Fragmentation of Na$_2^+$ dimer ions in kilo-electron-volt collisions with He: A coupled wave-packet study

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The dynamics of the fragmentation of Na$_2^+$ dimer ions in keV collisions with He is investigated theoretically in the framework of the semiclassical coupled wave-packet method. The fast collisional motion is treated classically, whereas both the electronic motion and the vibrational or dissociative motion of the dimer are treated quantally. The frozen vibrational and rotational approximations are used to lighten the computational effort. The method is able to describe both the impulsive and electronic fragmentation mechanisms. The calculations are undertaken in a basis of 14 electronic states of the Na$_2^+$-He system. Aside from the entrance $\Sigma_g^3s$ channel, the main contributions to the Na$_2^+$ fragmentation are those of the $\Sigma_u^3s$, $\Sigma_u^3p$, and $\Pi_u^3p$ channels. For each electronic state dissociation probabilities as functions of the impact parameter are presented for various dimer orientations to extract physical insight in the fragmentation mechanism. This analysis shows in particular that the contribution of the electronic mechanism is due to collisions where the He atom passes between the two Na nuclei. Doubly differential cross sections for dissociation are calculated for the $v=0$ initial state of the dimer and for the distribution of vibrational states. Good agreement with experiment is obtained assuming a small amount of initial vibrational excitation of the dimer. [S1050-2947(99)03101-7]

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I. INTRODUCTION

Fragmentation of molecules or clusters by making them collide with atoms is a way of studying the dynamics of energy deposition and its subsequent distribution in polyatomic objects. Schematically, there are two main mechanisms by which collision-induced fragmentation can occur [1–3]. The first mechanism involves energy or momentum transfer from the relative collisional motion to internal vibrational and rotational degrees of freedom of the molecule (or cluster). If the transferred energy lies above the binding energy of an atom or a group of atoms in the molecule (or cluster) the latter may be freed and move apart. A particularly simple example of this mechanism is when the atomic projectile hits, in a close binary encounter, a specific atom or group of atoms in the molecule (or cluster) and kicks it out. This mechanism is called an impulsive mechanism [1–3]. Another simple example is when an initial binary kick is followed by successive caroms; the transferred energy is shared among several degrees of freedom of the molecule (or cluster), which may yield many-body fragmentation or delayed fragmentation as evaporation. The second mechanism involves an electronic transition to a dissociative or predissociative state of the molecule (or cluster), which automatically entails its fragmentation. Most known examples of such an electronic mechanism are those of dissociative charge exchange. The review of Ref. [4] and more recent works of Refs. [5,6] may help the reader trace the evolution of the experimental and theoretical investigations of this special case of molecular collisions.

A step forward in the experimental investigation of collision-induced fragmentation has been made recently by combined time-of-flight and multiparametric coincidence techniques [1–3]. Applied to the study of Na$_n^+$ ($2\leq n \leq 9$) cluster fragmentation in keV (laboratory energy) collisions with He this technique has made it possible to analyze how the impulsive and electronic mechanisms manifest themselves in the various Na$_{n-p}^+ +$ Na$_p$ fragmentation pathways [2]. For the Na$_3^+$+He collision, which is the main subject of the present work, the latter experimental technique has made possible the complete measurement of all observables characterizing the collision-induced dissociation process. Such achievements are highly challenging for theory.

When considering the problem from a theoretical point of view, it should be kept in mind that a detailed quantum-mechanical description of translational-to-rovibrational energy transfer is far from being a trivial routine task in actual atom-molecule collision systems. The problem is dramatically complicated when dissociation and electronic transitions come, individually or together, into play. However, it has long been known that the use of classical or semiclassical approximations removes many of those difficulties and can provide, to a certain extent, reasonable descriptions of the dynamics of nuclei in a polyatomic system. This is the basis of the so-called quasiclassical trajectory (QCT) approach [7] also known as the adiabatic molecular-dynamics method (AMD) [8]. In that method all heavy particles in the collision system obey classical laws of motion under forces deriving from a unique Born-Oppenheimer potential-energy surface, usually that of the ground state. For nonadiabatic collisions, leading to electronic transitions (which are intrinsically quantum events), the QCT-AMD approach has to be modified. It is a very old idea that in such cases semiclassical treatments may be used in which the heavy particles move classically along prescribed trajectories while the electrons are treated quantally and obey a time-dependent Schrödinger
The time dependence of the electronic problem is introduced by the classical motion of the heavy particles. Inasmuch as in such nonadiabatic collisions the system is simultaneously in several quantum electronic states, a unique potential governing the classical motion of the nuclei does not in principle exist. It has been suggested among other proposals [7,8] that the expectation value of the electronic Hamiltonian, determined by using the actual coherent superposition of the populated electronic states, could provide the unique potential sought. The interest of this proposal is that it ensures conservation of the total average energy of the system and thus introduces some energy transfer between classical and quantum degrees of freedom. While the method has met with some success in the calculation of integral cross sections for electronic transitions, it has known flaws when differential cross sections are considered. Namely, the scattering angle of the projectile and the kinetic energy of the heavy particles are independent of the actual quantal electronic state in which the system is. This is because the classical part of the system “knows” only the average state of its quantal part. While the scattering angle deficiency is a minor one in energetic collisions at small angles, the internal energy content of the molecule at the end of the collision is a serious issue especially when studying fragmentation. In a recent study of the Na$_2^+$+He collision-induced dissociation (CID) problem [3] such a method has been applied and its above-mentioned drawbacks have been met. An ad hoc “projection” procedure then had to be applied to patch up the theoretical treatment.

In the present work we revisit the problem of dimer fragmentation in the Na$_2^+$+He collision. From the outset, the internal vibration and electronic motions of the molecule are handled quantally in the framework of the semiclassical coupled wave-packet technique [5,6,9]. This approach has been designed originally to handle dissociative nonadiabatic molecular collisions and has been applied since to a variety of problems in molecular reaction dynamics at rather low energies [5,6,9,10]. The comparison of characteristic collisional and vibrational-rotational times then leads us to introduce a sudden approximation. The computation of transition amplitudes and differential cross sections of dissociation is described in this context. The results are compared with experiment and are scrutinized to gain more knowledge in the dissociation mechanisms.

The outline of the article is as follows. Section II sets up the theoretical framework. Section III deals with the method used to determine the relevant interaction potentials and couplings and presents some of their salient features. Section IV analyzes the results at various stages of the calculation and discusses the comparison with experiments. The main findings are summarized in Sec. V.

II. THEORETICAL FRAMEWORK

We consider the collision of the Na$_2^+$ dimer ion with He at $E_{lab}=1$ keV, i.e., $E_{cm}=80$ eV. Various relevant coordinates and parameters are shown in Fig. 1. Here $\vec{R}(t)$ is the relative vector between He and the center of mass of the dimer. The dimer vector $\vec{r}$ is characterized by the bond length $r$ and the orientation $\theta, \phi$ in fixed space. The fixed space reference frame has its Z axis parallel to the incident direction of the relative velocity vector $\vec{v}$ and its Y axis parallel to the impact parameter vector $\vec{b}$.

A. Principle equations of motion

Owing to the large reduced mass $\mu_{coll}$ of the Na$_2^+$-He collision system and the importance of the considered collision energy, the relative motion can be treated classically. For each impact parameter it is thus considered to evolve along a trajectory $\vec{R}(t)$. The total wave function of the system $\Psi(\{\vec{p}\},\vec{r},t)$ then depends on time via this trajectory and thus obeys the time-dependent Schrödinger equation

$$i \frac{\partial \Psi}{\partial t} = \left( -\frac{1}{2\mu} \Delta_{\vec{r}} + H_{el} \right) \Psi. \quad (1)$$

In the above $\{\vec{p}\}$ represents collectively the set of electronic coordinates, $\mu$ is the Na$_2^+$ reduced mass, and $H_{el}$ is the electronic Hamiltonian of the system. Equation (1) expresses the quantal evolution of the rotational and vibrational motions of the molecule together with the electronic motion of the system along a prescribed trajectory $\vec{R}(t)$ to be specified below.

The corresponding rovibrionic wave function can be expanded over a set of electronic basis functions $\phi_j(\{\vec{p}\};r,\gamma,R)$ determined for fixed positions of the nuclei; the $\phi_j$'s thus depend parametrically on the three relative coordinates $r, \gamma,$ and $R:

$$\Psi(\{\vec{p}\},\vec{r},t) = \sum_j P_j(t,\vec{r}) \phi_j(\{\vec{p}\};r,\gamma,R). \quad (2)$$

Each $P_j(t,\vec{r})$ function constitutes a wave packet that describes the instantaneous rovibrational motion of the system in the $j$th electronic state. Substitution of expression (2) into Eq. (1) and projection onto the $\phi_j$ basis functions leads to a well-known set of coupled partial differential equations for the wave packets:

$$i \frac{\partial P_j(t,\vec{r})}{\partial t} = -\frac{1}{2\mu} \Delta_{\vec{r}} P_j(t,\vec{r}) + \sum_k H_{jk}(\vec{R}(t),\vec{r}) P_k(t,\vec{r}). \quad (3)$$

In the above we have made use of the notation
\[ H_{jk}(\vec{r}, \vec{r}) = \langle \phi_j | H_{el} | \phi_k \rangle \langle \phi_k | \phi_j \rangle = H_{ek}(\vec{r}, \vec{r}). \]  

(4)

Equation (3) actually assumes that the \( \phi_j \) basis functions form a diabatic representation, i.e., that the \( \langle \phi_j | d/dt | \phi_k \rangle \) coupling matrix elements are sufficiently small to be neglected [11].

Following Ref. [12], the trajectory of relative collisional motion \( \vec{R}(t) \) is obtained at each time \( t \) from the average potential

\[ \vec{V}(\vec{R}, \theta, \varphi) = \sum_{j,k} \langle P_{j}(t, \vec{r}) | H_{jk}(\vec{R}(t), \vec{r}) | P_{k}(t, \vec{r}) \rangle, \]

(5)

using Hamilton’s equations

\[ \vec{\dot{r}} = \frac{\vec{K}}{\mu_{\text{coll}}}, \quad \vec{\ddot{r}} = -\vec{V}_{\vec{K}}. \]

(6)

While the use of a common trajectory to describe the scattering in all channels \( j \) is a rather crude procedure in general, it will be seen in Sec. IV A that it is legitimate in the present case because (i) when the electronic transitions are sizable they take place predominantly at small scattering angles where the trajectory does not matter very much and (ii) at large scattering angles where the impulsive mechanism is dominant, the system is predominantly in one electronic state (ground state \( \phi_i \)). The use of a common trajectory to describe the scattering for all \( r \) values is justified by the fact that the \( r \)-average potential is very close to the actual \( r \)-dependent potential.

### B. Sudden approximation

It has been rightly argued in Ref. [3] that, for the \( \text{Na}_2^+ \)-He collisions in the \( E_{\text{cm}} \approx 10^7 \text{ eV} \) energy range, typical interaction times \( (t_{\text{coll}} \approx 10^{-15} - 10^{-16} \text{ s}) \) are at least one order of magnitude shorter than a typical vibration period of the \( \text{Na}_2^+ \) dimer, itself two orders of magnitude smaller than the typical \( \text{Na}_2^+ \) rotation period. Accordingly, the \( \text{Na}_2^+ \) dimer barely vibrates or rotates during the collision time. This has been checked in the early stages of the present work [13] by studying the earliest encounters when the He atom undergoes a head-on collision with a nucleus of the molecule. In the most extreme conditions investigated the molecular bond distance varied by less than 7% and its orientation by less than 5° over an interaction time of 100 a.u. (\( \approx 2.4 \times 10^{-15} \text{ s} \)). One can thus confidently make use of the sudden approximation in which the \( \vec{r} \) vector is considered as a fixed parameter during the collision [6,9]. As pointed out in Ref. [9], this essentially amounts to discarding the kinetic energy of the molecule in Eq. (3), i.e.,

\[ \frac{\partial P_{j}(t, \vec{r})}{\partial t} = \sum_{k} H_{jk}(\vec{R}(t); \vec{r}) P_{k}(t, \vec{r}). \]

(7)

The picture that emerges from this description is that of a quantum evolution of the electronic part of the problem, as a result of the classical relative atom-molecule motion, for fixed values of the parameter \( \vec{r} \). Notwithstanding the latter frozen bond vector approximation, the molecule actually gains momentum during the collision along its vibrational and rotational degrees of freedom; this will appear below.

### C. Wave-packet analysis

From the solution of Eq. (7), one obtains for each impact parameter \( b \) the probability amplitudes \( a_{jm}(\epsilon, b) \) that \( \text{Na}_2^+ \) dissociates in the electronic state \( j \) and the rotational state \( lm \), with the dissociation energy \( \epsilon \):

\[ a_{jm}(\epsilon, b) = \langle g_{ejl}(r) | Y_{lm}(\theta, \varphi) | P_{j}(t_{\text{final}}; \vec{r}, \theta, \varphi) \rangle r, \theta, \varphi. \]

(8)

\( g_{ejl} \) is the continuum wave function obeying the isolated molecule radial Schrödinger equation

\[ \left( \frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + H_{jj}(R \rightarrow \infty, r) - H_{ij}(R \rightarrow \infty, r \rightarrow \infty) \right) g_{ejl}(r) = \epsilon g_{ejl}(r). \]

(9)

Regardless of the rotational state of \( \text{Na}_2^+ \), the dissociation probability density (i.e., probability per energy unit) is

\[ \tau_{j}(\epsilon, b) = \sum_{l,m} |a_{jm}(\epsilon, b)|^2. \]

(10)

To circumvent the tedious task of explicitly handling the rotation quantally, it is possible to approximate the exact \( g_{ejl} \) wave function in Eq. (9) by \( g_{ejl}(\vec{r}) \), where \( \vec{r} \) is a fixed value. Using this approximation together with the closure relation over the spherical harmonics leads to

\[ \tau_{j}(\epsilon, b) = \int \tau_{j}(\epsilon, b; \theta, \varphi) \sin \theta \ d\theta \ d\varphi, \]

(11)

where

\[ \tau_{j}(\epsilon, b; \theta, \varphi) = \langle g_{ejl}(r) | P_{j}(t_{\text{final}}; \vec{r}, \theta, \varphi) \rangle t_{\text{final}}. \]

(12)

In expression (12) the integration is carried out over \( r \) only. The validity of such an approximation requires the fixed \( \vec{r} \) value to be representative of all the \( l \) components of \( P_{j}(t_{\text{final}}; \vec{r}, \theta, \varphi) \). The distribution of the \( l \) components may actually be very broad and it is generally not possible to find any representative value \( \vec{r} \) of the whole final wave packet. The breadth of this distribution can be understood classically. If \( b, \theta, \) and \( \varphi \) are such that there is a hard He-Na+ core collision leading to a transfer of momentum perpendicular to the \( \text{Na}_2^+ \) bond, \( l \) becomes very large. Conversely, for the same impact parameter, if \( \theta \) and \( \varphi \) are such that the He trajectory remains always far from the Na+ core, only a few rotational level will be populated and \( l \) is low. Hence the calculation of \( \tau_{j}(\epsilon, b; \theta, \varphi) \) according to Eq. (12) is expected to provide good results when \( \vec{r} \) is the \( (\theta, \varphi) \)-dependent classical value of the angular momentum

\[ \vec{T}^2(b; \theta, \varphi) = \frac{P^2}{\sin^2 \theta} \]

(13)

obtained from the classical equations of motion
\[ \frac{dP_\theta}{dt} = -\left( \frac{\partial \tilde{V}}{\partial \theta} - \frac{P_\phi^2 \cos \theta}{\mu r^3 \sin^3 \theta} \right), \quad \frac{dP_\phi}{dt} = -\frac{\partial \tilde{V}}{\partial \phi}, \] 

(14)

where the average bond distance is defined similarly to Eq. (5).

\[ \tau(t, \theta, \varphi) = \sum_{j,k} \langle P_j(t; r, \theta, \varphi) | r | P_k(t; r, \theta, \varphi) \rangle, \] 

(15)

Knowing \( \tau(e, b; \theta, \varphi) \), the differential cross sections for dissociation in each channel \( j \) for each orientation \( (\theta, \varphi) \) may hence be obtained semiclassically as [14]

\[ \sigma_j(e, \chi; \theta, \varphi) = \sum_{\beta} \frac{b_{\beta} \tau(e, b_{\beta}; \theta, \varphi)}{\sin \chi \frac{d\chi}{db}_{b=b_{\beta}}}, \] 

(16)

where use is made of the classical deflection function \( \chi(b) \) stemming from Eq. (6). The sum in Eq. (16) extends to all branches \( \beta \) of the multivalued function. Near the coalescence point of two branches (rainbow) we have resort to the textbook Airy function approximation [15]. Finally, the observable differential cross sections are obtained by the average of \( \sigma_j'(e, \chi; \theta, \varphi) \) over dimer orientations \( (\theta, \varphi) \):

\[ \sigma_j(e) = \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} \sigma_j'(e, \chi; \theta, \varphi) d\varphi. \] 

(17)

**D. Implementation**

Equation (7) is solved using an adapted version of the coupled wave-packet code of Refs. [6,10], which was designed to solve Eq. (3) for vibronic problems [i.e., cases when the molecule orientation is held fixed [9] or treated classically [6(b)]]. The set of equations (7) is obviously much less computationally demanding that those considered in the just cited literature. Further, significant computational efficiency can be gained by making the change of function

\[ P_j(t; \vec{r}) = Q_j(t; \vec{r}) \exp\{i \eta_j(t; \vec{r})\}, \] 

(18a)

with

\[ \eta_j(t; \vec{r}) = -\int_{t_{\text{initial}}}^t H_{jk}(\vec{R}(t'); \vec{r}) dt'. \] 

(18b)

Indeed, while the \( P_j \) wave function can exhibit very-short-wavelength components in the \( r \) coordinate, especially when the collision gives rise to a large momentum transfer, the \( Q_j \) wave functions are always quite smooth and can be described with a large stepsize in the \( r \) grid.

Equation (7) then becomes

\[ i \frac{\partial Q_j(t; \vec{r})}{\partial t} = \sum_{k \neq j} H_{jk}(\vec{R}(t); \vec{r}) \exp\{i[\eta_k(t; \vec{r}) - \eta_j(t; \vec{r})]\} Q_k(t; \vec{r}). \] 

(19)

For a given impact parameter \( b \) and a molecule orientation \( (\theta, \phi) \), the \( Q_j(t; r, \theta, \phi) \) and \( \eta_j(t; r, \theta, \phi) \) functions are determined simultaneously for a whole set \( \{\vec{r}\} \) of \( r \) values.

To solve Eqs. (7) and (19) we choose as the initial condition

\[ P_j(t_{\text{initial}}; \vec{r}) = Q_j(t_{\text{initial}}; \vec{r}) = \delta_{j1} \chi_c(r). \] 

(20)

Equation (20) specifies that the system is initially in the \( \text{Na}_2^+ \) electronic ground state \( \phi_1 \) and \( \chi_c \) vibrational state \( \chi_c \). An isotropic initial rotational state is assumed for simplicity. It is noteworthy that Eqs. (7) and (19) may be made independent of the actual choice of \( \chi_c \). This is effected by writing

\[ P_j(t; \vec{r}) = C_j(t; \vec{r}) \chi_c(r) = A_j(t; \vec{r}) \exp\{i \eta_j(t; \vec{r})\} \chi_c(r), \] 

(21a)

\[ C_j(t_{\text{initial}}; \vec{r}) = A_j(t_{\text{initial}}; \vec{r}) = \delta_{j1}, \] 

(21b)

so that

\[ i \frac{\partial A_j(t; \vec{r})}{\partial t} = \sum_{k \neq j} H_{jk}(\vec{R}(t); \vec{r}) \exp\{i[\eta_k(t; \vec{r}) - \eta_j(t; \vec{r})]\} A_k(t; \vec{r}). \] 

(22)

Equations (21) and (22) are quite useful because the knowledge of the \( C_j(t; \vec{r}) \) functions provides the relevant \( P_j(t; \vec{r}) \) functions for arbitrarily chosen initial vibrational states \( \chi_c(r) \), i.e., the calculations need not in principle be done for every \( \chi_c \) taken into consideration.

Clearly, in the case of an electronically elastic collision \( [H_{ij}] = 0 \) entailing \( A_i(t; \vec{r}) = \delta_{ij} \) the effect of the collision is the accumulation of phase \( \eta_j(t; \vec{r}) \). This illustrates again that, although the \( \vec{r} \) vector is held fixed during the encounter, the molecule gains vibrational momentum, which in this case amounts to \( \partial \eta_j(t; \vec{r}) / \partial r \).

**E. Technicalities**

The solutions of Eq. (22) for the quantum part of the problem and Eqs. (6) and (14) for the classical part are obtained in the following way. At each time \( t \) the propagation of Eq. (22) during the time step \( dt \) provides the values of the \( P_j \) wave packets at time \( t + dt \). The average potential \( \tilde{V} \) is obtained using Eq. (5) and these updated values of \( P_j \). With this potential Eqs. (6) and (14) are propagated during the time step \( dt \).

To solve Eqs. (6) and (14) the Runge-Kutta integrator is used. The initial conditions are

\[ \vec{R} = \begin{pmatrix} 0 \\ b Z_{\text{initial}} \end{pmatrix}, \quad \dot{\vec{R}} = \begin{pmatrix} 0 \\ 0 \sqrt{2E_{\text{coll}} / \mu_{\text{coll}}} \end{pmatrix}. \]

The impact parameter \( b \) is sampled over 120 equidistant values in the range \( 0 - 6a_0 \). The starting point of He motion is \( Z_{\text{initial}} = -12a_0 \). The time of propagation is 700 a.u. From
the final velocity vector $\vec{R}_{\text{final}}$ we obtain a classical scattering angle $\chi$. The final rotational state $I$ of the dimer is obtained from Eq. (13).

The propagation of the coupled equations [Eq. (22)] is done using a Lanczos scheme. The $r$ grid is made of by 32 equidistant points in the interval $r \in [5.8a_0, 8.5a_0]$. Such a moderate number of points is a consequence of writing the wave packets in the form of Eqs. (18a) and (18b).

A total of 150 dimer orientations, corresponding to values of $\theta$ in the range $0^\circ$–$90^\circ$ and $\phi$ in the range $0^\circ$–$180^\circ$ were considered. The $(\theta, \phi)$ grid was denser in the vicinity of $\theta = 90^\circ$ and $\phi = 0^\circ$ because of the importance of this region for the impulsive mechanism.

### III. Potential-Energy Surfaces and Couplings

In the present collision conditions only the outer electron of the Na$_2^+$-He system is expected to eventually undergo excitation during the collision. This is expected from earlier studies of atom-atom systems such as Na-He and Na-Ne in similar conditions [16]. Accordingly, we have chosen to describe the effect of the two Na$^+$ cores of the dimer on the outer active electron using Na-centered $l$-dependent pseudopotentials [17]. The spectator electrons of the He partner are explicitly considered in the calculation, although the corresponding orbitals are held frozen. The effect of He on the outer electron is not only a He-centered short-range (screened Coulomb-Hartree plus exchange) potential but also an orthogonality constraint imposed by the Pauli principle.

To build the diabatic representation required in the derivations presented in Sec. II we follow the lines of the already cited work on the Na-He and Na-Ne collisions [16]. The strictly diabatic basis obeying $\langle \phi_i | \partial/\partial R$ or $\partial/\partial \gamma | \phi_i \rangle = 0$ [11] would be made, in the present problem, of the orbitals of the isolated Na$_2^+$ dimer. To take into account the above-mentioned orthogonality constraint we make these orbitals orthogonal to the $1s_{1\text{He}}$ orbital using the Schmidt procedure. In doing so, the orbitals are ordered with the $1s_{1\text{He}}$ orbital first and then the Na$_2^+$ orbitals follow by order of increasing energy. While this procedure introduces slight $\partial/\partial R$ and $\partial/\partial \gamma$ coupling matrix elements, it was shown in Ref. [16] that these couplings are not important in the description of the electronic excitation process. It may be noted in passing that in the above we have not concerned ourselves with $\langle \phi_i | \partial/\partial r | \phi_i \rangle$ matrix elements since $r$ enters the proposed dynamical treatment of Sec. II B only as a fixed parameter, as opposed to $R$ and $\gamma$, which evolve during the encounter.

In practice the (nearly) diabatic basis considered is made of the lowest 14 eigenstates of the Na$_2^+$ molecule: $\Sigma_u 3s$, $\Sigma_u 3p$, $\Sigma_u 3p$, $\Pi_u 3p$, $\Pi_u 3p$, $\Sigma_u 3d$, $\Sigma_u 3d$, $\Pi_u 3d$, $\Pi_u 3d$, $\Delta_g 3d$, $\Delta_g 3d$, $\Sigma_g 4s$, $\Sigma_g 4s$. The Na$_2^+$-He calculations are restricted to the $A^\prime$ irreducible representation of the $C_2$ point group, that is, to states that are symmetric in the plane containing the three atoms. Excluding $A^\prime(\Pi_{\Sigma_s}, \Delta_{g,u})$ states from the dynamics calculations amounts to making the approximation that Coriolis coupling, which arises from the tumbling of the triatomic plane, is negligible. Therefore, this approximation may have an effect on the $\Pi$ and $\Delta$ states if at all.

The orbitals considered are expressed as linear combination

![FIG. 2. Potential-energy curves of isolated Na$_2^+$ relevant to the present study. Superimposed on the ground-state curve is the probability density $|\chi_0|^2$ of the corresponding $v=0$ vibrational state. The related Franck-Condon zone is shown by dashed lines. The inset in the bottom of the figure shows the probability density for the $v=6$ vibrational level (oscillating curve) and for an incoherent superposition of vibrational states issued from the distribution of Sec. VI B (two-lobe curve).](image)
dinate equal to the equilibrium distance \( r_e \), of the isolated \( \text{Na}_2^+ \) dimer. The highest energy in this figure was chosen to be equal to the collision energy \( (E_{\text{cm}} = 80 \text{ eV} \approx 2.94 \text{ a.u.}) \). It shows that the classically forbidden region is a sphere with radius \( \approx 1\alpha_0 \) centered at the position of the \( \text{Na}^+ \) core \( (r/2 = r_e/2 \approx 3.55\alpha_0) \). Another noticeable feature of this figure is that there is a lot of room between the \( \text{Na}^+ \) cores where the He atom can easily pass through. It should be noted that for the energy scale of the figure, all the other \( H_{jj}(r, \gamma, \rho) \) potentials look nearly the same. This justifies the approximation that a common potential may be used to treat the encounter.

Figures 3(b)–3(d) show samples of \( |H_{1j}(r, \gamma, \rho) / [H_{jj}(r, \gamma, \rho) - H_{11}(r, \gamma, \rho)]| \) functions for fixed \( r = r_e \) \( (r/2 \approx 3.55\alpha_0) \). The importance of the coupling to the energy difference ratio is a measure of the likeliness of a transition. It is seen that excluding the classically forbidden region [see Fig. 3(a)], these ratios are sizable in the region between the \( \text{Na}^+ \) cores and not outside. Electronic excitation is thus expected to occur for collision trajectories that pass in between the cores. Figure 3(a) indicates that such trajectories correspond to soft collisions in which the trajectory should not be deflected significantly. Another interesting feature of Figs. 3(b)–3(d) is that the \( |H_{1j}/(H_{jj} - H_{11})| \) ratios reflect, actually through \( H_{1j} \), characteristics of the interacting \( \text{Na}_2^+ \) electron clouds: the \( \Sigma_g 3\Sigma_g p \) interaction builds around the Na-Na axis and maximizes halfway between the cores; the \( \Sigma_g 3\Sigma_g 3\Sigma_g 3s \) interaction also builds along the Na-Na axis but, owing to symmetry, it vanishes and changes sign midway; the \( \Sigma_g 3\Sigma_g \Pi_g 3p \) interaction builds between the \( \text{Na}^+ \) cores but off axis. Finally, it may also be noted that the \( \Sigma_g 3\Sigma_g \) and \( \Sigma_u 3\Sigma_g \) potential surfaces undergo a diabatic crossing that appears in Fig. 3(c) as a truncated hollowed out cylinder. This is somewhat reminiscent of a similar feature in the He-H$_2$ system [21].

IV. RESULTS

Results will first be presented for the collision-induced dissociation (impulsive mechanism) and dissociative electronic excitation (electronic mechanism) for \( \text{Na}_2^+ \) ions in their ground vibrational state. The case of vibrationally hot \( \text{Na}_2^+ \) ions will be examined next. It is generally found that four electronic states among the considered 14 (Sec. III) are populated significantly, namely, the \( \Sigma_g 3\Sigma_g \) ground state and the \( \Sigma_u 3\Sigma_g p \), \( \Pi_u 3\Sigma_g p \) states.
Collisions with smaller and larger impact parameters than $b = r/2 \approx 3.5a_0$ produce two similar branches of the $\tau_1(\varepsilon, b; \theta, \phi)$ probability density. Dissociation does not occur for $b \leq 1.2a_0$ and $b \geq 5.6a_0$. For these ranges of impact parameters the He atom passes at distances larger than $2a_0$ from a Na$^+$ core and the transferred momentum is insufficient to vibrationally excite the dimer up to dissociation.

The evolution of the dissociation probability density with $\phi$ for $\theta = 90^\circ$ [Figs. 4(a)–4(c)] shows that the maximum energy of the fragments, as well as the corresponding impact parameter, decreases as the dimer axis is twisted out of the collision plane. As $\phi$ increases, the smallest distance of approach of a Na$^+$ core to He increases, thereby reducing the momentum transfer to the dimer. For $\phi > 30^\circ$ this smallest distance of approach becomes larger than $2a_0$ and no dissociation in the $\Sigma_g^+3s$ state is possible any longer.

More generally, the evolution with orientation of the impact parameter dependence of the dissociation probability density can be roughly deduced from Figs. 4(a)–4(c), keeping in mind the image that the He atom has to fall within a sphere, centered around one Na$^+$ core, of radius $\approx 2a_0$; the closer the He atom gets to the center of the sphere the larger the transferred momentum and the relative energy of the fragments. Thence the decrease of $\theta$ from $90^\circ$ holding $\phi = 0$ will give rise to a pattern, similar to Fig. 4(a), except that the maximum fragmentation energy moves to smaller $b$ values. This is understood with the above-discussed picture: The center of the sphere is hit for an impact parameter $b = r/2 \sin \theta$. Of course, $\theta$ should not be too small for the other Na$^+$ core to be disregarded.

Let us briefly mention that a kinematic event has been erased artificially from Fig. 4. This is the very specific case when the He atom bounces off one Na$^+$ core and then faces the second one. This case occurs for a very narrow range of impact parameters and gives rise to much larger fragmentation energies than those considered experimentally [Fig. 9(a)]. In the final cross-section calculation (Sec. IV A 4) this effect is actually included, but cannot be seen in the $(\varepsilon, \chi)$ window considered.

### 2. Dissociative electronic excitation

As in Sec. IV A 1, the probability density $\tau_1(\varepsilon, b; \theta, \phi)$ of dissociation (with energy $\varepsilon$ of the fragments as a function of impact parameter $b$ for orientation $\theta$ and $\phi$) when the system has undergone an electronic excitation $\phi_1 \rightarrow \phi_2$ is obtained from the computed probability amplitude $P_{\phi_1(\varepsilon, b; \theta, \phi)}$ using Eq. (12). It is found that the $\Sigma_g^+3p$, $\Sigma_u^+3p$, and $\Sigma_g^+3p$ states are systematically far more populated than the other electronic states considered (Sec. III).

Figures 5(a)–5(c) show the dissociation probability densities for these states as functions of impact parameter at the fixed orientation $\theta = 90^\circ$ and $\phi = 0^\circ$. The whole pattern is concentrated in the small-impact-parameter range $0 \leq b \leq 2a_0$. From Fig. 3 and Sec. III it is obvious that the electronic excitation takes place when the trajectory of the He atom passes in between the Na$^+$ cores. The symmetry characteristics of the electron clouds, already discussed in Sec. III, also reflect themselves in the plots of Figs. 5(a)–5(c). Thus, for $b = 0$, $\theta = 90^\circ$, and $\phi = 0^\circ$, the (HeNa)$_2^+$ system forms an isosceles triangle that transforms according
the $C_{2v}$ symmetry point group. For such an arrangement the $\Sigma_u^3p$ and $\Pi_u^3p$ states have the same $A_1$ symmetry as the entrance $\Sigma_u^3s$ state and can thus be populated at $b=0$; the $\Sigma_u^3s$ state having $B_2$ symmetry cannot. On the other hand, as soon as $b$ becomes different from zero these selection rules disappear. Indeed, the $(\text{HeNa}_2)^+$ system has then planar symmetry only ($C_2$ point group); the $\Sigma_u^3s$ and $\Sigma_u^3p$ states now belonging to the same $A'$ irreducible representation may thus interact [see Fig. 3(c)]. This is nicely illustrated in Fig. 5.

The $\varepsilon$ ranges characterizing the dissociative electronic excitation processes are governed by vertical transitions as a result of the sudden collision conditions discussed in Sec. II B. At the smallest impact parameters they are roughly determined by the Franck-Condon zone and the related reflection principle [7]. Accordingly, the closeness to $\varepsilon=0$ of the $\Pi_u^3p$ structure is a consequence of the particular shape of the corresponding Na$_2^+$ potential-energy curve in the Franck-Condon region (Fig. 2). The positions of the $\Sigma_u^3p$ and $\Sigma_u^3s$ structures at $\varepsilon \approx 1$ eV are consistent with this interpretation scheme as well.

When the impact parameter increases beyond $b \approx 0.8a_0$ the patterns clearly depart from the Franck-Condon expectation. This is due to the closer passage of the He atom to one of the Na$^+$ cores: The larger the $b$, the closer this encounter and the larger the transferred momentum. Hence the observed tails extending towards large $\varepsilon$ values in the patterns of Figs. 5(a)–5(c) are nothing but a manifestation of the impulsive mechanism in the electronically excited channels.

Figures 5(a)–5(i) show the evolution of the $\Pi_u^3p$, $\Sigma_u^3p$, and $\Sigma_u^3s$ dissociation probability densities as functions of impact parameter for $\theta=90^\circ$ when $\varphi$ increases. As was the case in Sec. IV A 1, one observes the progressive reduction of the impulsive tails. The progressive extinction of the $\Sigma_u^3s$ process as $\varphi$ approaches $90^\circ$ [Figs. 5(c)–5(f), and 5(i)] has again to do with symmetry: For $\varphi=90^\circ$ the $(\text{HeNa}_2)^+$ system keeps a $T$ shape (isosceles triangle) for all impact parameters. As argued above as well as in Sec. III, the $\Sigma_u^3s$ and $\Sigma_u^3p$ states having respectively $A_1$ and $B_2$ symmetry in this arrangement do not interact.

### 3. Comparison of the dissociation mechanisms

Figure 6 gathers the $\tau_\varepsilon(e,b;\theta,\varphi)$ dissociation probability densities for the ground $\Sigma_u^3s$ and excited $\Sigma_u^3s$, $\Sigma_u^3p$, and $\Pi_u^3p$ processes at $\theta=90^\circ$ and $\varphi=0^\circ$. The $\Sigma_u^3s$ process results exclusively from the impulsive mechanism and is characterized by the two branches around $b \approx r/2$. The $\Sigma_u^3p$ and $\Sigma_u^3s$ structures appear in a close $(e,b)$ neighborhood. Their impulsive tails are seen to merge and display asymptotically the same slope as the $\Sigma_u^3s$ purely impulsive process. It is clearly seen from this figure that the dissociative electronic excitation and impulsive dissociation (whether in the ground or excited states) take place in distinct impact parameter ranges.

### 4. Differential cross sections for dissociation

In practice, it is not the $\tau_\varepsilon(e,b;\theta,\varphi)$ functions that are accessible to experiment but rather the doubly differential cross section in the scattering angle of the projectile $\chi$ and the relative energy of the fragments $\epsilon$ [Eq. (16)]. The transformation of the $\tau_\varepsilon$ functions into the $\sigma_j$ ones is achieved
through Eqs. (16) and (17). Figure 7 shows samples of deflection functions $\chi(b; \theta, \varphi)$ that enable one to effect the latter transformation. For a given orientation $(\theta, \varphi)$ of the dimer two impact parameters contribute to the same $\chi$: the two impact parameters merge into a single value at a limiting $\chi$ value. This is handled along the lines of the discussion following Eq. (16). Figure 8 shows examples of the way these rainbow features contribute to the cross section for dissociation in $\Sigma_g^+ 3s$ ground state.

Figure 9(b) shows the final cross section for dissociation including all important processes: $\Sigma_g^+ 3s$, $\Sigma_u^- 3s$, $\Pi_u^- 3p$, and $\Pi_u^+ 3p$. In this figure one can easily distinguish three main structures, corresponding to different channels of dissociation. As expected from Figs. 6 and 7, the dissociation in the $\Sigma_g^+ 3s$ electronic state appears at large scattering angles ($\chi \approx 20^\circ$) and displays a trend similar to the impulsive structure of the experimental cross section [Fig. 9(a)]. Dissociative electronic excitation takes place at small scattering angles ($\chi \approx 10^\circ$): Excitation of the $\Pi_u^- 3p$ weakly bound state forms a structure at the ($\epsilon \approx 0, \chi \approx 0$) region, while the $\Sigma_u^- 3s$ and $\Sigma_g^- 3p$ states are responsible for the structure at $\epsilon \approx 1–1.3$ eV. The general appearance of the plot shows many qualitative similarities to the experimental data of Refs. [1,3] presented in Fig. 9(a).

B. Case of vibrationally excited Na$_2^+$ dimers

Though the $v=0$ cross section of Sec. IV A [Fig. 9(b)] bears a qualitative resemblance to the experimental data of Refs. [1,3] [Fig. 9(a)], a few differences are noticeable. First, the computed $\Sigma_g^+ 3s$ impulsive contribution extends too much towards high $\epsilon$ values as compared to experiment where it exhibits greater localization around its maximum near $\epsilon \approx 0.2$ eV. Second, instead of the distinct structures $\Sigma_g^- 3p$ and $\Sigma_u^- 3s$, appearing, respectively, at $\epsilon \approx 1$ and 1.3 eV in the theory, the experiment shows a single structure at $\epsilon \approx 0.9$ eV. Actually, the above comparison disregards the fact that in the experimental conditions the Na$_2^+$ dimer ions have a vibrational state distribution $w(v)$ and so the actual cross section results from an incoherent superposition of initial vibrational states

$$\langle \sigma(\epsilon, \chi) \rangle = \sum_v w(v) \sigma^v(\epsilon, \chi). \tag{24}$$

In Eq. (24) $\sigma^v(\epsilon, \chi)$ is the doubly differential dissociation cross section for each vibrational state $v$ initially present in

FIG. 6. Contour maps of the probability density $\tau(\epsilon, b; \theta, \varphi)$ of dissociation summed over all electronic channels $j$ as a function of the energy $\epsilon$ of the fragments and the impact parameter $b$ for $\theta = 90^\circ$ and $\varphi = 0$.

FIG. 7. Classical scattering angle $\chi(b; \theta, \varphi)$ determined from the classical relative motion as a function of impact parameter $b$ for dimer orientations defined by $\theta = 90^\circ$ and different $\varphi$ values indicated in the figure.

FIG. 8. Contour maps showing the $\sigma^v(\epsilon, \chi)$ contributions of the dimer orientations $\theta=90^\circ$ and $\varphi = \{20^\circ, 25^\circ, 30^\circ\}$ to the doubly differential cross section $\sigma_j(\epsilon, \chi)$ [see Eq. (17)] for dissociation in the entrance state $\phi_j(\Sigma_g^+ 3s)$: (a) classical cross section with diverging rainbows and (b) result of the treatment of the rainbow regions by Airy functions. Darker areas indicate higher intensities.
FIG. 9. Contour maps of the doubly differential cross section \(\sigma(\epsilon,\chi)\) for dissociation irrespective of the final electronic state: (a) experimental result of Refs. [1,3], (b) cross section \(\sigma(\epsilon,\chi)\) obtained for Na\(_2^+\) assumed to be initially in the ground vibrational state, and (c) cross section \(\sigma(\epsilon,\chi)\) for the distribution of vibrational states of Na\(_2^+\) discussed in the text. Darker areas indicate higher intensities.

the Na\(_2^+\) beam. Yet the actual vibrational state distribution \(w(v)\) is unknown. An average internal energy \(\approx 0.2\) eV of the dimer ions was tentatively proposed in Ref. [3] to make the simple binary encounter kinematics model of impulsive dissociation reproduce the overall trend of the experimental data. This value seemed to receive support from more involved classical trajectory calculations [3]. Still, as such, this estimate is insufficient to make the evaluation of a formula such as Eq. (24) possible. We have thus proceeded as described below.

The Na\(_2^+\) dimer ions are produced in the experiment of Refs. [1,3] by the bombardment of a Na\(_2\) neutral beam by fast (40-eV) electrons. Thus the \(w(v)\) distribution is merely reflecting, through the Franck-Condon principle, the vibrational distribution \(w_0(v_0)\) in the parent Na\(_2\) neutral beam:

\[
w(v) = \sum_{i=0}^n w_0(v_0)\langle \chi_0 | \chi_{v_0}^i \rangle^2,
\]

where \(\chi_0\) and \(\chi_{v_0}^i\) are, respectively, vibrational wave functions of the ionized and neutral dimers. In the experimental conditions of Refs. [1,3] the neutral Na\(_2\) dimers are likely to have \(v_0\) in Eq. (25) bounded by \(v_0 \approx 2\). For simplicity, we make the working assumption that

\[
w(v) \approx \langle \chi_0 | \chi_{v_0}^0 \rangle^2.
\]

It has occurred that the maximum of this distribution is located near \(v = 6–7\) and its width at half maximum encompasses states in the range \(3 \leq v \leq 10\). Its mean vibrational energy

\[
\langle E_{\text{ vib}} \rangle = \sum_v w(v) E_v
\]

is \(\langle E_{\text{ vib}} \rangle = 0.096\) eV. In Fig. 2 we compare the initial distribution of \(r\) values for the corresponding incoherent superposition of vibrational states to the initial probabilities \(|\chi_{v_0}|^2\) for \(v = 0\) and 6 vibrational levels.

We have determined the \(\sigma(v,\chi)\) cross sections for \(v\) in the interval \(v \in [3,10]\) as described in Sec. II C Eqs. (21) and (22), using the relevant \(P_i = \chi_v\) initial vibrational wave functions. The corresponding average [Eq. (24)] over the distribution \(w(v)\) [Eq. (26)] is displayed in Fig. 9(c). The result definitely improves the comparison with experiment. The \(\Sigma_{3s}\) impulsive structure is now more concentrated in a narrower \(\epsilon\) range than Fig. 9(b) and the \(\Sigma_{3p}\) and \(\Sigma_{3s}\) structures have merged into a single one properly located at 0.9 eV. While all details of the new pattern do not have a general straightforward explanation, the way in which the electronic structures have evolved has a transparent interpretation. As seen from Fig. 2, the \(\Sigma_{3s}\) energy curve is more repulsive than the \(\Sigma_{3p}\) one. Dissociation energies in vertical electronic transitions are thus more sensitive in the former than in the latter case to the \(r\) location where the transition takes place. Moreover, the vibrationally excited states can roughly be viewed as essentially made of two lobes placed around the turning points of classical motion (see Fig. 2). Actually, the outer lobe gives rise more efficiently to an electronic transition than the inner lobe. This is most probably related to the smaller energy difference for the electronic transition at the outer lobe than at the inner one. These characteristics are sufficient to explain why the \(\Sigma_{3p}\) and \(\Sigma_{3s}\) structures move to lower dissociation energy with vibrational excitation and the more so for the latter than for the former.

The comparison with experiment still indicates that the breadth and intensity of the structure at \(\epsilon \approx 0\) and \(\chi \approx 0\), which actually originate from dissociation in the \(\Pi_{3p}\) state (Sec. IV A 2), are rather underestimated in the calculation. Again, this issue can be examined in terms of vertical transitions from the electronic ground state. Two possible explanations related to the comparative flatness of the \(\Pi_{3p}\) energy curve in the Franck-Condon region of the distribution of vibrational states considered can be proposed: (i) Higher accuracy of this curve than what was considered reasonable in Sec. III can change the relative importance of what goes
into (bound) vibrational excitation and dissociation in this state or (ii) a different vibrational distribution emphasizing small-\(\nu\) values further can yield more dissociation. Another possibility could lie in one of the approximations made in Sec. II to lighten the computational effort. More specifically, it is not clear by now what the effect of disregarding Coriolis coupling in the present work (Sec. III) could have on the discrepancy discussed.

V. SUMMARY AND CONCLUSION

One of the incentives to undertake the present work was to apply a state-of-the-art method for treating the dynamics of Na\(_2^+\) fragmentation in collisions with He, a process that has been the subject of a detailed experiment in Refs. [1,3]. From the latter study it appeared that fragmentation can occur with different characteristics either as a vibrational excitation above the dissociation limit in the initial electronic ground state of Na\(_2^+\) or as a result of an electronic excitation to a dissociative state. This implied the use of a nonadiabatic molecular collision framework to treat the corresponding dynamics. The semiclassical coupled wave-packet approach that treats electronic and vibrational (whether bound or dissociative) motions quantally and the remaining motions classically is to date the most developed theory of that kind. Yet this method is computationally quite demanding, especially in the collision energy range in which the experiments of Refs. [1,3] have been carried out. It turns out that for the latter collision conditions one can advantageously make use of an approximation in which the dimer neither vibrates nor rotates during the encounter. This approximation has actually made the present work affordable. While the dimer is held frozen, as just stated, it actually accumulates momentum and may actually undergo electronic transitions as the He atom passes by. This accumulated momentum reveals itself in a postcollisional stage and contributes to the final vibrational- (eventually dissociative) rotational motions of the dimer in each of the final electronic state produced by the collision. In the work reported the information on the accumulated vibrational momentum of the dimer is contained in the bond length dependences of the electronic transition probability amplitudes. Likewise, the information on the accumulated rotational angular momentum is contained in the dependences of these electronic amplitudes upon the orientation of the dimer. Nevertheless, to simplify the computation we have extracted this information from classical equations of motion as discussed in Sec. II C.

It may be stated right away that the reported results confirm the analysis of Refs. [1–3] of the different structures observed in the experimental fragmentation cross section. Conversely, the general agreement of the present results, taking a plausible initial vibrational distribution of the Na\(_2^+\) ions into account, with experiment is in strong support of the cogency of our theoretical treatment. From this agreement we are inclined to infer that the Na\(_2^+\) ions in the experiment of Refs. [1,3] were cooler than what was initially thought.

Concerning the fragmentation mechanism, collisions leaving the Na\(_2^+\) dimer ion in its electronic ground state \(\Sigma_g^3s\) lead to dissociation at large scattering angles (\(\chi \geq 20^\circ\)). This corresponds to important momentum transfer, justifying its designation as impulsive mechanism in Refs. [1–3]. The momentum transfer actually occurs most efficiently when the He trajectory passes close to one of the Na\(^+\) cores: typically within a sphere of radius \(= 2a_0\). Most salient features and trends of this CID mechanism correspond to what may be predicted from classical mechanics. Details such as the shape, breadth, and importance of dissociation probability densities actually depend on the initial quantal state and quantal projection.

Collisions that bring the Na\(_2^+\) dimer in an excited electronic state (\(\Sigma_g^3s, \Sigma_g^3p, \) and \(\Pi_g^3p\)) occur for He trajectories going into the region between the nuclei and thus contribute mainly to relatively small scattering angles. For these dissociative electronic excitation processes the gross features of the probability densities correspond to what may be predicted from Franck-Condon overlaps between the initial vibrational state and the final dissociation continuum. Still finer details, for instance, the extension of dissociative electronic excitation structures by impulsive tails, arise from the detailed dependence of the electronic transition probability amplitudes upon the Na\(_2^+\) bond distance.

Further work on collision-induced fragmentation of larger alkali-metal cluster ions, such as Na\(_3^+\)He [2], should show which aspects of the present semiclassical treatment will survive the dimensionality increase of the system.

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