Eur. Phys. J. D **30**, 363–368 (2004)
DOI: 10.1140/epjd/e2004-00109-0

THE EUROPEAN
PHYSICAL JOURNAL D

Charged cores in ionized ^{4}He clusters III: A quantum modeling for the collisional relaxation dynamics

E. Scifoni[1,2], E. Bodo[2], G. Dellepiane[1], and F.A. Gianturco[2,a]

[1] Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, 16146 Genoa, Italy
[2] Department of Chemistry and INFM, University of Rome "La Sapienza", Piazzale A. Moro 5, 00185 Rome, Italy

Received 24 March 2004 / Received in final form 15 June 2004

Abstract. When a pure ^{4}He droplet is ionized by electron impact, the most abundant fragment detected in mass spectra after ionization is He_2^+. All the models that have been proposed thus far to explain the experimental evidence therefore involve the formation of the He_2^+ molecular ion. The understanding of the interactions between this ion and the surrounding He atoms in the cluster and of their dynamical behavior during cluster break-up is an important element for the modeling of the cluster evolution after the ionization event. In previous works [1,2] we have computed and described the Potential Energy Surface (PES) of the electronic ground state for the He_3^+ system that provides the required forces between He_2^+ and He. After ionization He_2^+ is presumably formed by association of an He^+ and any of the neutral atoms in the cluster via a 3-body collision process. The ensuing vibrational quenching of the "hot" molecular ion may release the energy necessary to evaporate the entire droplet, or most of it, and give the fragmentation patterns detected by experiments. We present here a model quantum dynamics that generates vibrational deexcitation cross-sections and the corresponding rate coefficients for the collision of He_2^+ with He. A timescale of the cluster evaporation due to vibrational relaxation is estimated and the present findings are compared with earlier studies on the same system.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 34.50.Ez Rotational and vibrational energy transfer – 36.40.Wa Charged clusters

1 Introduction

When an helium droplet is ionized by electron impact the resulting mass distribution observed experimentally [3] tends to be dominated by the presence of very small fragments even when the initial cluster size is very large. In particular, regardless of the initial size of the cluster the He_2^+ moiety turns out to contribute more than 40% of the relative peak intensities. Various theoretical hypotheses have been put forward over the last 20 years in order to describe the likely processes taking place in a helium cluster after ionization [4–6] and to explain through them what is experimentally observed [3,7–9].

The initial effect of a photon or a fast electron impinging on a relatively large ($100 < N < 10^6$) helium droplet is the ionization of one of the atoms. This ionization can occur randomly throughout the outer cluster layers because the mean-free path of fast electrons into the helium droplets is rather large [3]. The secondary electrons generated by the primary process are not energetic enough to induce additional ionization because of the large ionization potential of He and of the very large mean free path of slow electrons in such diluted systems [4]. Moreover, alternative ionization mechanisms such as indirect ionization via decay of helium excited states or direct ionization to He_n^+ species formation are considered to be inefficient under experimental conditions [3]. After ionization a large number of atoms in the cluster evaporates, leading to He_2^+ and other small fragments to be observed (e.g. see Refs. [4,7]). This effect can be explained by a multistep mechanism:

- after the formation of the atomic ion by electron impact, the charge may migrate by resonant charge transfer among the various atoms: see, for example, the discussion in references [8,10] and the model calculations of references [5,6] for the time scales of this charge-hopping process. The most recent model calculations [10] indicate different values to occur depending on the initial position of the He^+ ion in the cluster. They estimate that any single charge transfer hop may take place in about 9.5×10^{-15} s;
- after a certain amount of time which we will discuss below more in detail, a 3-body collision may lead to the formation of He_2^+ in a highly vibrationally excited state. In fact, there is some theoretical evidence for

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[a] e-mail: `fa.gianturco@caspur.it`

considering the He_2^+ the main outcome of such a charge localization process: in the study of large ionic helium cluster structures [11], the dimeric molecular ion turns out to be the center of nucleation around which the remaining atoms are structured, although a triatomic core He_3^+ is found to be possible when the aggregates become markedly smaller [11]. We have further seen that, in the photoionization of He_3^+ [12], a highly excited He_2^+ dimer is the dominant outcome. The earlier calculations of references [5,10] have also probed this point, as we shall further discuss below;

- after the formation of He_2^+, the vibrational de-excitation process, due to further collisions, may be the chief cause for the large atomic losses seen by experiments. Recently, however, a new interpretation of the fragmentation has been put forward [3] in which the possibility that the He_2^+ molecule is ejected from the cluster right after its formation without any thermalization process should also be a possible option. We shall show below that our present calculations surmise that the formation of translationally "hot" dimer ions, necessary for their direct ejection seems to be less likely than the efficient transfer of its internal energy to surrounding atoms which therefore acquire additional translational energy and are more likely to leave the cluster.

Another set of experiments [8,9,13,14], have looked at the cluster fragmentation when the latter is doped with a neutral molecular impurity. In such experiments the parent ion of the dopant usually becomes the most intense peak in the mass spectrum. A reasonable explanation is that, for doped clusters, the charge initially located on one of the helium atoms gets to be transferred to the impurity residing in its center (where charge stability increases) since most molecular dopants have a lower ionization potential when compared to He. In this case the inelastic processes involving the collisional cooling of the final ionized molecular impurity seem to lead to the evaporation of the entire cluster structure. It is therefore very important to theoretically estimate the various time scales in which all these processes can take place in order to establish whether an electron impact over He clusters produces at the end either ionization of the dopant molecule (when present) or the direct formation of He_2^+ (in the pure helium droplets) bound to some remaining neutral atoms.

In various earlier papers [4,6,9], the time span in which charge migration can occur before the formation of the He_2^+ or of an ionic molecular impurity, has already been surmised to be of the order of 10^{-12} s that could correspond to several molecular vibrations. Recently however, there has been some theoretical evidence [5,10,12] that suggests that the He_2^+ moiety might get formed in a much shorter time: the simulations of the short time electronic dynamics in smaller aggregates found that the He_2^+ is formed after about 10^{-13} s [5]. The charge localization process on He_2^+ is particularly efficient when the primary ionization site is near the surface of the cluster [10]: in such a case the ionization does not lead to significant charge migration before formation of He_2^+ and this can partly explain the fragmentation patterns observed in the mass spectra. Furthermore, a simple kinetic estimate which uses the three-body association rates, measured earlier [15] and recently calculated [16] for the reaction $He^+ + 2He \rightarrow He_2^+ + He$, yields even shorter times for the formation of He_2^+. Since at low temperatures, the above rate constant is between 5×10^{-32} and 5×10^{-31} cm^6 s^{-1} (values that are consistent with the data in Fig. 5 of Ref. [16]), if we assume that the neutral helium density in the droplet is constant during the reaction and is at most equal to the experimental value of liquid helium[1], we obtain that the available time span leading to the He_2^+ formation is between 4×10^{-15} and 4×10^{-14} s.

It therefore follows that the time available to resonant charge hopping discussed before is very short. Thus, one might look for alternative mechanisms by which the charge may migrate through the cluster and eventually reach the impurity, if it exists. For example, charge migration may take place by atom exchange collisions of He_2^+ and the surrounding atoms or by simple transport of the He_2^+ moiety: none of these processes, however, have been either directly measured or put to test in actual calculations. A classical approach to evaluating the collision rates of $He_2^+ + He$ has been applied by Bosanac and Murrell [17], who obtained (at a collision energy of 0.1 eV) probabilities for the resonant atom exchange of about 12.7% under single collision conditions.

In view of the above discussion we believe that it is still very important to be able to estimate the time scale needed for the vibrational quenching of He_2^+ because it determines the lifetime of the cluster i.e. that time during which, in doped clusters, a dynamical process such as non-resonant charge transfer to the existing impurity can occur. In the present work we thus provide, using an approximate quantum dynamical method, estimates of the time scale and the efficiency of the inelastic collisions once the "hot" He_2^+ dimer has been formed inside the pure helium clusters. In Section 2 we shall present the dynamical method chosen to study this system while in Section 3 we will show and comment on the results found for the vibrationally inelastic cross-sections. Finally, in Section 4 we show our computed cooling rates and extract from them a time estimate for the relaxation process that would bring the vibrationally "hot" He_2^+ down to the bottom of its potential well. The conclusions are summarized in the last Section 5.

2 The quantum dynamical model

The first step in the study of the quantum dynamics of the title system requires the evaluation of the Vibrorotational-to-Translational (V,R-T) couplings that stem from the three-dimensional PES when convoluted over the asymptotic He_2^+ vibrational functions $\{\varphi_i(r)\}$:

$$\langle \varphi_i(r) | \, V(r, R, \theta) \, | \varphi_j(r) \rangle = V_{ij}(R, \theta) \qquad (1)$$

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[1] The number density of bulk liquid helium is 2.18×10^{22} atoms cm^{-3}. The density that is attained in the largest droplets, $n > 100$, is very similar to that of the bulk value [23].

where (r, R, θ) are the three Jacobi coordinates. The vibrational couplings for this system have been extensively reported in reference [2] where they were shown to be very strong and rather long-ranged. As a results of this, and because of the strong rotational anisotropy of the present PES [2], an exact calculation with a full Coupled Channel (CC) [18] model would require too many ro-vibrational levels to obtain numerical convergence especially when the initial vibrational state is very high. We have first attempted to apply a simplified scheme in which the vibrational states are treated exactly while the rotational states are modelled by an Infinite Order Sudden approximation (VCC-RIOS, e.g. see Ref. [19]), but even such a reduced coupling turned out to be too strong to provide satisfactorily converged state-to-state inelastic cross-sections. We have therefore resorted to further simplifications as briefly outlined below.

The collisional process we are studying can be written down as follows

$$\mathrm{He}_2^+(\nu) + \mathrm{He} \rightarrow \mathrm{He}_2^+(\nu' < \nu) + \mathrm{He} \quad (2)$$

where the initial values for ν are taken to be the highest vibrational levels of the molecule (ν from 17 to 22). The coupled channels equations for a structureless atom and a closed shell Σ molecule in a space-fixed (SF) reference frame are well-known [18] and stem from the usual expansion of the total wavefunction onto asymptotic roto-vibrational state of the target times unknown radial coefficients, $g^{J\nu jl}_{\nu''j''l''}(R)$, determined via such equations and the coupling potential terms U's reported below are related to our computed couplings reported in paper II of this series 2 [18]

$$\left[\frac{d^2}{dR^2} + k^2_{\nu'j'} - \frac{l'(l'+1)}{R^2}\right] g^{J\nu jl}_{\nu'j'l'}(R) = \sum_{\nu''j''l''} U^J_{\nu'j'l',\nu''j''l''}(R)\, g^{J\nu jl}_{\nu''j''l''}(R). \quad (3)$$

where the labels refer to the asymptotic states and the coupled angular momenta of the atom-diatomic case [18]. The molecular angular momenta and the vibrational quantum numbers can now be fully decoupled [19] by rewriting the above equations as parametrically dependent on the relative orientation $\theta = \arccos(\hat{R} \cdot \hat{r})$ and on the diatomic bond distance r:

$$\left[\frac{d^2}{dR^2} - \frac{l'(l'+1)}{R^2} + k^2_j\right] F^{l'}_j(R;\theta,r) = U^{l'}(R;\theta,r) F^{l'}_j(R;\theta,r) \quad (4)$$

where $U^{l'}(R,\theta)$ is now a "rigid rotor" potential obtained by keeping the internuclear distance of the target fixed during the collision.

Equation (4) is therefore solved numerically using $j = 0$ and by keeping fixed the values of θ and r for the necessary values of l. The physical simplifications introduced by the present scheme, although dictated by necessity, have a physical justification if one takes into account the ambient conditions in the ionized droplet and when one considers that, due to the low temperature of the droplets, the diatomic ion is presumably formed rotationally "cold", but vibrationally excited. Since He_2^+ is produced in one of its highly excited vibrational states, the nodal structure of the corresponding vibrational wavefunction describes the two partners atoms to be localized mostly in the outer regions of the potential where the nuclear motion is "slow": this would allow the collision to occur on a locally shorter timescale than the one corresponding to a full vibrational coupling.

The numerical integration was started in the inner, classically forbidden region of relative distances and the solution was then propagated using a log-derivative scheme up to a suitable (and large) value of R where the usual boundary condition is imposed in order to generate the corresponding S-matrix, as fully described by reference [20]:

$$F^l(R;\theta,r) \rightarrow k^{-\frac{1}{2}} \left(e^{-i(kR-l\pi/2)} - S^l(\theta,r) e^{i(kR-l\pi/2)}\right). \quad (5)$$

The resulting T-matrix was then fitted over the radial variable r using cubic splines and integrated over the vibrational states $\phi_\nu(r)$, thereby leading to the θ dependent matrix elements:

$$T^l_{\nu\nu'}(\theta) = \langle \phi_\nu(r) |\, T^l(r|\theta)\, | \phi_{\nu'}(r) \rangle. \quad (6)$$

The calculation has been repeated for all the necessary values of l in order to obtain fully converged r-fixed T-matrix elements. The integral cross-sections have been then obtained by summing over all the contributing partial waves and integrating over the angular variable θ:

$$\sigma(\nu' \leftarrow \nu) = \frac{\pi}{2k^2_\nu} \int_0^{\pi/2} \sum_l (2l+1) \left|T^l_{\nu\nu'}(\theta)\right|^2 d\theta. \quad (7)$$

In spite of its simplicity, we think that, under the experimental conditions and for our modelling purposes such an approximation may possibly be appropriate. In any event, in this way we were able to yield converged estimates for the cross-sections because in such a simple model the vibrational and rotational couplings are not dynamically active during the collision but are instead adiabatically included.

3 The computed de-excitation cross-sections

Although a theoretical modelling of the gas-phase reaction

$$\mathrm{He}^+ + 2\mathrm{He} \rightarrow \mathrm{He}_2^+ + \mathrm{He} \quad (8)$$

leading to the formation of He_2^+ has been recently proposed [16] and yielded fairly good agreement with the existing in-cell measurements [15], we lack any information on the possible vibrational population after the 3-body collision in the droplet environment. This is a key piece

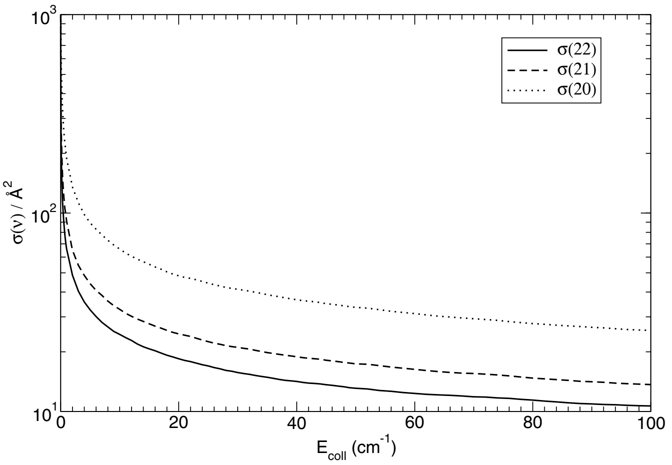

Fig. 1. Computed de-excitation cross-sections, from the $\nu = 22$, 21 and 20 initial vibrational levels of He_2^+, summed over all final lower levels.

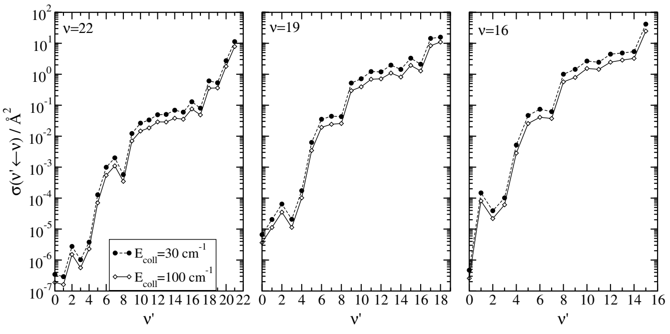

Fig. 2. $\sigma(\nu' \leftarrow \nu)$ as a function of ν', i.e. the final vibrational population after a single collision event. The cross-sections are given for three different initial He_2^+ vibrational states. The collision energies are indicated in the legend.

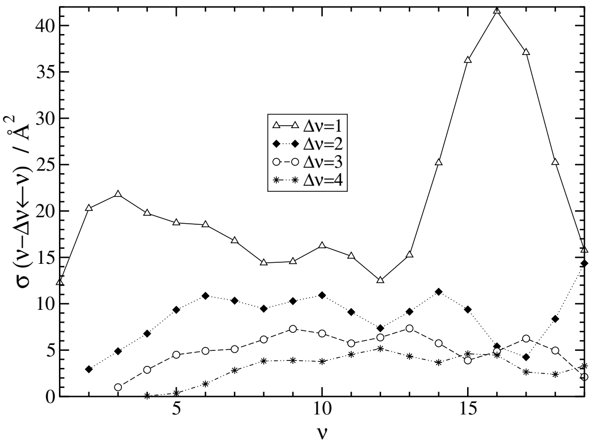

Fig. 3. $\sigma(\nu - \Delta\nu \leftarrow \nu)$ as a function of ν for different values of $\Delta\nu$. The collision energy is 30 cm $^{-1}$.

of information in order to generate reliable data for the ensuing vibrational deexcitation process. We have, therefore, decided to include all the vibrational levels that are compatible with our simplified model for the dynamics in order to glean some further light on the relative efficiency of such cooling processes. Although the final state-resolved 3-body recombination rates are not known, it seems reasonable to assume that the molecular ion will be formed in a fairly high vibrational state. Moreover, in order for it not to escape from the droplet, its entrance channel kinetic energy should be very low and therefore we expect that the association collision would be dominated by s-wave scattering, thereby leading to the chief formation of $j = 0$ molecules: this last assumption is also implicit in our present model for the collisional dynamics as we have discussed above: we have therefore analyzed the collisional quenching for all the possible vibrational levels of He_2^+ starting from the top ones.

In Figure 1 we report, for three of the higher vibrational states, the total quenching cross-sections obtained by summing over all the final vibrational states:

$$\sigma(\nu) = \sum_{\nu' < \nu} \sigma(\nu' \leftarrow \nu) \tag{9}$$

where $\sigma(\nu' \leftarrow \nu)$ are the state-to-state relaxation cross-sections. In our calculation scheme summing over all the final rotational states is also carried out implicitly. The collision energy ranges from 10^{-3} to 100 cm^{-1}. The relaxation cross-sections reach very large values at low collision energy because of the onset of the Wigner's law which states that the cross-section for inelastic processes becomes inversely proportional to the initial relative velocity as the collision energy tends to vanish [21]. The reported cross-sections, however, remain appreciably large at the higher kinetic energy values sampled in our calculations: indeed, they turn out to be of the order of 50 Å^2 even at 80−100 cm^{-1}. It is interesting to note that the largest contribution comes here from the $\nu = 20$ cross-section and not from the higher ones. This effect is also clearly seen when we report the state-to-state cross-sections as a function of the final state (see Fig. 2). The state-to-state cross-sections as a function of the final quantum number ν represent the final vibrational population right after a single collision event. The collision process is thus seen to produce in our case an He_2^+ with an anti-Boltzmann distribution, where the lower lying vibrational states are only slightly populated. After the initial collision, the excited molecules may undergo multiple collisional quenching before cluster break-up. The computed vibrational populations reflect also the fact that the efficiency of the vibrational deactivation processes, in which multiple quanta exchanges can occur, are comparable with the single quantum vibrational relaxation process. The relative sizes of the cross-sections that involve the exchange of one or more vibrational quanta is shown by Figure 3 where the cross-sections are now plotted as a function of the initial vibrational level, for a fixed number of exchanged vibrational quanta.

In general, we notice the following:

- all the cross-sections have a smooth energy dependence (see Fig. 1);
- as can be seen from Figure 3 by looking at the single quantum deexcitation cross-sections as a function of

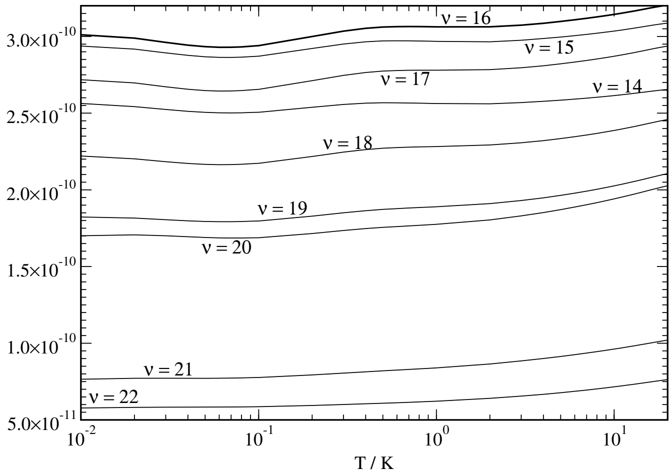

Fig. 4. Summed collisional cooling rates in cm^3 s^{-1} as a function of temperature and for different initial vibrational levels.

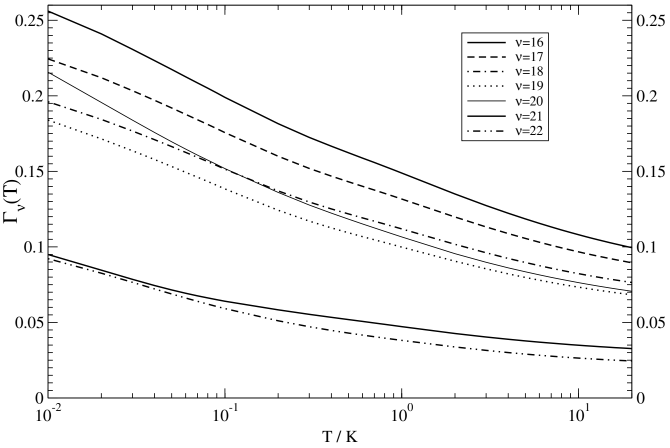

Fig. 5. Temperature behaviour of the ratio between inelastic rates and total collision rates, for different initial vibrational levels of He$_2^+$. See main text for the definition of Γ_ν.

the initial vibrational level, such cross-sections reach a maximum value when the initial state is $\nu = 16$. The lower efficiency of the deactivation from the higher energy vibrational states is possibly due to a less efficient overlap between the wavefunctions of the higher neighboring states. This type of behaviour persists over the considered energy range of this study, although the actual cross-section values may change;

- the relaxation cross-sections with multiple quantum jumps present a smoother dependence on the initial vibrational quantum number. Such cross-sections are also seen to be comparable in magnitude to the single jump ones;
- in the case of single quantum jumps, starting from the $\nu = 1$ level, the cross-section values remain all fairly large as the initial quantum number ν varies, while those for multiple jumps become smaller as the target initial state gets closer to its ground vibrational level.

4 Computed relaxation rates

The temperatures of the ionized helium droplets are known experimentally to vary from about 0.4 K to 10−20 K [3,8]. Using the cross-sections computed in our work we have therefore calculated the rate coefficients for the relaxation processes by averaging their energy dependence over a Boltzmann-type velocity distribution. The initial state dependent rate $R_\nu(T)$ is therefore obtained as:

$$R_\nu(T) = \sqrt{\frac{8k_BT}{\pi\mu}}(k_BT)^{-2}\int_0^\infty \sigma_\nu(E)e^{-E/k_BT}EdE \tag{10}$$

where k_B is the Boltzmann constant, μ the reduced mass of the system, v is the relative velocity between the two colliding partners and $\sigma_\nu(E)$ is the vibrational quenching cross-section of Figure 4. We have plotted the rates for different initial quantum states over a range of temperatures consistent with the collision energy range explored by our calculations and broader than the one which is expected to apply for the ionized helium droplets. They are seen to slightly increase with temperature, but remain of the order of 10^{-10} cm^3 s^{-1} over the whole range if we exclude the upper two levels. The largest rates produced in the present work occur when the relaxation takes place from level 16, as we had seen to happen for the cross-sections. The dependence of the rate constants on the initial vibrational level is rather weak, a result that is opposite to what has been found for the vibrational de-excitation in neutral systems at ultra-low temperatures [22].

Finally, in Figure 5 we report the ratios $\Gamma_\nu(T)$ between the quenching and the total collision rates (inelastic + elastic) as a function of temperature:

$$\Gamma_\nu(T) = \frac{R_\nu(T)}{R_\nu(T) + R_{\nu\nu}(T)} \tag{11}$$

where the quantities $R_{\nu\nu}(T)$ are the elastic rates arising from an equation analogous to the 10 with the elastic cross-sections $\sigma_{\nu\nu}$. Our results tell us that the collisional de-excitation is likely to occur with sizable probability within the droplet, although at temperatures higher than about 0.1 K the elastic collisions are still the dominant process.

A simple estimate of the time needed by the quenching process may be obtained through evaluating the following quantity

$$\tau_\nu(T) = \frac{1}{R_\nu(T)n_{\mathrm{He}}} \tag{12}$$

where n_{He} is the number density of helium. From equation (12) we get that, in the range of temperatures between 10^{-2} and 20 K and considering different initial vibrational states, the quenching of approximately one vibrational quantum takes between 1.4×10^{-13} ($\nu = 16$, $T = 20$ K) and 7.1×10^{-13} ($\nu = 22$, $T = 10^{-2}$ K), or $2.5 \times 10^{-13}(\nu = 20)$ s, if we exclude the upper two levels. We therefore see that the time scale depends very weakly on the initial vibrational state and on the temperature, and it represents a very fast relaxation for the collisional cooling process. This value is remarkably close to the qualitative guess for the same processes surmised in the recent literature (e.g. see Ref. [10] and other work quoted therein) and suggests that the high quenching efficiency occurs right after the short initial step of He_2^+ formation. If we assume that full relaxation is taken to have occurred when the hot target molecules have lost at least 10 vibrational quanta, then a full vibrational cascade will take about 10^{-12} s. This value suggests that a surprisingly high quenching efficiency, even under droplet conditions, must exist after the short-time He_2^+ formation step.

5 Conclusions

We have analyzed in detail the vibrational quenching of the $\mathrm{He}_2^+ + \mathrm{He}$ system using a relatively simple approach to the quantum scattering dynamics. We have obtained reasonable values for the relevant vibrational quenching cross-sections which, in turn, yielded considerably large relaxation rate coefficients: this is seen to happen even for multiple-quanta deexcitation processes. Our results therefore suggest that the collisional cooling of vibrationally hot, nascent He_2^+ molecules formed after the initial electron impact event is a competitive process with respect to its evaporative ejection from the cluster and could happen on a time scale that makes it also competitive with the charge hopping process on the initially fast time scale. The time scale during which collisional quenching for vibrationally excited He_2^+ occurs, in fact, turns out to be rather short and of the order of 10^{-12} s. This is an important result since we believe that such a time scale might be the measure of the lifetime of the cluster after ionization, especially if the He_2^+ formation takes place, as we have suggested before, right after electron impacting onto the neutral helium cluster. Our findings therefore provide for the first time estimates for the collisional quenching process from ab-initio data and a modeling of the quantum dynamics. They indeed suggest that the cooling of the initially “hot” He_2^+ formed within the droplet could very well provide the energy necessary for the rapid cluster break-up observed in experiments, with the corresponding detection of stable He_2^+ ionic fragments.

The financial support of the CASPUR Supercomputing Center, of the Scientific Research Committee of the University of Rome “La Sapienza” and of the INFM is gratefully acknowledged.

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