by a shift of the $\text{ArI}_2(X)$ PES of only 26 cm^{-1} , an amount clearly smaller than the error nowadays obtained in any *ab initio* calculation on this system. However, the change in the relative dissociation energies proposed by Miller *et al.*³⁶ introduces a very important change in the energetic of the B state, of $\approx 1/3$ of the binding energy. Thus, the $\Delta v = -2$ would be accessible by vibrational predissociation, while there is no experimental evidence on this fact. In this work, we do not consider EP and, therefore, some other arguments should be found to try to harmonize all the experimental data. For this purpose we use the DIM PT1 model since it describes simultaneously and reasonably well the dissociation energies of the T-shaped isomer with respect to Levy and co-workers^{45,46} and the binding energy

of the linear isomer when compared with the data of Miller *et al.*³⁶ With this assumption, the problem resides on the link between the well depths of the two isomers in the ground electronic state and, in this work, we will discuss several alternatives. The error is of the order of 30 cm⁻¹ in the spectral shift, which can be considered as an inaccuracy which is not too important.

In the present context, the use of the MP4 PES for ArI₂(X) is, therefore, found to be inadequate to study the absorption to the *B* electronic state when, for the latter, the DIM PT1 PES is used. Hereafter, we shall discuss the results obtained using the DIM PT1 PES's for both, ground and excited, electronic states.

Eigenstates with energies above -123 cm⁻¹ have significant amplitude in the near-linear geometry and are expected to show up in the spectra due to favorable Franck-Condon factors with the initial linear *X* bound state. However, the energy spacing between eigenstates with significant amplitude in colinear geometry (typically 1 cm⁻¹) is one order of magnitude lower than energy spacing between the peaks appearing on the spectra of linear isomer. In order to explain this fact, we calculated the following approximate spectra:

- a “three-dimensional” spectrum, where all I₂(*B*,*v*) ← I₂(*X*,*v*=0) Franck-Condon factors have been set to zero except one, so that the oscillator strength is due to a single vibrational level.
- a “two-dimensional” spectrum, similar to the 3-D one but for a fixed colinear geometry $\theta=0$ of the system.
- an even simpler “one-dimensional” model, similar to the 2-D one with the further simplification that all couplings between *B* vibrational levels are zero.

The 1-D, 2-D and 3-D results are compared in Fig. 6 for the ArI₂(*B*,*v*=20) ← ArI₂(*X*,*v*=0) transition. In the 1-D model the straight lines correspond to bound states, appearing at collinear geometries because the potential shows a minimum along the *R* distance. These bound states take a significant part of the oscillator strength. However, the continuum above the I₂(*B*,*v*) threshold also absorbs significantly: Indeed, a vertical transition from the initial state falls into the repulsive part of the excited PES (the vdW minimum distance *R* being smaller for the *X* state than for the *B* one, see Table I). Thus, absorption remains significant even for high product translational energy, as can be seen on Fig. 6 from the slow decrease of the 1-D direct continuum absorption curve as a function of energy.

When the vibrational couplings are included (2-D model), the bound states give resonances, and new peaks corresponding to quasibound states of the *v* (≠ 20) manifolds appear. The 3-D spectrum is very similar to the 2-D. As a result, most peaks which appear on the 3-D results can be correlated to bound states on the 1-D model at different *v*'s. one-dimensional bound state energies are only slightly lower than peak maxima. This correlation allows us to assign approximate quantum numbers (*v*, *n_s*) to the resonances analogous to those defined in Eq. (7) for the initial vibrational state and associated to the I₂ vibration and *R*-stretching mode. The quantum number *n_b* associated to bending is left

FIG. 6. Absorption spectrum for the linear ArI₂(*B*,*v*=20) ← ArI₂(*X*,*v*=0) transition neglecting all Franck-Condon factors except the I₂(*B*,*v*=20) ← I₂(*X*,*v*=0) one and for different dimensionalities: One-dimensional (top panel), two-dimensional (middle panel) and three-dimensional (bottom panel). See text for a description of the models.

undefined. Indeed, a single peak on the spectrum probably results from the contribution of several closely spaced (see Fig. 3) bound states with different, but always small, bending excitations. The degree of this bending excitation is given by the difference between the energies of the peaks and those of the 1-D bound states: It is of the order of a few wave numbers only.

This simple interpretation of resonances can be complicated when several zero-order states are close to the one reached by optical excitation because of IVR.^{57,76} This is illustrated in Fig. 7, where we show the absorption spectra for the T-shaped isomer in two different energy intervals. For each transition there are several peaks. In these energy intervals, three vibrational quanta are required to break down the complex, and the zero-order bound states belonging to a particular I₂(*B*,*v*) manifold are facing some other zero-order levels of the *v*-1 and *v*-2 manifolds. These levels interact

FIG. 7. Absorption spectra from the T-shaped $\text{Ar-I}_2(X)$ isomer. The top panel corresponds to the IVR bands of $v=21$, while the bottom to those of $v=29$. In the top panel dashed lines corresponds to the spectrum multiplied by 100.

with each other, and the oscillator strength, originally associated to the ground and first two excited vdW levels for each v manifold, is shared among several peaks, giving rise to the so-called IVR bands. Because of the anharmonicity of I_2 , as total energy increases, the energy difference between vibrational levels decreases and their mutual coupling increases. That is why the IVR bands become broader and less intense with increasing total energy. This is particularly clear in the bottom panel of Fig. 7 for which the absorption spectrum intensity is of the order of that associated to the linear isomers.

Since the first and second excited zero-order vdW levels are only separated by $\approx 7 \text{ cm}^{-1}$ (see Fig. 3), in some cases, the two IVR bands overlap, as it is observed in the bottom panel of Fig. 7. This may be the reason why the emission spectra obtained from these two bands were found to follow a similar pattern by Burke and Klemperer.²² The authors, however, interpreted this fact as a proof of IVR in the statistical limit.

B. Vibrational distributions

Concerning the calculation on the product state distributions, all the results presented in the following have been obtained using the DIM PT1 PES's. In Fig. 8 we compare the I_2 vibrational distributions obtained in this work for

T-shaped isomers with the experimental results by Johnson *et al.*⁴⁷ for $v=16$, 21, and 24. The energies at which the vibrational distributions were calculated correspond to the maximum of the most intense peak of the IVR band associated to the ground vdW level. The agreement is rather good. In all cases the first open vibrational channel, $\Delta v=-3$, is dominant. However, the percentage of the $\Delta v=-3$ channel decreases as the initial vibrational excitation increases because of the increase of the vibrational couplings. This trend is rather general for all the v 's studied and also for the IVR bands associated with the first and second excited vdW levels.

The final vibrational state distributions obtained from linear isomer, in Fig. 8, become broader as initial excitation increases, as for the T-shaped isomer. However, the distributions for the linear isomer are much broader than for the T-shaped one, and in many cases their maxima are not located at the first open vibrational channel. Such a situation is not only due to the strong efficiency of vibrational-translational energy transfer occurring at collinear geometries. Also, direct excitation to a given v spreads over a wide energy range, as already mentioned in Sec. IV A. Thus, at a given energy, the oscillator strength corresponds to a large mixture of vibrational levels. The theoretical vibrational distributions shown in Fig. 8 were calculated at the energies corresponding approximately to experimental measurements by Miller *et al.*,³⁶ i.e., $E_v - 166 - 1 \text{ cm}^{-1}$, where E_v is the $\text{I}_2(B,v)$ diatomic energy, 166 is the dissociation energy of the linear $\text{ArI}_2(X)$ isomer, and one wave number is the detuning from the bare I_2 transition. The comparison is rather good at low v 's and the closing of the $\Delta v=-2$ channel occurs approximately at the same v . This results from the good agreement between the DIM PT1 $\text{ArI}_2(X)$ linear dissociation energy and the experimental one (172 cm^{-1}). The agreement at higher v 's is, however, not so good, and in particular, the theoretical results are not able to reproduce a so-large shift of the vibrational distribution maximum towards lower v 's. This may be due to some inaccuracies on the $\text{ArI}_2(B)$ PES. Also, in the present model, EP process is not considered. Such a process should be more efficient when the dissociation after VP is slower, as it is the case for the highest open vibrational channels.³⁶ Therefore, the probabilities of the highest vibrational channels should decrease when including the competing EP process, yielding a better agreement with the experimental data.

C. Rotational distributions

Even much more detailed information can be obtained from the product rotational state distribution of the $\text{I}_2(B,v)$ fragments which were recently measured by Burroughs and Heaven⁵⁴ for both linear and T-shaped isomers. In Fig. 9 an example is shown corresponding to an energy of 2685 cm^{-1} , consistent with a photon excitation energy of 18513 cm^{-1} .⁷⁷ For $v=21$ the experimental distribution is compared with the present results showing an excellent agreement. Due to the relatively fast dissociation occurring for the linear ArI_2 isomer, the rotational distributions are rather smooth and independent of the available energy for different final vibrational state of $\text{I}_2(B)$. It is interesting to note, however, that as the

FIG. 8. I₂(B,v') product vibrational state distributions obtained from the T-shaped and linear ArI₂(X) isomers. In the T-shaped isomer cases (indicated by a T), the energy corresponds to the main resonance of ArI₂(B,v), where v is shown in each panel. For the linear isomer cases (indicated by an L), the energy corresponds to $D_0 \approx 166 \text{ cm}^{-1}$ below the I₂(B,v) threshold, where v is shown in each panel. Full squares are the present results. Empty squares are experimental data, from Johnson *et al.*⁴⁷ for T-shaped isomer and from Miller *et al.*³⁶ for linear isomer. The sum of all available final states have been renormalized.

available kinetic energy increases (i.e., final v decreases) the rotational distribution gets slightly colder showing that there is nearly no energy transfer to rotation.

To stress this fact, in Fig. 9 corresponding to $v = 23$ and the linear isomer, the final rotational distribution is compared to the decomposition of the initial wave packet, $\mathbf{d} \cdot \mathbf{e} \Psi_i$, on the final I₂(B,v,j) rovibrational states. The later is narrower and slightly shifted towards lower j 's. The differences are due to small forces acting on the rotational degree of freedom during dissociation. This effect could be described in terms of the rotational reflection principle.⁵⁵ As a consequence, the final rotational distribution of the products becomes rather insensitive to the details of the PES for ArI₂(X) and in the two PES's considered here they are pretty similar.

By contrast, for the T-shaped ArI₂(X) isomer, the product rotational distributions are highly structured because of IVR.^{52,57} The quasibound states of the v manifold interacts with other states of the $v - 1$ and $v - 2$ manifolds which are highly excited in the vdW modes. Thus, highly oscillating rotational distributions were also obtained in Ref. 52 from quantum calculations. In Fig. 9 several final rotational distributions are compared with recent experimental data of Burroughs and Heaven.⁵⁴

Aside from the fast oscillations, the main trends of the experimental distributions are, in general, well reproduced by the present calculations for nearly all cases considered. To explain the disappearance of the fast oscillations, theoretical calculations should be performed for different total angular momentum J , symmetry blocks, etc. The average over-rotational transitions should provide more definite comparison with experimental data. Such an average may wash out the fast theoretical oscillations if distributions depend significantly on these quantities. We have done calculations up to $J = 2$ and the results present little influence of J on the rotational distribution. This is due to the small efficiency of the Coriolis coupling for such low J on a so-heavy system. However, the ArI₂(X) rotational sublevels (i.e., those states corresponding to different K projection of J for an asymmetric top) exhibit important differences in their rotational decomposition, and, in turn, in the corresponding product rotational distributions.

V. DISSOCIATION ENERGIES OF LINEAR AND T-SHAPED ISOMERS

There is a good agreement between the experimental value of Miller *et al.*³⁶ and the different potentials used, DIM

Linear isomer

T-shaped isomer

$I_2(B, v, j)$ product rotational state

FIG. 9. $I_2(B, v', j)$ product rotational state distributions: Four top panels correspond to the linear isomer after excitation with $h\nu = 18\,513\text{ cm}^{-1}$ [the four different panels correspond to the various final vibrational states considered. Black dots for $v=23$ correspond to the simple overlap model (see text)], while the six bottom panels correspond to the T-shaped isomer obtained after excitation to $\text{ArI}_2(B, v)$ band at the main peak and $v' = v + \Delta v$, as marked in each panel. In all cases, the dashed lines correspond to the experimental data from Burroughs and Heaven (Ref. 54).

PT1 and MP4, to establish that the dissociation energy for the linear isomer for $\text{ArI}_2(X)$, $D_0(X, L)$, is about $172 \pm 10\text{ cm}^{-1}$, as listed in Table I. For the T-shaped isomer, however, there are two different experimental values for $D_0(X, T)$, 142 cm^{-1} by Miller *et al.*³⁶ and 237 cm^{-1} by Blazy *et al.*⁴⁶ The theoretical potentials used in this work also give different T-shaped dissociation energies: 209 and 168 cm^{-1} for the DIM PT1 and MP4, respectively, as listed in Table I. This difference has significant effects on the dissociation dynamics and it is important to clarify which of the dissociation energies is the correct one.

It should be stressed that all experimental spectra obtained for the T-shaped isomer are in agreement,^{36,47,54} espe-

cially in what refers to final vibrational distribution of $I_2(B)$. The difference arises in the interpretation of the new results obtained by Klemperer and co-workers.^{22,26,36} Blazy *et al.*⁴⁶ assume that all energetically accessible final states of $I_2(B, v)$ were populated. Thus, the determination of the vibrational level at which the $\Delta v = -3$ channel becomes closed allows a pretty accurate determination of $D_0(B, T)$, so that knowing the spectral shift with respect to the bare I_2 transitions, the $D_0(X, T)$ could be determined.

The procedure followed by Miller *et al.*³⁶ to determine $D_0(X, T)$ is rather different and their arguments can be summarized as following:

TABLE I. Minima of the $W^a(r, R, \theta)$ X and B potentials used in the present paper. r is fixed at the equilibrium distance $r_{\text{eq}}=2.7$ Å for the X potentials and $r_{\text{eq}}=3.0$ Å for the B potentials. Experimental results are given for reference and discussion.

		Linear isomer			T-shaped isomer		
		D_e/cm^{-1}	D_0/cm^{-1}	$R_0/\text{Å}$	D_e/cm^{-1}	D_0/cm^{-1}	$R_0/\text{Å}$
X potential	DIM PT1	189	166	5.2	233	209	3.9
	MP4 ^a	206	179	5.1	187	168	4.1
	experiment ^{b,c}					237	
	experiment ^d		172			142	
B potential	DIM PT1	145 ^e		5.5	249	222	3.8
	experiment ^{b,c}					224	
	experiment ^d					128	

^aReference 37.

^bReference 46.

^cReference 54.

^dReference 36.

^eSaddle point: Minimum as a function of R , maximum as a function of θ .

- (1) A direct measurement of $D_0(X, L)$ for linear isomer, following a procedure similar to that followed by Blazy *et al.*⁴⁶ for T-shaped isomer;
- (2) The assumption of Boltzmann thermal equilibrium in the jet between linear and T-shaped isomer;
- (3) The estimation from fluorescence intensity ratio of the T-shaped to linear population ratio in the beam as the ratio of integrated intensities of quasidiscrete and quasi-continuum absorption (roughly a factor of 1:3).

They obtained a $D_0(X, T)$ 95 cm⁻¹ smaller than the result of Blazy *et al.*⁴⁶ and 26/67 cm⁻¹ smaller than the MP4/DIM PT1 theoretical ones. Let us discuss possible explanations for such large differences, on the basis of our present calculation. Let us consider each item just mentioned in the reasoning of Miller *et al.*

1. All values obtained for $D_0(X, L)$ are in good agreement and, therefore, we have no reason to question the measured D_0 for linear isomer.
2. Our present calculation does not provide any indication on the validity of the thermal equilibrium hypothesis, which remains an opened question. According to Burroughs and Heaven,⁵⁴ "it is quite common to find that the internal degrees of freedom of a molecule are not in thermal equilibrium in the downstream region of a seeded expansion." On the other hand, collisions with surrounding Ar atoms may promote linear to T-shaped isomer conversion giving fast thermal equilibrium.⁷⁸
3. Our computed spectra have some distinctive features which should be taken into account when estimating population ratio from fluorescence ratio. For T-shaped isomer, the intensity among the most intense IVR bands is not negligible as compared to that of linear isomer even far in energy from the resonance maximum. For linear isomer, dissociation is not only a direct process, vibrational predissociation also contributes and induces peaks on the energy dependence of the spectra (see Figs. 4 and 5). These two aspects are rather different from the assumptions made by Burke and Klemperer²⁶ to establish

the 1:3 ratio of T-shaped versus linear isomer population. In Fig. 10 the intensity ratio between the linear and T-shaped spectra at the same energies is shown. In the vicinity of IVR bands this ratio presents a minimum because the T-shaped spectrum always dominates. On the contrary, the maxima of the ratio correspond to the maxima of the linear isomer spectrum. In between these two extreme situations, the ratio oscillates between 1 and 100 and the base line clearly approaches 1 as energy increases. Moreover, when considering higher total angular momentum, the rotational bands associated to the T-shaped isomer get much broader, which makes the assignment of the spectra to the isolated linear isomer even more difficult. Based on these results, it is relevant to address the question about the possibility of distinguishing the spectra associated to linear and T-shaped isomers. More elaborate estimation of intensity ratio between the linear and T-shaped spectra could have an important effect on the relative population of two ArI₂(X) isomers.

FIG. 10. Ratio between the linear vs T-shaped isomers spectra.

VI. CONCLUSIONS

We have computed spectra and product state distributions on semiempirical and *ab initio* electronic potential energy surfaces for both linear and T-shaped $\text{ArI}_2(X)$ isomers. Whereas the T-shaped isomer dynamics is dominated by resonances, dissociation of the linear isomer involves competition between a fast direct process and slower vibrational predissociation of near-linear resonances, which have been characterized. In view of these rather complex dissociation mechanisms, we suggest the experimental determination of the linear to T-shaped isomer population ratio be reinvestigated. In particular, according to Klemperer,⁷⁹ the two experimental results for the binding energies of the perpendicular isomer could actually agree, if saturation effects are taken into account. Since the T-shaped spectrum consists of sharp lines, its absorption can be more easily saturated. This would change the perpendicular/linear isomer proportion, which was based on their relative absorption, hence modify their relative binding energy.

Although the present results are fully quantum mechanical ones, they are approximate in the sense that electronic couplings between excited electronic states which induce electronic predissociation have been neglected. Electronic predissociation is an experimentally well-established process, which Miller *et al.*³⁶ use to explain discrepancies between their perpendicular isomer dissociation energy and the one from Blazy *et al.*⁴⁶ A full picture of the ArI_2 dissociation process could, therefore, be obtained by performing dynamical calculations on several coupled excited states. Work along this line is currently in progress.

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