Eur. Phys. J. D 4, 321–330 (1998)

THE EUROPEAN PHYSICAL JOURNAL D

Nonadiabatic fragmentation of excited molecular ions: An exploratory study for N_2H^+

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Received: 6 March 1998 / Revised: 7 March 1998 and 17 June 1998 / Accepted: 23 June 1998

Abstract. The photodissociation of N_2H^+ was studied in a one-dimensional approximation, with the aim of understanding the nonadiabatic features of the fragmentation dynamics. In the collinear arrangement of the system, the three lowest excited surfaces ($^1\Sigma^+$ states) interact *via* two avoided crossings outside the Franck-Condon region, and they are strongly coupled radially by nonadiabatic terms. Electronic transition probabilities for the process $N_2H^+ + h\nu \rightarrow (N_2^+)^* + H$, with N_2^+ in one of the three lowest electronic states involved in the fragmentation, were calculated using the semiclassical multichannel S-matrix within the half-collision approach to photodissociation. The reliability of the semiclassical theory, for treating multichannel nonadiabatic processes was analyzed, and inelastic cross-sections for the three processes of electronically selected fragmentations were calculated. The structure found in the calculated absorption lineshapes reveals the marked influence of the nonadiabatic couplings between excited states in the fragmentation dynamics of this molecular ion.

PACS. 33.80.Gj Diffuse spectra; predissociation, photodissociation

1 Introduction

Fragmentation of ionic molecular systems has received renewed attention in the last years, being the subject of a large amount of both experimental and theoretical work. Modern experimental techniques have enabled us to prepare molecular ions in a well-defined initial state, to irradiate them with photons of proper wavelength in order to either excite or fragment them, and then to analyze the final state distribution of the fragments.

Ion photofragment spectroscopy begun in the late'70s with the first experiments of photodissociation of diatomic molecular ions [1], and at present it can be considered as one of the most powerful experimental tools for the study of the properties of such ions. Photofragment ions produced by the interaction of a laser with a fast beam can be detected with nearly unit efficiency, thus overcoming the well-known problems created when one would try to detect *directly* the emission, or the absorption [2], of radiation from these systems: the low density of the relevant ionic species. With photodissociation techniques it has been possible to determine bond dissociation energies, as well as vibrational spacings and rotational constants, not only for ionic diatomic systems, like O_2^+ [3] and CH^+ [4], but even for polyatomic cases, like NO_2^+ and CH_3I^+ [5]; besides, another application of the ion photofragment spectroscopy can be the preparation of molecular ions in selected internal states in order to use them in collisional studies.

Following the above advances, a series of theoretical models have been developed to treat such processes, and several methods have been applied in order to calculate photodissociation cross-sections and final vibrational-state distributions of the photofragments, including quantum time-dependent or time-independent treatments, as well as classical or semiclassical calculations. A review of these methods is available from reference [6]. It should be noted that they use there the same principles employed in the theoretical study of photodissociation of *neutral* systems (see, for instance, Refs. [7,8]).

In most cases, however, the theoretical calculations deal with a single potential energy surface (PES) as the only molecular state involved in the fragmentation. On the other hand, because of the high energies considered, and most of all because of the strong couplings existing in ionic systems between the excited electronic states, the real dissociation process could involve at least two excited electronic potential surfaces of the molecular ion, thus leading to possible *nonadiabatic fragmentations.* In order to treat such processes some basic difficulties arise. First of all the presence of more electronic channels in the dynamics severely complicates the theoretical treatment, because, instead of solving one Schrödinger equation for the motion of the nuclear framework, one has to solve n coupled equations, where n is the number of the electronic channels that are coupled during the process. Furthermore, even in the approximate methods that do

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not directly solve the coupled equations, what is required is the knowledge of the potential couplings between the relevant PES of the system. In the *adiabatic* representation these couplings are electronic integrals containing gradients of the electronic states with respect to the internal nuclear coordinates, and it is general practice, instead of calculating them, to abandon the adiabatic representation, constructing new *diabatic* electronic states, for whom the couplings are simply matrix elements of the potential operator [9]. This procedure is not trivial [10] and involves costly computational schemes.

The most common approach used in molecular dynamics involving the coupling between electronic and nuclear degrees of freedom is certainly the *semiclassical* approximation, known as the Landau-Zener-Stuckelberg treatment ([11], see also [12,13]) of the curve-crossing problem, and examined in a series of papers by Miller and George [14] (see also the theoretical work by Delos, Thorson *et al.*, [15]) in the ′70s. Furthermore, the diagrammatic expression for the semiclassical nonadiabatic S-matrix, formulated by Child [16] and refined by Nakamura and coworkers [17,18], has also allowed an easy application of the semiclassical theory to nonadiabatic collisions, producing results usually found to be in good agreement with the quantal ones. The method could be applied [17a] to the study of molecular fragmentations involving more electronic surfaces, provided that one works in the context of the “half-collision” approach [7,8] for the photodissociation processes. Even in this case what is expected is fairly good agreement between the results coming from the semiclassical theory and the ones obtained from a full quantumechanical treatment.

In this work we therefore discuss new results we have obtained by applying the semiclassical S-matrix method to the study of the nonadiabatic fragmentation dynamics of N_2H^+. This molecular ion has received in the past decade great attention, both experimental [2] and theoretical [19,20], and it can be considered as the prototype for a wide class of ionic systems. From recent, very accurate calculations [21] reported for the lowest energy states of this ion one can see that the first excited surface ($2^1\Sigma^+$ in the $C_{\infty v}$ geometry) is lying not far away from the ground state ($1^1\Sigma^+$), and very near in energy to the higher ones. This closeness in energy gives rise to a number of interactions, showing up as avoided crossings between states of the same symmetry ($3^1\Sigma^+$,$4^1\Sigma^+$), and allowed crossings between Σ and Π states. Thus, in order to study the fragmentation dynamics of the excited N_2H^+, we are forced to regard more electronic excited states as the final products thereby considering the possible nonadiabatic processes

$$N_2H^+{}_{g.s.} + h\nu \rightarrow (N_2H^+)^* \begin{cases} \rightarrow (N_2)_{g.s.} + H^+ \\ \rightarrow N_2^* + H^+ \\ \rightarrow (N_2^+)_{gs} + H \\ \rightarrow (N_2^+)^* + H. \end{cases}$$

The nonadiabatic (*i.e.* electronically inelastic) fragmentation probabilities have been computed extracting the outgoing part of a full semiclassical S-matrix, which has been obtained in turn from the electronic potential surfaces *via* two different set of calculations:

- simple WKB solutions of the different electronic states far from the crossing regions;
- semiclassical connection formulae localized in the crossing regions.

This paper is organized as follows. In Section 2 we analyze the PES we have used to treat the dynamics, with special attention to the equilibrium geometry of N_2H^+ in its ground state and to the correlations of the excited molecular states with the fragments N_2 and N_2^+. In Section 3 we describe the theoretical approach employed, that is the semiclassical S-matrix in the context of the half-collision approximation for photodissociation processes, while the mathematical details and the results of the calculations are presented in Section 4. The conclusions are given in Section 5.

2 Ionic potential energy surfaces

The PES we have employed here have been evaluated earlier on by Gianturco, Kumar and Schneider [21], who performed an *ab initio* MRDCI (Multireference Configuration Interaction, see Ref. [22]) calculation for the ground-state and for some of the low-lying surfaces of the complex N_2H^+. They chose the $C_{\infty v}$ and C_{2v} geometries to perform the calculations, *i.e.* they fixed at the values of 0° and 90° the θ angle, *i.e.* the internal angle between the vibrational ($\mathbf{r}$) and the translational ($\mathbf{R}$) vectors of the triatomic system. For each geometry the calculations were done at 8 values of r (the N−N distance) and 11 values of R (the N−H distance in the $C_{\infty v}$ geometry, while in the perpendicular approach R was chosen as the distance between H and the N_2 center of mass). Very recently, Mahapatra *et al.* [18] have also presented the results of a rigid-rotor (RR) calculation for the full ground-state PES (7 angles between 0° and 90°), obtained by fixing the N−N distance at its equilibrium value, *i.e.* $r = 2.08a_0$. This surface, as it turns out, shows a deep well ($\Delta E \simeq 0.2$ a.u.), and has been found [20] to be able to support 163 bound states.

In Figure 1 we have plotted the results of the rigid-rotor calculations for the minimum of the potential well at each value of θ: as it is clear from the figure, the collinear geometry is the most stable for the ion in its ground state. This result can be further combined with the Franck-Condon (FC) approximation to be valid during the photon absorption and with the additional assumption (see, for instance, Ref. [23a]) that the body-fixed angle remains unchanged during the fragmentation dynamics. Hence, in this initial study we can begin by choosing the $C_{\infty v}$ geometry surfaces as those of greatest interest for our model calculations. It is worthwhile to point out here that the assumption of fixing the internal angle during the dynamical processes for a triatomic system (*i.e.* one with three internal degrees of freedom) finds its physical explanation in the fact that the energies involved in these processes are much greater than the internal rotational energies

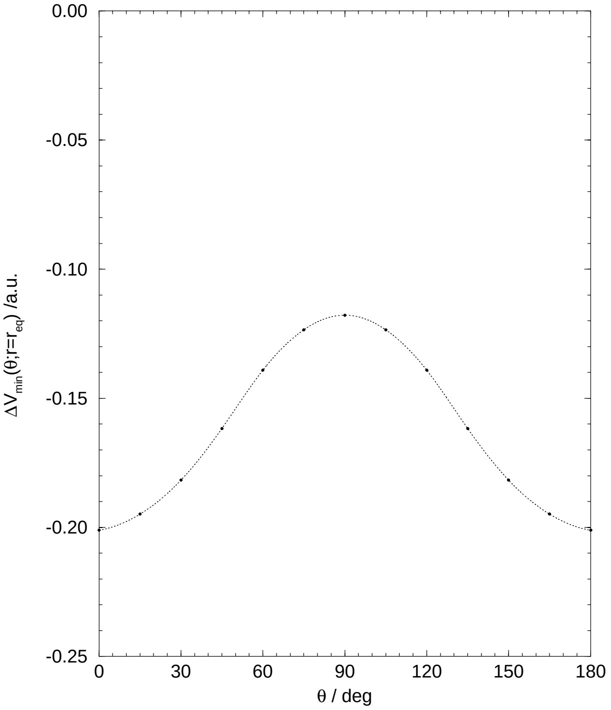

Fig. 1. Minimum energy profile of N_2H^+ ground electronic state for different values of θ, and r fixed at the equilibrium distance of $2.08a_0$.

of the systems (see, for this purpose, the IOS approximation for collisional cases, Refs. [24,25]). The further use of the FC scheme is also related to the sudden occurrence of the excitation process.

Our present purpose has been to establish a possible correlation between the electronic states of the bound-system N_2H^+ and those of its fragment-systems, $N_2 + H^+$ and $N_2^+ + H$. This was an interesting issue in itself from the point of view of the collision dynamics of the fragments [26], while also helping with investigating the possibility of a charge-transfer reaction between N_2 and H^+. As it has been pointed out elsewhere [21], the ground-state PES of N_2H^+ correlates with the ground state of the N_2 molecule, while the first molecular excited state correlates with the ground state of N_2^+. Our investigation on the upper electronic states has already shown [21] the additional, important result that *the lowest-lying excited states of the molecular ion* N_2H^+ *are mainly made up of electronic* N_2^+ *states*, while the first excited state of N_2 is located much higher in energy.

To make this point pictorially clearer, we have reported again, on the left of Figure 2, the cuts of the $C_{\infty v}$ surfaces at the largest value of the N−H distance that was considered in the MRDCI calculations [21], *i.e.* $R = 7.5a_0$. These cuts have to be compared on the right with the potential energy curves available from the same calculations for the molecular fragments N_2 and N_2^+, that should represent the same states with the H partner removed to infinity. From this comparison we see that the fragmentation of the molecular ion allows for the following asymptotic correlations:

$$\begin{aligned} 1^1\Sigma^+ &\rightarrow 1^1\Sigma_g^+(\mathrm{N_2}) + \mathrm{H}^+ \\ 2^1\Sigma^+ &\rightarrow 1^2\Sigma_g^+(\mathrm{N_2^+}) + 1^2S(\mathrm{H}) \\ 1^1\Pi &\rightarrow 1^2\Pi_u(\mathrm{N_2^+}) + 1^2S(\mathrm{H}) \\ 3^1\Sigma^+ &\rightarrow 1^2\Sigma_u^+(\mathrm{N_2^+}) + 1^2S(\mathrm{H}) \\ 4^1\Sigma^+ &\rightarrow 2^2\Sigma_u^+(\mathrm{N_2^+}) + 1^2S(\mathrm{H}). \end{aligned}$$

Hence, the fragmentation dynamics of N_2H^+ can be studied as if it were to follow the dynamics of two separate systems, depending on which potential surface describes the entrance channel (*i.e.* after the photon absorption): $N_2 + H^+$ if the dissociation process starts in the ground state, $N_2^+ + H$ if it starts in one of the ionic upper states. In the latter case, due to the strong couplings between the upper states of the molecular ion, there is also the possibility for the system to end up into different electronic final channels.

Supposing now that the photon beam ($E > 15$ eV) has brought the bound N_2H^+ to the first excited state, $2\Sigma^+$, with $N_2^+ + H$ as the final products of the fragmentation, then the following question arises: in which electronic state will the ion N_2^+ be produced? To try to answer this question has therefore been the purpose of the present work.

To summarize here the relative energetics of the involved states, we have reported in Figure 3 the ground-state and some of the lower-lying $C_{\infty v}$ electronic states resulting from the MRDCI [21] calculations, at the equilibrium value ($r = 2.08a_0$) for the molecular bond. In this first study of the N_2H^+ fragmentation dynamics we have not yet included the coupling with the vibrational degrees of freedom of the system thereby treating the N_2^+ fragment as a rigid rotor in which the bond has been kept fixed at its equilibrium value ($r = 2.08a_0$). The problem is therefore initially reduced to a 1D case where we use the cuts of Figure 3 as the starting points to perform the dynamical calculations. It is important to stress here that at least at the seams, *i.e.* when the dynamics behaves nonadiabatically, the approximation of fixing one of the two radial coordinates (r, R) is completely justified [27], and indeed we have found the R coordinate to be the one mostly responsible for the nonadiabatic couplings between the electronic channels. Furthermore, we have initially considered only *internal* couplings, *i.e.* those generated by the motion of the nuclei in the BF frame, neglecting the couplings between angular momenta of nuclei and electrons (or *rotational* couplings: see, for this purpose, Ref. [17a, 28, 29]). This restriction, fully justified by the great difference in strength between the two kinds of couplings [30], has allowed us to exclude from the dynamics those molecular states of symmetry different from $^1\Sigma^+$. Hence we can thus focus on the lowest three excited $^1\Sigma^+$ states of N_2H^+ (see Fig. 3) as the molecular states along which the nonadiabatic fragmentation would be mostly likely to take place. The explicit dependence of the process on the molecular coordinate will be further analyzed in a later study [31].

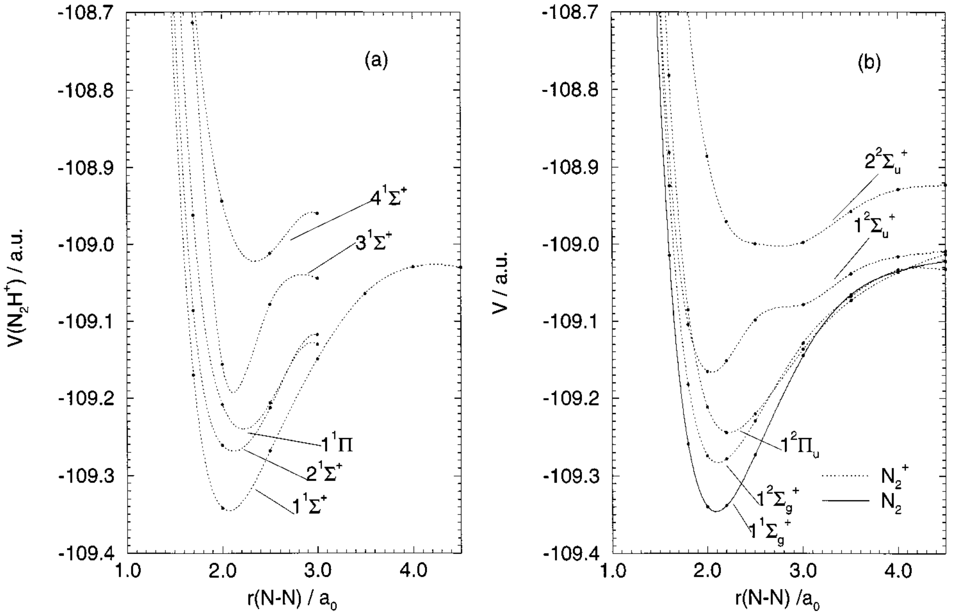

Fig. 2. Correlations between the electronic states of the molecular ion N_2H^+ and the asymptotic states of its fragments N_2 and N_2^+: (*a*) cuts of the $C_{\infty v}$ PES (collinear geometry) of N_2H^+ at $R = 7.5a_0$ as a function of r; (b) potential energy curves of N_2 and N_2^+ (the latter being shifted by 0.5 a.u.).

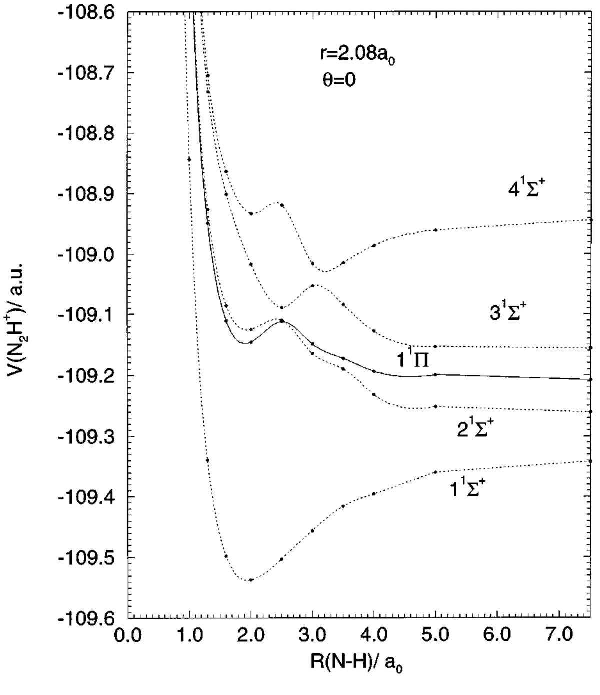

Fig. 3. Cuts of the $C_{\infty v}$ PES of N_2H^+ at the equilibrium distance between the N atoms ($r = 2.08a_0$).

3 Semiclassical theory: an outline

3.1 Half-collision approximation for fragmentation processes

Following the so-called half-collision approximation, one could imagine a photodissociation process consisting of two steps: first, the photon absorption, and, second, the nonadiabatic dissociation on the three excited potential energy surfaces. In the half-collision approximation for *adiabatic* photodissociations [7], instead of solving the coupled equations for the molecular system interacting with a photon beam, one reduces the problem to the determination of a dipole-transition integral over the wavefunctions of the initial and final electronic states, and to the evaluation of the half-collision matrix elements relative to the dissociative state only. In a 2D problem (*e.g.* a triatomic system in which the internal orientation angle is kept fixed), this can be easily seen if one substitutes, in the expression for the absorption cross-section [32],

$$\sigma_{vv'} = \frac{4\pi}{3\lambda} \sum_n \Gamma(d,n,E|g,v,v') \tag{1}$$

the partial widths $\Gamma(d,n,E|g,v,v')$ as [7]

$$\Gamma(d,n,E|g,v,v') = 2\pi|\sum_{n'} S^{HC}(n,n')O(d,n',E|g,v,v')|^2 \tag{2}$$

where n, n' are two continuum states of the electronic dissociative state (d), while v, v' are the separate vibrational eigenfunctions (one for the R-space, the other for the r-space) of the ground-state (g). $O(d,n',E|g,v,v')$ are a set of two-dimensional integrals that can be reduced, in the Condon approximation, to Franck-Condon integrals times the dipole moment [32], $S^{HC}(n,n')$ is the half-collision matrix element

$$S^{HC}(n,n') = \delta_{nn'} - i\pi T_{nn'} \tag{3}$$

while the corresponding full-collision matrix-element would be

$$S(n,n') = \delta_{nn'} - 2i\pi T_{nn'} \tag{4}$$

with $T_{nn'}$ an element of the **T** transmission matrix [24].

When one has more than one dissociative state, as in our case, the problem is more complicated and therefore one needs to apply some further approximations. What we have done here is to set equal to 1 the Franck-Condon integrals of equation (2). This is often not very physical but it should be fairly realistic in the present instance of little N_2 bond deformation [21]. The problem has then been reduced to the search for the matrix-elements of an $\mathbf{S}^{HC}$ matrix over different electronic states. We have accomplished this search by choosing the *semiclassical* description of electronically inelastic processes, *i.e.* by extracting the half-collision part of a full-collision inelastic S-matrix that has been derived within the semiclassical approximation.

3.2 Semiclassical multichannel S-matrix

The semiclassical solution to a scattering problem involving one electronic state (and one scattering coordinate) is an S-matrix of the form [14]

$$S_l(k) = \exp(2i\eta_l(k)) \tag{5}$$

in which the phase-shifts $\eta_l(k)$ are computed in the WKB approximation [33], *i.e.*

$$\eta_l(k) = \int_{R_T}^{\infty} [k_l(R) - k_l(\infty)]dR - k_l(\infty)R_T + (l+\frac{1}{2})\frac{\pi}{2} \tag{6}$$

where R_T is the classical turning point, l is the lth partial wave, and $k_l(R)$ is the effective wave-number with the Langer-modification [33,34]:

$$k_l(R) = \frac{1}{\hbar}\sqrt{2m[E-V(R)] - (l+\frac{1}{2})^2\frac{\hbar^2}{R^2}}\,\cdot \tag{7}$$

When more electronic channels are involved in the problem, the semiclassical expression for the off-diagonal elements of the scattering matrix is [15c,17e]

$$S^l_{ij} = A^l_{ij}\exp[i(\eta^l_i + \eta^l_j)] \tag{8}$$

where, besides the elastic phase-shifts relating to the different electronic curves, there are also the crossed-terms $A^l_{ij}(k)$, often referred to as the elements of a *reduced* scattering matrix. The semiclassical theory for electronically inelastic processes describes the nuclear motion by WKB waves from the different electronic states in the full coordinate space, except for the *transition points*, where the couplings between the curves reach their maximum values and where the nonadiabatic transitions are assumed to be *localized* [14a]. That's why [12] the theory basically holds for electronic surfaces *radially* coupled (*i.e.* exhibiting avoided crossings), with complex crossing points. Here the semiclassical solutions (WKB) acquire a phase-factor, due to the passage into the complex region of the coordinate space, that gives rise to the crossed terms in equation (8).

For the simplest case of $l = 0$, these terms are [14a]

$$A_{ij} = (p_S)^{1/2}(1-p_S)^{1/2} = \sqrt{exp(-2\delta_S)}\sqrt{1-\exp(-2\delta_S)} \tag{9}$$

where δ_S is the Stuckelberg integral [11c] originating from the complex nuclear trajectories between the two electronic surfaces:

$$\delta_S = i\int_{\mathrm{Re}(R_*)}^{R_*} [k_2(R) - k_1(R)]dR \tag{10}$$

$\mathrm{Re}(R_*)$ being the real part of the complex crossing point.

The procedure of the semiclassical theory, in electronically inelastic processes, is then to *connect*, in the complex crossing regions, the WKB wavefunctions of the different electronic curves, that are still proper solutions of the Schrödinger equation in the semiclassical limit ($\hbar \to 0$, see [12]) *far* from the crossings. The approximation of localizing a transition at the complex crossing point is supported by quantum mechanical considerations [12,17a], and the calculation of the (quantumechanical) dynamical couplings between the adiabatic states [9,28]

$$\langle i|\frac{\partial}{\partial R}|j\rangle \tag{11}$$

is now replaced by the complex integration of the classical actions at the crossings.

3.3 "Diagrammatic" approach to the semiclassical S-matrix

In order to extract the half-collision part from the full semiclassical S-matrix presented up to now, one needs the full matrix in a "diagrammatic" form, just as that devised by Child [16b] for inelastic scattering problems.

Using the *comparison equation* method [33,35], in the spirit of the path-integral [14a, 36] formulation, it is possible to show [17a] that the matrix-elements (8) are originating from a matrix (for two states which cross at the complex point R_*, with $R_X = \Re(R_*)$)

$$S = P^+_{\infty X} O_X P_{XTX} I_X P^-_{X\infty} \tag{12}$$

where the P-matrices are adiabatic propagation matrices containing incoming (P^-) and outgoing (P^+) WKB-functions for the 2 curves:

$$\begin{aligned}[P^+_{\infty X}]_{nm} &= [P^-_{\infty X}]_{mn}\\ &= \delta_{nm}\exp\left(i\lim_{R\to\infty}\left[\int_{R_X}^{R} k_n(R')dR' - k_n(\infty)R\right]\right),\end{aligned} \tag{13}$$

and

$$[P_{XTX}]_{nm} = \delta_{nm} \exp\left(2i \int_{t_n}^{R_X} k_n(R) dR + i\frac{\pi}{2}\right), \quad (14)$$

and t_n stands for the turning point of the nth state.

The outgoing matrix O_X at the crossing is

$$O_X = \begin{pmatrix} (1-p_{12})^{1/2}\exp(i\phi) & -p_{12}^{1/2}\exp(-i\sigma) \\ p_{12}^{1/2}\exp(i\sigma) & (1-p_{12})^{1/2}\exp(-i\phi) \end{pmatrix}, \quad (15)$$

where

$$p_{12} = \exp(-2\delta) \quad (16)$$

and δ and σ are the real and imaginary part of the Stuckelberg integral (10):

$$\sigma + i\delta = \int_{R_X}^{R_*} [k_1(R)dR - k_2(R)]dR \quad (17)$$

i.e.

$$\delta_S = \delta - i\sigma. \quad (18)$$

In the *diagonal* elements of these matrices appears the Stokes-phase ϕ [33,36]

$$\phi = \frac{\pi}{4} - \gamma(1 - \gamma ln\gamma) - \arg\Gamma(1 + i\gamma), \quad (19)$$

with $\gamma = \delta/\pi$ which originates from the connection, at the crossings, between asymptotic solutions of the *same* electronic curve.

The incoming matrix I_X at the crossing is the O_X transposed:

$$I_X = \tilde{O}_X. \quad (20)$$

The expression can be generalized [17a] to a 3-coupled states problem with two crossing points, R_A and R_B: in this case the expression is

$$S = P^+_{\infty A} O_A P^+_{AB} O_B P_{BTB} I_B P^-_{BA} I_A P^-_{A\infty}, \quad (21)$$

where the meaning of the P-matrices is straightforward and, provided that R_A is the position of the crossing between the curves 2 and 3, and R_B is that of the crossing between the curves 1 and 2, the matrices at the crossing are:

$$O_A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & (1-p_{23})^{1/2}\exp(i\phi_{23}) & p_{23}^{1/2}\exp(i\sigma_{23}) \\ 0 & -p_{23}^{1/2}\exp(-i\sigma_{23}) & (1-p_{23})^{1/2}\exp(-i\phi_{23}) \end{pmatrix} \quad (22)$$

$$I_A = \tilde{O}_A \quad (23)$$

$$O_B = \begin{pmatrix} (1-p_{12})^{1/2}\exp(i\phi_{12}) & p_{12}^{1/2}\exp(i\sigma_{12}) & 0 \\ -p_{12}^{1/2}\exp(-i\sigma_{12}) & (1-p_{12})^{1/2}\exp(-i\phi_{12}) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (24)$$

$$I_B = \tilde{O}_B. \quad (25)$$

The meaning for δ, σ and ϕ is the same already seen in the 2-states problem.

From this expression of the scattering matrix one can easily extract the outgoing part relative to the fragmentation process. However one has to evaluate first the region of the coordinate space where the system is found after the absorption of the photon: from the Franck-Condon principle this region will be the equilibrium distance for the system in its ground-state, and we will call it R_{fc}. One then constructs a P-matrix from that radial point up to the first crossing point. The rest of the half-collision matrix will be just the outgoing part of the total S-matrix: for a 3-states problem one then has

$$S^{HC} = P^+_{\infty A} O_A P^+_{AB} O_B P^+_{BR_{fc}}. \quad (26)$$

It is worthwile to note here that the semiclassical information contained in the S and S^{HC} matrices are the *probability amplitudes* relative to the different molecular processes considered, and from a superposition of these amplitudes [14a] one expects to obtain the correct quantum behaviour of the fragmenting ionic system.

4 Present calculations

4.1 Numerical details

In order to calculate the half-collision matrix depicted in equation (26), one has to evaluate:

- simple WKB integrals (P matrices) of the electronic curves far from the crossings;
- contour integrals in the complex region at the crossings (O matrices).

The numerical integration in the real space is obviously an easy task while the bulk of the numerical work is to evaluate the complex integrals (17). For this purpose, one usually assumes having an "averaged" trajectory [28] between the two that are defined from the two different electronic curves, then one switches from the *adiabatic* representation to new *diabatic* states [9] and finally one assumes the diabatic curves to be linear in the crossing region and to have there a constant coupling. These three steps [14c] give rise to the Landau-Zener approximation [11a, 11b] for the Stuckelberg integral (10):

$$p_{LZ} = \exp(-2\delta_{LZ}) = \exp\left(-\frac{2\pi}{\hbar v}\frac{V_{12}^2(R_0)}{|\Delta V'(R_0)|}\right) \quad (27)$$

where v is the "average" velocity of the nuclei at the crossings, V_{12} the diabatic couplings, and $\Delta V'(R_0)$ the difference between the slopes of the diabatic curves, with R_0 the real part of the crossing point.

Recently, Nakamura and coworkers [17d–17f] have proposed new formulae to evaluate the Stuckelberg integral for nonlinear potentials. The approximation of neglecting the real part (σ) of the Stuckelberg integral is removed, and a nonunique diabatization, with the following approximation for the new potentials (linear model), is not required anymore. Furthermore, when using these formulae to calculate the phase-integrals σ and δ there is no need to perform analytic continuations into the complex plane and to use contour-techniques to solve them [27]. This is because σ and δ are now [17f] simple functions of two diabatic parameters, a^2 and b^2, related respectively to the coupling strength between the electronic curves and to the energy difference, which can be extracted directly from the information on the adiabatic curves near the crossings [17d]. See also reference [38].

In the Landau-Zener (linear potential) model, these parameters [37] appear in equation (27) as

$$p_{LZ} = \exp\left[-\frac{\pi}{4a|b|}\right] \tag{28}$$

where

$$a^2 = \frac{\hbar^2}{2m}\frac{F(F_1F_2)}{8V_{12}^3} \tag{29}$$

and

$$b^2 = (E - E_x)\frac{F_1 - F_2}{2FV_{12}}, \tag{30}$$

with

$$F_1 = V_1^{'}(R_0); F_2 = V_2^{'}(R_0); F = \sqrt{|F_1F_2|}; V_{12} = V_{12}(R_0). \tag{31}$$

Now, a^2 and b^2 can become "adiabatic": their expressions related to adiabatic parameters of the curves are contained in reference [17f], and the relations between these adiabatic parameters and the quantities of interest for the S-matrix, *i.e.* σ and δ, are in references [17d, 17e]. Once δ is known, the Stokes-phase is defined *via* equation (19). We have used these formulae to build the O matrices equations (22, 24). Later, combining them with the transmission matrices P, by the direct product in equation (26), we have computed the S^{HC}-matrix for the energy range considered in the present study. It is worth reminding ourselves at this point that the curve crossings we are discussing here is classified to be of the NT-type in reference [17].

4.2 Results and discussion

To describe the fragmentation dynamics we have looked first at the equilibrium geometry of the molecular ion in its electronic ground state ($1^1\Sigma^+$): this is [20] $\theta = 0$, $r = 2.08a_0$, $R = 1.954a_0$. Our approach has been to set N_2H^+ at *its equilibrium geometry for what concerns the* θ *and* r *coordinates*, and to consider the dynamics along the R coordinate only. We found the equilibrium distance of the first bound state of N_2H^+ at ($\theta = 0, r = 2.08a_0$) to be $R = 2.006a_0$: according to the Franck-Condon principle, we have therefore chosen this R value as the starting point for the evaluation of the S^{HC}-matrix elements.

The cuts of the $C_{\infty v}$ excited surfaces ($^1\Sigma^+$) at $r = 2.08a_0$ (Fig. 3) show two avoided crossings at distances ($R_B \simeq 2.5a_0$, $R_A \simeq 3.0a_0$) greater than $R_{fc} = 2.006a_0$, thereby revealing that it is necessary to include in the fragmentation dynamics at least the three low-lying excited states $^1\Sigma^+$. The half-collision matrix was then a 3×3 matrix, just as that depicted by equation (26).

The semiclassical approximations are expected to work at sufficiently high energies as far as the *adiabatic* part (WKB approximation, see [33]) is concerned while the *localization* of the nonadiabatic couplings is a further approximation usually working well over a broad range of energies [14a]. To compare our results we have therefore chosen an energy interval between 15 eV, where the three dissociative channels start to be open, up to about 50 eV.

In Figure 4a we have reported the results for the nonadiabatic state-to-state dissociation probabilities, obtained as the squared moduli of the S^{HC} matrix off-diagonal elements:

$$|S_{ji}^{HC}(E)|^2 = P_{ij}(E) \tag{32}$$

where $P_{ij}(E)$ is the probability that the system, once excited in the ith state by the photon absorption at energy E, dissociates by exiting into the jth state.

The shapes of the nonadiabatic transition probabilities come up from the physical assumptions of the semiclassical multichannel theory. Once the system has been brought by the photon absorption to a given excited state, it fragments as a WKB outgoing wave of this state until it reaches a crossing region. Here the nuclear trajectory is allowed to branch into complex space and it will continue on either one or the other of the two relevant electronic states. The wavefunction will thus acquire a different factor according to which state it has moved into. These factors are contained in the crossing-matrices O_A and O_B equations (22, 24), and their largest contributions are given by the *one-passage probabilities* equation (28),

$$p_{ij} = \exp(-2\delta_{ij}) \tag{33}$$

due to the imaginary part of the Stuckelberg integral δ_S (10). The one-passage probabilities, now being calculated beyond the Landau-Zener approximations, are expected to provide a more correct physical picture.

At the crossings the wavefunctions also acquire new phase-factors which originate from the real part of the complex integral and appearing in the crossing-matrices (22, 24) as the phases σ and ϕ. These phases are included in the semiclassical formulation we have adopted while they would be neglected in a simpler Landau-Zener treatment.

While studying the behaviour of the P_{ij}'s in Figure 4a, we found that, as it was expected from the analytical formulation of the S^{HC} matrix (see Sect. 3), our results are

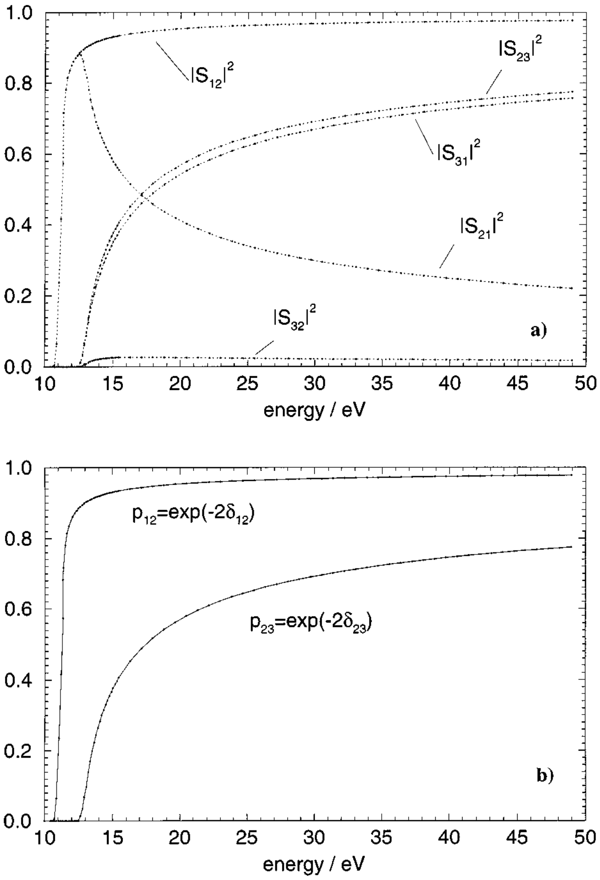

Fig. 4. Nonadiabatic transition probabilities for the fragmentation of N_2H^+ as a function of the photon energies (a). In (b) the one-passage probabilities for the two transitions $2^1\Sigma^+ \to 3^1\Sigma^+$ (p_{12}) and $3^1\Sigma^+ \to 4^1\Sigma^+$ (p_{23}) are reported.

simple products of the one-passage probabilities at the crossings. More precisely, one has

$$P_{12} = |S_{21}|^2 = p_{12}(1 - p_{23}) \tag{34}$$

$$P_{21} = |S_{12}|^2 = p_{12} \tag{35}$$

$$P_{23} = |S_{32}|^2 = (1 - p_{12})p_{23} \tag{36}$$

$$P_{32} = |S_{23}|^2 = p_{23} \tag{37}$$

$$P_{13} = |S_{31}|^2 = p_{12}p_{23} \tag{38}$$

$$P_{31} = |S_{13}|^2 = 0. \tag{39}$$

From the equations (34–39) it is readily seen that the phase-factors do not appear in the squared moduli of the half-collision matrix, while they would have appeared in the P_{ij}'s for a full-collision problem [37]. Then, the occurrence of an inelastic dissociation process depends only on the one-passage probabilities at the crossings.

In Figure 4b we have plotted the values of the one-passage probabilities p_{12}, p_{23} as a function of the energy. At every energy p_{12} is stronger than p_{23}. This result was already expected, in the light of the Landau-Zener formula (Eq. (25)), while observing the cuts reported in Figure 3, where the curves $2^1\Sigma^+$ and $3^1\Sigma^+$ are much closer in energy than the $3^1\Sigma^+$ and $4^1\Sigma^+$. With the adiabatic calculations for p_{12} and p_{23} (*i.e.* for δ_{12} and δ_{23}) we have thus obtained a quantitative estimate for this behaviour. Furthermore, the values of p_{12} and p_{23} are seen to vary from energies lower than the energies at the crossings (E_X = 11.37 eV for the 1–2 transition, E_X = 12.74 eV for the 2–3 transition) where they do not become zero as would have wrongly prescribed the Landau-Zener formula. In fact, in order to calculate the Stuckelberg-integral δ_s, we have used analytical formulae available for nonlinear potentials and for energies not only above the well bottom for the upper curve, E_b (Eq. (3.34) of Ref. [17d]), but also below the dissociation limit of the lowest curve, E_t, (Eq. (3.8) of Ref. [17d]) and between E_t and E_b (Eq. (3.23) of Ref. [17d]) (for each of these equations the two adiabatic parameters a^2 and b^2 are available in Ref. [17d]).

The p_{ij} behaviour in the crossing regions will become of crucial importance for the understanding the electronically inelastic cross-sections, provided that the exit channel corresponding to the process considered will be open, although the one-passage probability has no meaning at energies lower than the bottom of the upper adiabatic potential.

In order to obtain from the P_{ij}'s the nonadiabatic absorption cross-sections, we have followed the relation [24]

$$\sigma_{ij}(E) = \frac{\pi}{k_j^2(E,\infty)}|S_{ji}(E)|^2 = \frac{\pi}{k_j^2(E,\infty)}P_{ij}(E) \tag{40}$$

where

$$k_j(E,\infty) = \sqrt{\frac{2\mu}{\hbar^2}(E - V_j(\infty))} \tag{41}$$

and $V_j(\infty)$ is the asymptotic potential of the molecular fragmentation state j.

As already mentioned, the molecular fragments were found to be N_2^+ and H, with N_2^+ in its electronic states $1^2\Sigma_g^+$ (ground state), $1^2\Sigma_u^+$ and $2^2\Sigma_u^+$. These asymptotic states start to be open at energies of 7.29 eV, 9.00 eV and 15.13 eV respectively, while the one-passage probabilities (see Fig. 4b) become zero for energies lower than $\simeq$ 10 eV.

In Figure 5 we have reported the results for the state-selected, electronically inelastic absorption cross-sections, obtained from equation (40) with $i = 1$ ($2^1\Sigma^+$; Fig. 5a), $i = 2$ ($3^1\Sigma^+$; Fig. 5b) and $i = 3$ ($4^1\Sigma^+$; Fig. 5c) as the initial states involved in the fragmentation.

For each initial state i where the system is found after the photon absorption, the calculated cross-sections are seen to differ by a factor of almost 10 between the state i and the state $i + 1$. For each initial state the calculated absorption lineshapes show a stronger peak when the final state of the fragmentation is $2^2\Sigma_u^+$(state 3: see Figs. 5a, 5b), while nonadiabatic fragmentations bringing the system to the other two states turns out to be much more broadened.

We have not reported the results for the nonadiabatic cross-section σ_{31}, that is systematically zero at every energy: according to the theory, in fact, there is no way for the system to dissociate back into the first electronic state

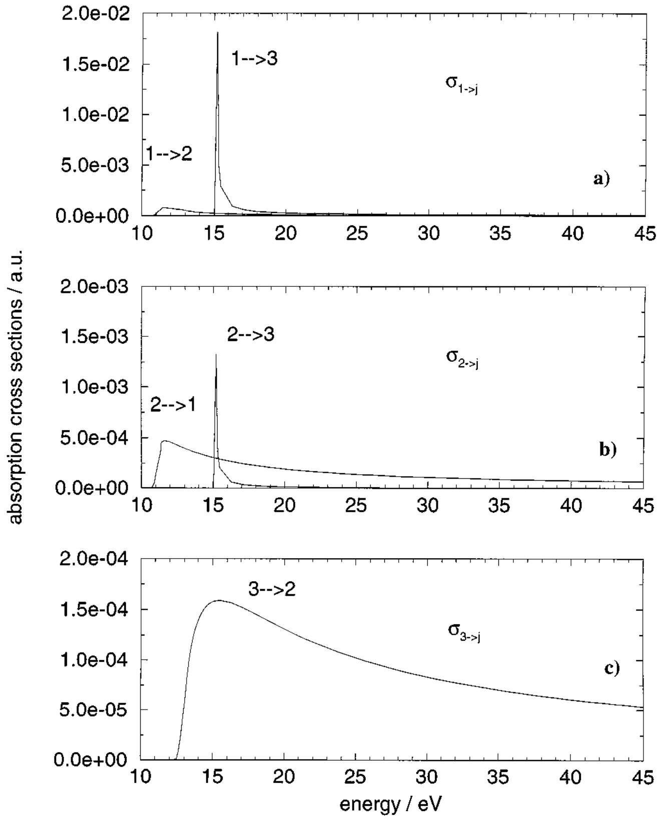

Fig. 5. Nonadiabatic fragmentation cross sections for the three asymptotic channels $2^1\Sigma^+$ (a), $3^1\Sigma^+$ (b) and $4^1\Sigma^+$ (c), as obtained from the half-collision matrix semiclassical calculations discussed in the main text. See there for the meaning of all symbols.

once has been excited to the third, because the avoided crossing between the curves 1 and 2 is at smaller R values with respect to the one between the 2 and 3 electronic states.

The occurrence of a maximum in each nonadiabatic cross-section depends on the behaviour of the one-passage probabilities from which the P_{ij}'s in equation (40) originate, and it is expected to exhibit some structure in the total absorption cross section whenever one is considering the off-diagonal contributions that we have calculated in the present treatment.

Finally, one should mention also the fact that we are currently analyzing the present process using a time-dependent-wave-packet (TDWP) approach [39]. In that case, however, the inclusion of nonadiabatic effects into the evolution of the wavepacket creates additional, and non-trivial, numerical problems which are avoided by the present treatment.

5 Conclusion

Dissociation of N_2H^+ after photoexcitation can be an interesting test for the applicability of the semiclassical theory to the study of molecular fragmentations involving several electronic energy surfaces that are coupled during the dynamics.

For this exploratory study we have included in the N_2H^+ fragmentation dynamics three electronic coupled channels, which are the three lowest $^1\Sigma^+$ excited surfaces of the system, and we have computed a 3-states half-collision S-matrix. For each matrix-element we have calculated the probability factors at the crossings and the right phases, the adiabatic ones as well as those arising from the crossings. The calculations were done in the spirit of the path-integral formulation, by using the analytical formulae [17] for the Stuckelberg integral.

The dependence of the nonadiabatic cross-sections on the photon energies has been examined, and it was found that peaks in the partial cross sections indeed arise at energies near the crossings. This is a direct consequence of the occurrence of a nonadiabatic transition in the region of an avoided crossing between two surfaces.

These calculations were aimed at treating an electronic *multichannel* problem: we have considered contemporarily *three* electronic states being coupled during the dynamics, by using the semiclassical idea of decomposing an overall event into a sequence of simpler two-state events. A possible way to improve on the present treatment would be provided by including in the calculations the multidimensionality of the problem (r and θ dependence), and by correctly evaluating the dipole-moment integrals appearing in the expression of the cross-sections within the half-collision approximation. The present results, on the other hand, are already capable of giving us some specific predictions on the selective population of different final electronic states of the charge-transfer products (N_2^{+*}) depending on the energy involved during the photon absorption. Although it still remains to analyze more in detail the possible effects of nonlinear initial ions and vibrationally "hot" initial ions on the final fragment populations, the present study is already allowing us to link the features of a realistic set of electronic potential energy surfaces with the possible outcome of the photofragmentation process by using a semiclassical, time-independent treatment of the physics involved.

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