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Influence of electronic excitations on the thermodynamics of small carbon clusters: the example of C_3^+

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Abstract. We illustrate the influence of the thermalization of electrons on the linear-cyclic isomerization of small carbon clusters by model Monte Carlo calculations of C_3^+ at 3500 K. It is shown that the inclusion of the electronic degrees of freedom, in such systems with several low-lying excited states, can significantly change the relative isomer populations and energy distributions, as compared with equivalent electronic ground-state simulations.

PACS. 71.15.Dx Computational methodology (Brillouin zone sampling, iterative diagonalization, pseudopotential construction) – 05.10.Ln Monte Carlo methods – 73.22.Dj Single particle states – 82.60.Qr Thermodynamics of nanoparticles

1 Introduction

Together with the very specific fullerenes and nanotubes, small carbon clusters have attracted a wide attention both theoretically and experimentally (for a review, see for instance Weltner an Van Zee [1], Campbell [2], Van Orden and Saykally [3]). One of the motivation comes from astrochemistry [4] since carbon chains and clusters are supposed to be present with other carbon-based systems in the interstellar and circumstellar medium. The structure of small carbon clusters with sizes $n < 10$ has been rather widely investigated and the most stable structures of the smaller ones are known to be either linear or cyclic [5–7]. This is true for neutrals and singly charged cations. However, pure carbon clusters correspond to half band filling and strongly unsaturated bonds. As a consequence, those systems are characterized by low-lying excited states, sometimes even quasi-degenerate with the ground state, situation further enhanced by rather high symmetry. This is even the case for C_2 for which a $^3\Pi_u$ state only lies around 0.25 eV above the $^1\Sigma_g^+$ ground state. This deneracy situation extends to all small carbon clusters, depending on the electron filling as well in cyclic forms as in linear forms, for which the true electronic state is not always completely elucidated (see C_8 for instance [8]). Such quasi-degeneracy and the possibility of electronic excitation is likely to significantly affect the thermal properties of those systems, even at temperature below the melting temperature of bulk carbon ($T_{melt} \approx 4000$ K for graphite). While most molecular dynamics or Monte Carlo simulations concerned with thermal properties of clusters are in general dedicated to motion on the electronic ground state surface [6,9], the present paper applies a Monte carlo method previously introduced [10] to the case of C_3^+. It combines the nuclear motion (characterized by coordinates $\mathbf{R}_I$) with electronic excitation (characterized by the molecular orbital occupation numbers n_i). While its application in the case of sodium clusters for temperatures in the range 10−400 K was not found to have significant influence on the thermal properties [10], the present application to the case of C_3^+ enlights the possible influence of low-lying electronic states excitation on the sampling of geometrical configurations and determination of statistical averages in small carbon clusters. The present canonical scheme should be relevant to the simulation of the initial condition sampling in non selective experiments with respect either to spin state or isomer distribution.

2 Methodology

2.1 Energy calculations

The model used for the description of the C_3^+ cluster was developed [11] to successfully treat neutral and positively charged carbon clusters. It is a semi-empirical charge-consistent tight-binding model for valence electrons built along the following approximations: (i) it is a single-electron mean field approach, (ii) electronic exchange is neglected, and (iii) the atomic basis set ($2s$, $2p$) is considered orthogonal. The only two-electron integrals are

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Coulomb integrals, approximated via a single function v of internuclear distance for two-center contributions, and via a single repulsion term U for all one-center contributions. Those approximations are in the spirit of those used in Complete Neglect of Differential Overlap type methods [12], in AM1 or PM3 schemes [13], or the SCTB-DFT approximation [14]. If $\hat{\rho}$ is the electronic density matrix, $\hat{t}$ the pure tight-binding part of the Hamiltonian (atomic energies plus hopping terms), and n_I (resp. n_J) is the electron number on atom I (computed from the diagonal of $\hat{\rho}$), the potential energy of the nuclei system, as a function of their positions $\boldsymbol{R}_I$, reads

$$E(\{\boldsymbol{R}_I\}) = \mathrm{tr}(\hat{t}\hat{\rho}) + \frac{1}{2}\sum_{I\neq J}(n_I - Z)(n_J - Z)v(R_{IJ}) + \frac{U}{2}\sum_I (n_I - Z)^2 + V(\{\boldsymbol{R}_I\}),$$

where V sums up classical repulsive core-core contributions.

For strictly monoelectronic (non self-consistent) Hamiltonians, the excited states of the system are easily obtained from the initial diagonalization by specifying all the possible occupations number sequences consistent with the number of molecular orbitals and the number of electrons [10]. In the context of an N-body Hamiltonian as in the case of the present model, this is only an approximation. In the following, the excited electronic states will still be taken as simple determinants, substituting the ground-state occupied orbitals with virtual molecular orbitals (namely changing the occupation numbers $\{n_i\}$), nevertheless calculating the energy of the excited states as the expectation value of the full Hamiltonian above. This approximation actually neglects relaxation and correlation effects in excited states, but should not be too bad in the present context, for a presumably semi-quantitative approach of multi-state thermal effects. We have actually checked that it does not significantly differ from linear response (RPA) states in the cases presented here. The systematic calculation of RPA states [15] in extensive simulations, even with the present simplified Hamiltonian, occurred to be too much time-consuming.

While the electronic properties of trimers and even larger clusters have been approached via higher level methods [5,7,16,17], the final scope is to extend such treatment to larger size clusters in simulations involving extensive sampling, in which case a simplified model such as the one used here should be efficient.

2.2 Monte Carlo scheme

The Monte Carlo (MC) algorithm developed by Calvo and Spiegelman [10] treats the nuclear ($\mathbf{R}$) and electronic ($\mathbf{N}$) degrees of freedom (DOFs) on the same footing [10], by performing random moves on the generalized coordinates $\mathbf{Q} = (\mathbf{R}, \mathbf{N})$. Here $\mathbf{N} = \{n_i\}$ is the set of instantaneous integer occupation states, which evolve during the simulation according to the level statistics. A change from $\mathbf{Q}_{\mathrm{old}}$ to $\mathbf{Q}_{\mathrm{new}}$ due to a change in $\mathbf{R}$ is accepted with the Metropolis probability $\min[1, \exp(-\beta\Delta E)]$ where $\Delta E = E(\mathbf{Q}_{\mathrm{new}}) - E(\mathbf{Q}_{\mathrm{old}})$; if it is due to a change in $\mathbf{N}$, the acceptance probability is 1 if $E(\mathbf{Q}_{\mathrm{old}}) > E(\mathbf{Q}_{\mathrm{new}})$ and $(C_{\mathrm{old}}/C_{\mathrm{new}})\exp(-\beta\Delta E)$ otherwise. Since the MC moves involving $\mathbf{N}$ must keep constant the total number $\mathcal{N}$ of occupied states, we only allow permutation of population between occupied and unoccupied, *neighboring* levels: C_{old} and C_{new} in the latter formula are the numbers of possible such exchanges in the old and in the new configuration. For any given $\mathbf{R}$ this algorithm was shown to clearly converge to the electronic canonical distribution in the ergodic limit for the case of a true non-self-consistent tight binding scheme [10].

Local moves involving $\mathbf{R}$ and $\mathbf{N}$ are implemented in the framework of the Exchange Monte Carlo algorithm [18], performing simultaneous simulations at various temperatures. Exchange moves between configurations $\mathbf{Q}_i = (\mathbf{R}_i, \mathbf{N}_i)$ and $\mathbf{Q}_j = (\mathbf{R}_j, \mathbf{N}_j)$ at the inverse temperatures β_i and β_j, respectively, are attempted with a given probability p and accepted with the probability

$$\mathrm{acc}(\mathbf{Q}_i \rightleftharpoons \mathbf{Q}_j) = \min\{1, \exp(\beta_i - \beta_j)[E(\mathbf{Q}_i) - E(\mathbf{Q}_j)]\}.$$

In our case, such moves exchange both the nuclei positions and the occupation number sequence. With probability $1 - p$, the usual local moves are attempted for all trajectories. The EMC scheme generally improves the ergodicity [19]. Even in small systems like a trimer at temperatures below the isomerization barrier, it ensures more efficient thermalization in both basins whenever accessible. The EMC simulations were run at $T = 3500$ K, 5000 K, 7000 K and 15 000 K. Only the 3500 K results are discussed here. Trajectory and electronic exchanges are attempted randomly, in average every ten moves: this compromises between exhaustive sampling of the accessible configurations at a given temperature (equilibration between nuclei and electrons) and efficiency of the exchange algorithm. In the case of an exchange move from temperature i, the destination temperature is chosen from all other temperatures with an equal probability. The parallel trajectories are propagated along 10^6 steps.

Though not specifically interesting and partly trivial since it has only one nuclear DOF, C_2 was used as a simple system to validate the thermalization scheme. The equilibrium distance of the closed shell $\pi_u^4 \Sigma_g$ ground state of C_2 is $R_e = 2.36$ Bohr. That of the lowest excited state, namely $\pi_u^3\sigma_g^1\ \Pi_u$ located $\Delta E = 0.08$ eV above the ground state is $R_e = 2.43$ Bohr. The minimum of the next excited state, $\pi_u^2\sigma_g^2\ \Delta$ is located at $R_e = 2.48$ Bohr, $\Delta E = 0.24$ eV above the ground state minimum. First a simulation of thermalization at geometry-fixed C_2 ($R_e = 2.36$ Bohr), involving only the electronic DOF's (8 electrons), is compared to an exact theoretical calculation involving the determination of the partition function with the total energy levels and state degeneracies. It can be seen in Table 1 that the expected (discrete) theoretical values of the energy distributions and those obtained in the simulation are in excellent agreement. Analogous distributions at $T = 500$ K are shown in Figure 1, now exhibiting some broadening

Table 1. Normalized energy distribution for the MC simulation of nuclei-fixed C_2 at 500 and 1000 K. Exact values are shown in parentheses.

T	ground	first	second
500	0.9446	0.05516	0.00021
	(0.9459)	(0.05376)	(0.00028)
1000	0.5815	0.3937	0.0248
	(0.5870)	(0.3873)	(0.0225)

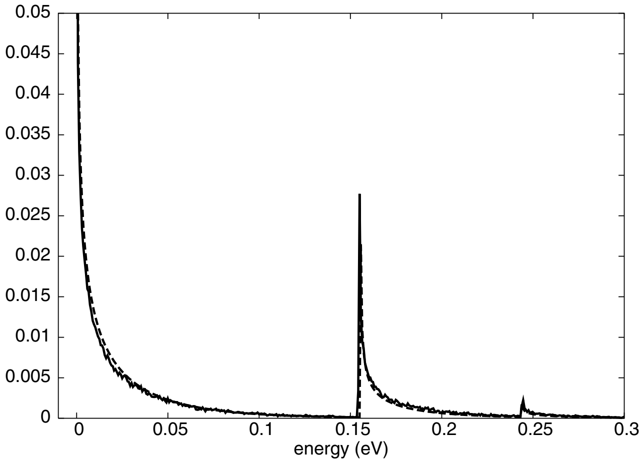

Fig. 1. Normalized energy distribution of C_2 with electronic thermalization at 500 K. Solid line: Monte Carlo; dashed line: direct calculation. The results are almost superimposed.

since the nuclear motion has been allowed. The above independent theoretical values have been obtained using the classical motion harmonic approximation of the nuclei DOS for each electronic state. There again, there is an excellent agreement between the theoretical and the simulated data.

3 Results

We now turn to the question of the effect of electronic thermalization on the relative population of C_3^+ isomers at $T = 3500$ K. The structure of the ground state PES of C_3^+ is pretty well accounted for in the present model. It has two characterized minima, one corresponding to a cyclic isomer with C_{2v} symmetry ($^2B_2$ electronic state, $r = R = 2.49$ Bohr, $a = 64$ degrees), the second one linear ($D_{\infty h}$ symmetry, $r = R = 2.45$ Bohr), the cyclic isomer being more stable by 0.17 eV (to be compared with the 0.09 eV separation in the accurate CCSD(T)/QCISD(T) investigation of Martin and Francois [20]). The C_{2v} minimum results from a conical intersection (D_{3h} configuration) located closeby. The harmonic approximation zero-point energy (HA-ZPE) of the linear isomer is lower than than that of the cyclic one (here 0.226 eV versus 0.242 eV) inverting the ordering given by the potential energy surface alone, as discussed by Martin and François [20]. In both cases, the HA-ZPE lies above the conical intersection, and clearly, even at low enough temperatures, two surfaces at least are likely to contribute to thermal properties. At $T = 3500$ K, several other surfaces contribute to a weaker extent. Figure 2 illustrates the ground state isomerisation path (present model) as a function of the bending angle a and the dissociation path as a function the elongating distance R. The conical intersection involving the two lowest potential energy surfaces and the various low potential energy surfaces are clearly visible.

Figure 2 shows the energy distributions corresponding to the EMC simulation of C_3^+ with and without electronic excitations enabled. The distribution corresponding to the adiabatic (without excitations) simulation is more strongly peaked above the energy of the linear isomer, and vanish more quickly than when electrons are able to thermalize. Moreover, the influence of electronic excitation is visible at low energy, resulting into a split peak corresponding to the ring isomer in the vicinity of the conical intersection.

The analysis of cluster geometry can be done in several ways. One typical way used in simulation is to perform quenches of the cluster along the MC "trajectory" and obtain so-called isomer-spectra [21]. However, here the situation is ambiguous since several potentials surface are involved, not necessarily having the same minima. We have thus used a geometry-based analysis involving the numbers of neighbours (defined via a cut-off distance $R = 4$ Bohr) per atom sorted in decreasing order: (2 2 2) corresponds to the cyclic isomer, while (2 1 1) stands for the linear isomer.

The relative population per isomer population of the system resulting from the two kinds of simulations are shown in Figure 3. The effect of electronic excitations is to inverse the relative abundances of the isomers of C_3^+. This effect can be related to differences between the (coordinate dependent) excitation spectrum in the respective basins of the cyclic isomer: the larger number of states associated with electronic excitation contributes much less to the total, for the linear isomer, than it does for the cyclic isomer, because of the much larger gap.

4 Conclusions

The energy distribution of C_3^+ at $T = 3500$ K was determined in the canonical ensemble via the classical Exchange Monte Carlo simulations including both nuclear and electronic degrees of freedom. At such a temperature, there is a possibility to populate the lowest excited states, especially, but not only, those involved in the conical intersection. This has an influence on the geometrical configurations sampling and affects the energy distributions. The determination of the full caloric curve for C_3^+ would be interesting, but requires a much larger sampling of temperatures. The relevance of including several states may be a general indication for larger carbon clusters with either cyclic or linear shape. The present study is still preliminary and mainly provides an illustration of the role of multi-state effects. Indeed it is seen that the potential energy surfaces (significantly anharmonic), the account of ZPE and the inclusion of several electronic states have

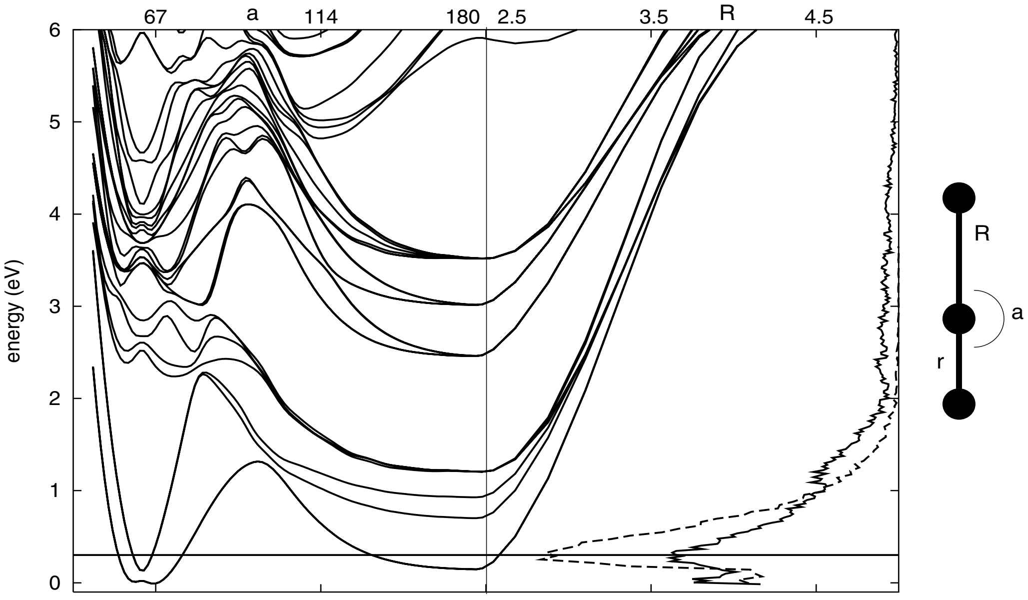

Fig. 2. Simulated energy distributions for C_3^+ at $T = 3500$ K (horizontal line) with and without electronic excitation. Left: ground state excited states of C_3^+; left of the vertical line: along the bending coordinate a (degree); right of the vertical line: along the linear dissociation coordinate R (Bohr) into C_2+C^+. Right: energy distribution with electronic excitation (solid line) and without electronic excitation (dashed line).

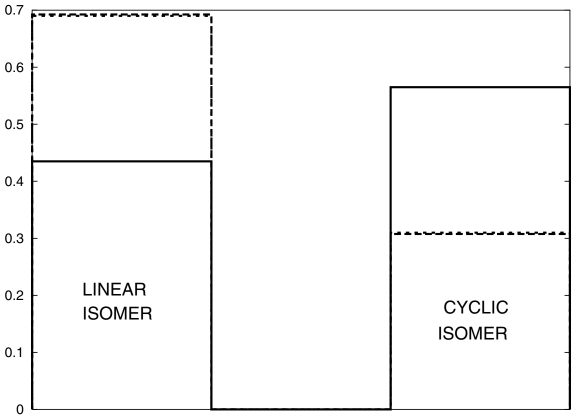

Fig. 3. Normalized isomer population for C_3^+ at $T = 3500$ K with (solid) and without electronic excitation (dashed line).

conflicting trends on the final isomer population and that the simulation should include all those effects. A detailed quantum treatment of the conical intersection would certainly be feasible for C_3^+ but would be almost impossible to extend to larger clusters in a thermodynamical context.

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