Theoretical study of the finite temperature spectroscopy in van der Waals clusters. III Solvated Chromophore as an effective diatomics

F. Calvo, F. Spiegelman
Laboratoire de Physique Quantique, IRSAMC, Université Paul Sabatier, 118 Route de Narbonne, F31062 Toulouse Cedex, France

J.-M. Mestdagh
CEA/DRECAM, CE Saclay, 91191 Gif-sur-Yvette Cedex, France

The absorption spectroscopy of calcium-doped argon clusters is described in terms of an effective diatomics molecule Ca–(Ar_\text{n})_\text{diatoms}, in the framework of semiclassical vertical transitions. We show how, upon choosing a suitable reaction coordinate, the effective finite-temperature equilibrium properties can be obtained for the ground- and excited-surfaces of the potential of mean force (PMF). An extension of the recent multiple range random-walk method is used to calculate the PMF over continuous intervals of distances. The absorption spectra calculated using this single-coordinate description are found to be in good agreement with the spectra obtained from high-statistics Monte Carlo data, in various situations. For CaAr_\text{13}, we compare the performances of two different choices of the reaction coordinate. For CaAr_\text{17}, the method is seen to be accurate enough to distinguish between different low-energy structures. Finally, the idea of casting the initial many-body problem into a single degree of freedom problem is tested on the spectroscopy of calcium in bulk solid argon.

I. INTRODUCTION

Polyatomic molecules can be electronically excited in a global or local way, depending on the chemical nature of the system, and on details of the excitation mechanisms, such as the characteristics or of the laser pulse. In many systems, the chemical bonds at various places of the same molecule favor local excitations. This situation typically occurs in chromophore-doped rare-gas clusters, where photons in the visible range may excite the chromophore but not the rare-gas atoms. This feature is especially useful because it allows a precise analysis by comparison with the isolated chromophore spectroscopy. Actually, even though the chromophore is locally excited, the geometric distortions and the vibrations of the solvent atoms act as a perturbation on its spectroscopic properties. From a theoretical point of view, these many-body effects are usually treated either with simple approximations or conveniently by simulation. In the previous papers of this series, we have presented an alternative approach to simulation, where the Gaussian theory of absorption by Wadi and Pollak was combined with the superposition approximation in the quantum regime at finite temperature. This method was applied to CaAr_n clusters of various sizes n in the range 2 \leq n \leq 146.

In these molecular systems, the calcium atom is energetically more stable when located on the surface of the argon cluster, rather than in a fully solvated site. At moderate temperatures, below the cluster melting point, the calcium atom gets the ability to glide over the argon cluster. The heterogeneous cluster CaAr_n can then be thought as an effective diatomic molecule, where the argon cluster would be replaced by a large pseudo-atom. Similar ideas have been previously used in chemical physics or condensed matter physics, as in the effective interactions between colloids or between polymers, or in the Girifalco or Gspann-Vollman interaction potentials between clusters of carbon or rare-gas atoms, respectively.

In this work, we investigate the possibility of treating the photoabsorption spectroscopy of CaAr_n clusters in this effective diatomics picture. For this purpose, we need to characterize the interaction on the ground- and excited-state potential energy surfaces in terms of a single reaction coordinate separating the calcium atom from the argon cluster. The effective absorption spectrum can then be constructed from the effective potential curves. The finite-temperature properties of a many-body system are conveniently expressed as ensemble averages in the canonical ensembles. It is possible to treat the reaction coordinate separately, and to perform some averages on the remaining degrees of freedom. The next stage consists of averaging over the reaction coordinate itself using its suitable statistical weight. In this context, the statistical average on the many-body system is reduced into a potential of mean force (PMF) calculation that will appear as a Helmholtz free energy. Several methods are available to get the computational solution to this problem, including umbrella sampling or constraint dynamics, or more recently the multiple-range random-walk algorithm which we have used in the present work.

The paper is organized as follows. In the next section, we describe the general method, and the algorithms used to calculate the effective properties of the Ca–(Ar_n) cluster as a function of an internal reaction coordinate. We then apply in Sec. the method to various cluster sizes, at several temperatures. In particular, the choice of the reaction coordinate may not be systematically obvious, and we show how more information can be obtained from a carefully chosen coordinate. For a suitable choice, ab-
II. FREE-ENERGY PROFILES FOR GROUND- AND EXCITED-STATES

Our system is a CaAr$_n$ cluster, described using the Cartesian atomic coordinates $\mathbf{R} = \{x_i, y_i, z_i\}$, where subscript 0 will be used for the calcium atom. We first present the main ideas and approximations of the method.

The photoabsorption spectrum of the cluster is calculated in a semiclassical way by assuming vertical transitions (Condon approximation) between the ground state surface $V_0(\mathbf{R})$ and several excited-state surfaces $V_k(\mathbf{R})$. At each configuration $\mathbf{R}$, the absorption cross section $\sigma_k(\mathbf{R})$ is proportional by the square of the transition dipole moment at this point, scaled by the transition energy. Excitation from the ground state surface thermalized at temperature $T$ leads to the unnormalized absorption intensity $\mathcal{I}_k(\omega)$ given by the sum over excited states, $\mathcal{I}_k(\omega) = \sum_k \mathcal{I}_k(\omega)$. The intensity of absorption from the ground state 0 to state $k$ is

$$\mathcal{I}_k(\omega) = \frac{1}{Z} \int \delta (\hbar \omega - [V_k(\mathbf{R}) - V_0(\mathbf{R})]) \sigma_k(\mathbf{R}) e^{-V_0(\mathbf{R})/k_BT} d\mathbf{R},$$

where the partition function $Z(T)$ is calculated on the ground state surface. For each excited surface $k$, and up to a constant factor, $\mathcal{I}_k(\omega)$ can be written as a canonical average on $V_0$:

$$\mathcal{I}_k(\omega) = \langle A_k(\omega, \mathbf{R}) \rangle,$$

with the notations

$$A_k(\omega, \mathbf{R}) = \sigma_k(\mathbf{R}) \delta (\hbar \omega - [V_k(\mathbf{R}) - V_0(\mathbf{R})]);$$

and

$$\langle O \rangle = \frac{1}{Z} \int O(\mathbf{R}) e^{-V_0(\mathbf{R})/k_BT} d\mathbf{R},$$

for any observable $O(\mathbf{R})$. In the following, and for clarity reasons, we shall drop the subscript $k$ indicating the excited state. The single excited surface will be denoted $V^*$.

Let now assume that a reaction coordinate or an order parameter $\xi(\mathbf{R})$ can be defined, which characterizes the overall location of ground state calcium with respect to the argon atoms. Possible expressions for $\xi(\mathbf{R})$ will be discussed at the end of the present section. At a given temperature $T$, calcium has a probability $p(\xi_0)$ of residing at coordinate $\xi_0$ given by the canonical average

$$p(\xi_0) = \langle \delta [\xi(\mathbf{R}) - \xi_0] \rangle.$$

This defines a potential of mean force (PMF) $W(\xi_0)$ according to:

$$W(\xi_0) = -k_BT \ln p(\xi_0).$$

The absolute value of the PMF is meaningful only if the probability distribution $p$ is normalized. It can be arbitrarily shifted by any additive term $W_0$, provided that a factor $e^{W_0/k_BT}$ is incorporated in the calculated observables.

Building upon these definitions, we can introduce the partial average $\bar{O}(\xi_0)$ of observable $O$ by restriction on the coordinate $\xi$:

$$\bar{O}(\xi_0) = \frac{\int O(\mathbf{R}) \delta [\xi(\mathbf{R}) - \xi_0] \exp[-V_0(\mathbf{R})/k_BT] d\mathbf{R}}{\int \delta [\xi(\mathbf{R}) - \xi_0] \exp[-V_0(\mathbf{R})/k_BT] d\mathbf{R}}.$$

$\bar{O}$ can also be written

$$\bar{O}(\xi_0) = \frac{\int O(\mathbf{R}) \delta [\xi(\mathbf{R}) - \xi_0] \exp[-V_0(\mathbf{R})/k_BT] d\mathbf{R}}{Zp(\xi_0)},$$

where $Zp(\xi_0)$ plays the role of a restricted partition function. By definitions of $p$ and $W$, Eqn. (8) effective surfaces $\bar{O}(\omega, \mathbf{R})$ can also be written

$$\langle A(\omega, \mathbf{R}) \rangle = \int \bar{A}(\xi) e^{-W(\xi)/k_BT} d\xi,$$

Importantly, Eq. (8) indicates that the PMF $W(\xi)$ plays the role of a Helmholtz free energy term corresponding to the deformation of the system along the single coordinate $\xi$. We have thus mapped the initial many-body problem into a simpler one-dimensional problem, where the initial ground-state potential has been replaced by the PMF, and the instantaneous observable by its partial average over all other, unrestricted degrees of freedom.

In the present context, further assumptions are needed in order to get the full picture of an effective diatomics to describe the CaAr$_n$ cluster. From expressions similar to Eq. (6) effective surfaces $\bar{V}_0(\xi)$ and $\bar{V}^*(\xi)$, as well as effective cross sections $\bar{\sigma}(\xi)$, can be constructed. The absorption intensity is then approximated as

$$\mathcal{I}(\omega) \approx \bar{\mathcal{I}}(\omega)$$

$$= \int \delta (\hbar \omega - [\bar{V}^*(\xi) - \bar{V}_0(\xi)]) \bar{\sigma}(\xi) e^{-W(\xi)/k_BT} d\xi,$$

A further approximation can be done, which will be checked later. We replace the function $e^{W_0/k_BT}$ by a Boltzmann weight over the effective ground-state surface $\bar{V}_0$. Hence

$$\mathcal{I}(\omega) = C \int \delta (\hbar \omega - [\bar{V}^*(\xi) - \bar{V}_0(\xi)]) \bar{\sigma}(\xi) e^{-\bar{V}_0(\xi)/k_BT} d\xi,$$

where the proportionality constant $C$ accounts for the normalization of $\bar{V}_0$:

$$C^{-1} = \int e^{-\bar{V}_0(\xi)/k_BT} d\xi.$$
In the following, we will only consider normalized absorption spectra, and $C$ will be dropped.

Using this extra approximation, Eq. (13) thus obtained is the complete analogue of Eq. (10) for a single-coordinate system. In order to use it in a practical situation, we need to calculate all effective quantities over a continuous range of the reaction coordinate $\xi$, starting with the free-energy profiles $V_0(\xi)$ and $V^*(\xi)$. For this purpose, we use the multiple range random walk method of Wang and Landau recently extended to the calculation of potentials of mean force and free-energies.

Briefly, we introduce a function $g(\xi)$ initially set to 1 in the range of accessible values of $\xi$, and we set $s(\xi) = \ln g(\xi)$. A Monte Carlo simulation is carried out using the following Metropolis acceptance rule between the old $R_{\text{old}}$ and new $R_{\text{new}}$ configurations:

$$\text{acc}(R_{\text{old}} \rightarrow R_{\text{new}}) = \min[1, \exp(-\Delta F/k_B T)], \quad (13)$$

with $\Delta F = F(R_{\text{new}}) - F(R_{\text{old}})$ and the (Landau) free energy $F(R) = V_0(R) - k_B T s(\xi(R))$. After the new configuration $R_{\text{new}}$ is visited, $s(\xi(R_{\text{new}}))$ is updated: $s(\xi(R_{\text{new}})) \rightarrow s(\xi(R_{\text{new}})) + \ln f$, or equivalently, $g$ is multiplied by $f$. Here $f$ is a fixed quantity, initially set to 2–2.5. After a large number of MC steps, a new iteration $m$ starts where $\alpha = \ln f$ is reduced by taking $\alpha_{m+1} = \alpha_m/2$. In this algorithm, the function $\Gamma(\xi) = -k_B T s(\xi)$ smoothly converges to the potential of mean force $W(\xi)$, up to an additive factor.

Once it has been calculated, the PMF gives also access to the restricted averages $A$ over a much wider range of $\xi$ than normally accessible. For this purpose each configuration in the Monte Carlo simulation is reweighted by the factor $\exp\{-W[\xi(R)]\}$. One should then get a uniform probability distribution for $\xi$. The flatness of this distribution can be used as a check of the PMF computed using the Wang-Landau method. The effective averaged observables are then obtained with the usual reweighting formulas.

We now turn to the choice of the reaction coordinate $\xi(R)$ in concern with absorption spectroscopy. A suitable coordinate should have a clear geometrical meaning. A straightforward definition is the “local” distance $d(R)$ between calcium and the closest argon atom:

$$d(R) = \min_{i \geq 4} \| \vec{r}_i - \vec{r}_0 \|, \quad (14)$$

where $\vec{r}_i$ denotes the position vector of atom $i$. This definition has the advantage that it reduces to the usual interatomic distance for the true diatomic molecule CaAr. Furthermore, this choice does not suffer any problem in a MC framework, in spite of the discontinuities that definition (14) introduces in the Jacobian. In contrast, this would not be the case in a molecular dynamics simulation and an alternative better choice would be the distance between the chromophore and the center of mass (com) of the argon cluster:

$$d_{\text{com}}(R) = \left\| \vec{r}_0 - \frac{1}{n} \sum_{i=1}^{n} \vec{r}_i \right\|. \quad (15)$$

Let us notice that the latter reaction coordinate is not practical in several cases, such as calcium in bulk argon. However, it can sometimes bring extra information with respect to the choice of $d$ above, Eq. (14), as will appear in the next section.

### III. APPLICATIONS TO Ca@Ar

We have applied the ideas developed in the previous section to two CaAr$_n$ clusters, namely CaAr$_{13}$ and CaAr$_{37}$. The 4$s^2$ ground state potential is modelled by simple pairwise terms, and the 4$s$4$p$ excited states are modelled using a Diatomic-In-Molecules (DIM) Hamiltonian. All details about the potentials and the parameterization are given in Ref. [4].

For all systems investigated here, the reference absorption spectra were obtained from classical parallel tempering Monte Carlo, using $10^6$ cycles after $2 \times 10^5$ initial cycles discarded for equilibration. For CaAr$_{37}$, we did not use parallel tempering because only the local properties of the isomers were needed. The potential of mean force was computed from the multiple range random walk algorithm using 20 iterations of each $10^6$ cycles following $2 \times 10^5$ thermalization cycles. The parameter $f$ was initially taken as 2.5, and the number of bins in the histograms of the reaction coordinate was set to 1000.

CaAr$_{13}$ is an obvious choice for testing the above methods, because the Ar$_{13}$ is icosahedral, hence nearly spherical, and because in this system calcium occupies a capping site of the icosahedral cluster. This is a virtual support to the effective diatomic picture. As seen in our previous papers, the calcium atom can jump into the icosahedral shell at moderate temperatures $T \sim 30$ K, but the spectroscopic signature of these isomerizations is rather weak.

In Fig. 4 we have represented the effective potential energy curves (ground and excited states) of CaAr$_{13}$ at $T = 30$ K, computed using the local distance $d$ between calcium and argon defined by Eq. (14). We have superimposed the (shifted) potential of mean force on the ground state effective surface. The two curves are rather close to each other, suggesting that approximating Eq. (10) by Eq. (13) is correct. All curves have similar variations as in the Ca–Ar diatomics, except a global shift to lower energies due to the additional argon-argon interaction energies. The excited state surfaces show a regular behavior, but we also note the presence of a crossing near $d \sim 10$ $a_0$ which is also present in the Ca–Ar pair. The corresponding effective absorption cross sections $\tilde{\sigma}(d)$ are displayed in Fig. 5. Except at small distances $d < 6$ $a_0$, they remain very close to their asymptotic atomic value. Hence the approximation $(AB) \approx \hat{A} \cdot \hat{B}$ in Eq. (10) should be satisfied.

The photoabsorption spectrum calculated using the diatomics picture and the effective potential surfaces is represented as a normalized histogram in Fig. 5, along with the result of classical Monte Carlo simulations.
FIG. 1: Effective potential surfaces of CaAr\textsubscript{13} at \( T = 30 \) K, as function of the local distance coordinate \( d \). \( V_0 \) and \( V^* \) are the ground- and excited-states surfaces, respectively. On the lower panel, the potential of mean force (PMF) is also represented, after shifting its asymptotic value to the ground-state potential.

FIG. 2: Effective absorption intensities of CaAr\textsubscript{13} at \( T = 30 \) K as function of the local coordinate \( d \). The agreement is remarkable, as far as the positions and widths of the peaks are concerned. The diatomics method introduces some additional noise due to the unaccuracy in the calculated effective potential curves. This noise could be partly reduced by taking a smaller number of bins in the interval of distances \( d \). However, this would also require one to reduce the number of bins in the histogram of the absorption spectrum.

As compared to our previous study using the superposition approximation, the absorption spectrum calculated using classical Monte Carlo does not show a significant signature of the isomers with calcium inside the icosahedral shell, the extra peak found in Ref.\textsuperscript{3} being replaced with a shoulder in the blue wing of the red peak. This prevents a clear identification of the possible isomers in the effective diatomics calculation.

The CaAr\textsubscript{37} cluster has a large number of stable low-energy minima, characterized by very different geometries. It’s global minimum is decahedral, and the next most stable isomer is a Mackay-type icosahedron. Due to their different spectroscopic signatures at low temperature, these two isomers provide a way of confronting the diatomics method to more detailed spectroscopic data. In Fig.\textsuperscript{4} we have represented the effective ground state potential curves as a function of the local coordinate \( d \), for the two decahedral and icosahedral isomers, at \( T = 5 \) K. At such low temperature, and using simple Monte Carlo, the cluster is expected to be trapped in its initial basin.\textsuperscript{4} As can be seen from Fig.\textsuperscript{4}, the icosahedral structure remains more stable than the decahedral minimum. The equilibrium distance is slightly shifted between the two isomers, which results from the different local arrangements of argon atoms near the calcium site. Neither the effective excited state potential curves nor the effective absorption cross sections are shown in this figure, as they display the same variations as in CaAr\textsubscript{13} with the same reaction coordinate. The normalized absorption spectra calculated with the effective diatomics approach are compared in Fig.\textsuperscript{5} to the reference Monte Carlo data. Besides the presence of residual noise, we find again a good agreement in the positions and widths of the absorption peaks for the two isomers. At temperatures higher than 5 K, multiple isomers become populated at thermal equilibrium,\textsuperscript{3} but they are separated by large energy barriers, making the sampling difficult even within the Wang-Landau approach. In an experiment, such a situation would correspond to the presence of several stable isomers in the cluster beam. Turning back
the choice of $d(\mathbf{R})$, which is very much guided by the kind of process we want to focus on. In CaAr$_{13}$, the distance $d_{\text{com}}(\mathbf{R})$ between the calcium atom and the center of mass of the argon atoms has essentially two values depending on the calcium atom being in a capping location over the argon icosahedron or inside the icosahedral shell. In the latter case, $d_{\text{com}}$ can actually take 4 different values, one for each icosahedral site, but the 4 values are close to each other (around 10\,a$_0$), and relatively far from the 13.5\,a$_0$ value in the global minimum.

The effective potential curves for CaAr$_{13}$ at $T = 30$ K using the $d_{\text{com}}$ coordinate are represented in Fig. 6. We could not extend the sampling of this coordinate below 8\,a$_0$ or beyond 18\,a$_0$ because of extensive noise. The effective ground state potential clearly shows the presence of two sets of minima, which can be attributed to the calcium (A) or argon (B) capping atom sketched in the lower panel of Fig. 6, depending on the outcome of a quenching procedure. Regions (A) and (B) are defined by the distance $d_{\text{com}}$ being larger or smaller than 12.01\,a$_0$, respectively. The effective excited states potential curves are also strongly influenced by this change in coordinate, and their variations reflect the two stable minima near 10\,a$_0$ and 13.5\,a$_0$, respectively. Therefore the $d_{\text{com}}$ reaction coordinate provides a structural order parameter that can distinguish between the different parts of the configuration space we are interested in. Being able to differentiate isomers (A) and (B) allows one to calculate the separate contributions of each region to the global absorption spectrum. We have reported in Fig. 7 the...
FIG. 7: Normalized simulated (solid line) and effective, diatomics-like (histogram) absorption spectra of CaAr$_{13}$ at $T = 30$ K, using the center-of-mass coordinate $d_{\text{com}}$. On the upper panel, the normalized spectra obtained by considering only regions A or B of the potential curves are represented (see Fig. 3).

total absorption spectrum and its individual contributions from (A) or (B). The overall agreement between the global spectrum and the Monte Carlo data is again good, and we notice that the blue shoulder near 23900 cm$^{-1}$ is larger than when using the local coordinate. This shows that the sampling of isomers (B) is more efficient, maybe even slightly too efficient with respect to the actual ergodic result. Longer simulations and a better sampling of region (A) would be needed to reduce this error.

By carrying the integral (11) over each region (A) or (B) separately allows for a spectroscopic distinction between the isomers. It can be seen that region (B) is responsible for the blue wing at 23900 cm$^{-1}$. The global spectrum is the weighted sum of the two separate contributions from (A) or (B), and the statistical weight of (B) was found to be around 25%, in agreement with the study in Ref. 14. It is interesting to discuss further the shape of the spectrum for each isomer. We discussed in Ref. 14 that the blue and red bands of spectra, similar to that shown in Fig. 3 for isomer A, are associated to exciting the 4p orbital perpendicular or parallel to the cluster surface, respectively. In the case of isomer A, because of the outer location of calcium the two possible parallel alignments of the 4p orbital are almost degenerated in average and lead to two merging bands. In contrast, calcium is closer to argon atoms in isomer B. As seen in Fig. 3 this corresponds to a larger the splitting between the two lower ($V^*$) potentials curves in the region that is accessible from the ground state isomer B. As a result, the red band in Fig. 3 is splitted into two components for isomer B. A splitted red band has actually been observed experimentally in a slightly different context, the $\text{Ba}(6s^2 \, 1S_0 \rightarrow 6s6p \, 1P_1)$ excitation on large argon clusters.

We just have seen that the spectroscopic properties of the chromophore are substantially affected by partial solvation in the argon cluster, that they appear as sensitive probe of the local environment of calcium and that they are satisfactorily described by the present effective diatomic picture. Going further in that direction, we consider a fully solvated Ca atom in an argon matrix as examined in the Monte Carlo simulations of Ref. 14. The present system is now a calcium atom surrounded by 107 argon atoms in a face-centered cubic lattice, at constant density $\rho = 1.562 \times 10^3$ kg.m$^{-3}$ and temperature $T = 20$ K. Bulk argon solvent is simulated using periodic boundaries conditions in the minimum image convention. The reaction coordinate is again the local distance from calcium to all other argon atoms, and the simulations were carried out with the same statistics as for clusters. The effective ground- and excited-states potential curves are displayed in Fig. 8. Since calcium remains fully solvated in an equilibrium position, the ground-state surface roughly has a distorted parabola shape, and cannot tend to zero at large distances $d$. As we expect, the excited-states surfaces are fully degenerated, giving rise to a dynamical Jahn-Teller effect in absorption.

The photoabsorption spectrum calculated from the effective diatomics approach is compared to Monte Carlo results in Fig. 8. The three excited potential surfaces lead to three absorption peaks, but they are quite broad, and the precise identification is less easy than with the MC data. Still we observe a surprisingly good agreement for the locations and overall widths of the peaks, suggesting that the effective diatomics method is adequate for
treating chromophore-doped inert systems with general shapes.

```
FIG. 9: Normalized simulated (solid line) and effective, diatomics-like (histogram) absorption spectra of Ca in solid argon at density $\rho = 1.562 \times 10^3$ kg.m$^{-3}$ and temperature $T = 20$ K, using the local coordinate $d$.
```

IV. DISCUSSION AND CONCLUSION

Spectroscopy of polyatomic molecules with many degrees of freedom is a difficult theoretical problem. Beyond simple harmonic approximations, the most convenient way to describe correctly the absorption intensity relies on numerical simulations based on relevant Hamiltonians for the potential energy surfaces. However, the complex, multidimensional character of the PES is a burden for simple physical interpretations of the results obtained by conventional methods. In this paper, we have presented a simple alternative approach based on the separate treatment of a single reaction coordinate, the many-body nature of the problem being thermally averaged into effective (free-)energy potential curves. By reducing the many-body problem into a single coordinate problem, the system is considered as a pseudo diatomics molecule, where the interactions implicitly depend on the thermodynamical conditions (temperature, but also pressure, and possibly chemical potential) and include the fluctuations within the averaged pseudo-atom. This point of view is best suited to the case of CaAr$_n$ clusters, where the visible photoexcitation is localized on the single calcium atom. In heterogeneous clusters, extra reaction coordinates could naturally appear. For instance, in CaKrAr$_n$, the two distances between calcium and krypton, and between calcium and the argon cluster could be treated on a same footing. In such cases, the present investigation could be easily generalized to provide effective hypersurfaces depending on several coordinates. In this picture the example chosen above would be considered as a pseudo triatomics Ca–Kr–Ar$_n$. Similar ideas could be applied to atom-diatom reactions solvated by an inert cluster.

Computationally speaking, the present method involves the preliminary calculation of the potential of mean force, which incorporates the statistical averages over all but one coordinates. The PMF is then used in a reweighting simulation to obtain the effective interactions and absorption cross section in a broad range of distances. The overall numerical cost is therefore heavier than in a conventional simulation, by one order of magnitude at the very least. However, the calculation of the PMF can be achieved conveniently, independently of the reaction coordinate chosen, using the multiple range random walk algorithm of Wang and Landau. Recently adapted to the problem of free-energy profiles, therefore the interest of the present approach mainly resides in the extra interpretations it provides. For instance, it could be used to assess or quantify the local character of the excitation. It also lays some ground for further spectroscopic investigations. In particular, more detailed studies of the excited states effective surfaces could be undertaken. The influence of temperature or the number of inert atoms on these curves, the related possible conical intersections offer examples of future research directions.

On a practical point, we have largely used a local distance coordinate $d$, namely the geometric distance (i.e. the lowest distance) between calcium and argon atoms. This order parameter is relevant to describe the CaAr$_n$ cluster as a pseudo Ca–(Ar$_n$) diatomics, for which most of the methodology developed here was meant. However, the separate effects of different isomers are essentially smoothed out and averaged, and it may be much more profitable to use other system-dependent coordinates to get a richer information about structure. In the case of CaAr$_{13}$, we have shown that the distance between calcium and the argon cluster center of mass was more appropriate in this purpose. In other, more complex clusters, one should take profit of the known structural information to design suitable reaction coordinates. For instance the bond order parameters $Q_4, Q_6, W_4$, or $W_6$, introduced by Steinhardt and coworkers, could be used to distinguish between icosahedral, octahedral, or decahedral isomers. One could then extend the present work to metallic clusters, where the energy levels can change upon global shape deformation and for which appropriate reaction coordinates could be the eccentricities or the Hill-Wheeler parameters.

Quantum vibrational effects are not accounted for in the present description, essentially because the corresponding treatment within path-integral finite temperature Monte Carlo is numerically demanding, and because reference calculations are not available. However, at moderate temperatures, the present approach could be straightforwardly applied to quantum-corrected potential energy surfaces using the Feynman-Hibbs effective potentials. [2]
At a more general level, the present approach gives the framework both to describe a reactive system in terms of deformations along a reaction coordinate and to calculate the corresponding energy variation. In that sense, the present calculation allows one to deal with the description of a chemical reaction in terms of the transition state theory in situations where part of the reactive system itself acts as a thermal bath. In the present case the reactive system is a calcium atom plus an argon cluster.

1. Y. J. Yan and S. Mukamel, J. Chem. Phys. 85, 5908 (1986).
2. H. Wadi and E. Pollak, J. Chem. Phys. 110, 11890 (1999).
3. F. Calvo, F. Spiegelman, and M.-C. Heitz, first article of this series.
4. F. Calvo, F. Spiegelman, and D. J. Wales, second article of this series.
5. F. Calvo, J. P. K. Doye, and D. J. Wales, J. Chem. Phys. 114, 7312 (2001).
6. L. A. Girifalco, J. Phys. Chem. 96, 858 (1992).
7. J. Gspann and H. Vollmar, in Rarefied Gas Dynamics, 8th Symposium, edited by K. Karamchti (Academic Press, New York, 1974), p. 261; in Rarefied Gas Dynamics, 11th Symposium, edited by R. Campargue (CEA, Paris, 1979), Vol. II, p. 1193.
8. M. P. Allen and D. J. Tildesley, Computer Simulations of Liquids (Oxford, 1987).
9. D. Frenkel and B. Smit, Understanding Molecular Simulation (Academic Press, NY, 1996).
10. G. M. Torrie and J.-P. Valleau, Chem. Phys. Lett. 28 578 (1974).
11. E. A. Carter, G. Ciccotti, J. T. Hynes, and R. Kapral, Chem. Phys. Lett. 156, 472 (1989).
12. F. Wang and D. P. Landau, Phys. Rev. Lett. 86, 2050 (2001).
13. F. Calvo, Mol. Phys. 100, 3421 (2002).
14. M. A. Gaveau, M. Briant, P. R. Fournier, J. M. Mestdagh, J. P. Visticot, F. Calvo, S. Baudrand, and F. Spiegelman, Euro. Phys. J. D 21, 153 (2002).
15. J. P. Visticot, P. de Pujo, J. M. Mestdagh, A. Lallement, J. Berlande, O. Sublimontier, P. Meynadier, and J. Cuvelder, J. Chem. Phys. 100, 158 (1994).
16. P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B 28, 784 (1983).
17. J. P. K. Doye, M. A. Miller, and D. J. Wales, J. Chem. Phys. 110, 6896 (1999).
18. J. P. Neirotti, F. Calvo, D. L. Freeman, and J. D. Doll, J. Chem. Phys. 112, 10340 (2000); F. Calvo, J. P. Neirotti, D. L. Freeman, and J. D. Doll, ibid. 112, 10350 (2000).
19. J. P. K. Doye, M. A. Miller, and D. J. Wales, J. Chem. Phys. 111, 8417 (1999).
20. C. Yannouleas and U. Landman, Phys. Rev. B 51, 1902 (1995).
21. R. P. Feynman and A. R. Hibbs, Quantum mechanics and path integrals (McGraw-Hill, New York, 1965).