

Multichannel dissociative recombination theory*

C. M. Lee[†]

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 7 July 1976; revised manuscript received 7 February 1977)

A theoretical multichannel treatment of dissociative recombination is presented, with application to $e + \text{NO}^+$ recombination. The conventional "indirect" and "direct" dissociative recombinations are treated together on the same footing. The physically meaningful eigenchannel parameters in the multichannel theory, for the NO system, are here determined by fitting to a wealth of spectroscopic data. The results are then compared with some previous theoretical predictions as well as recent experimental data, and a possible reconciliation is suggested for the discrepancy in the $(e + \text{NO}^+)$ recombination rates given by afterglow and stored-ion measurements.

I. INTRODUCTION

A unified treatment of perturbed series, continuous spectra, and collisions was recently reviewed by Fano,¹ who has summarized various applications to systems with quite different characteristics, such as diatomic molecules, neutral atoms, and negative atomic ions. The spectra of neutral diatomic molecular systems in the vicinity of ionization thresholds, mostly in the uv, usually contain discrete levels, autoionizing levels, and adjoining continua. The discrete levels and the autoionizing levels form Rydberg series which converge to different ionization thresholds, perturb each other strongly, and may also predissociate.

A traditional treatment of these levels via configurations and configuration mixing becomes formidable because of an infinite number of configurations involved here. It becomes appropriate to treat these levels from the point of view of collisions and thus to regard an excited or ionized diatomic molecule as consisting of a probing electron and a molecular ionic core which interact over a range of distances.

At large distances (i.e., the distance between the electron and the molecular ion is much larger than the distance between the two atoms of the molecule), the interactions between the probing electron and the molecular ion can be adequately described by a Coulombic potential. On the other hand, at small distances (i.e., within a reaction zone), the electron and the molecular ion form a complex through which both energy and angular momentum can be exchanged, and dissociations into two neutral atoms may occur.

From the point of view of collisions, the word "channel" here indicates a set of states consisting of a probing electron of arbitrary energy and of a target ion in a specified energy level, identifying a specification of the angular momenta of the elec-

tron and the molecular ion, and of their coupling. Therefore, wave functions of such an excited or ionized molecule can, in general, be expressed as superpositions of various channel functions. Particular sets of such superpositions are called eigenchannels. Outside the reaction zone (i.e., configuration space where either the probing electron is apart from the molecular ion or the two neutral atoms of the molecule dissociate apart), the eigenchannel wave functions can be written analytically through the eigenchannel parameters, which lump the dynamics of the "electron + molecular ion" complex within the reaction zone and thus serve as boundary parameters on the boundary of the reaction zone. At any energy within the range of interest, the energy eigenfunction is then expressed as a linear combination of the eigenchannel functions. For the Rydberg states, the level positions are determined analytically by imposing the appropriate boundary conditions at infinity. Here, the traditional treatment of the levels via configurations and configuration mixing is then replaced by the treatment via channels and channel mixing. Such treatment of Rydberg series as a whole permits further extension of its analysis, by extrapolating the properties of the series beyond the ionization limits to adjoining continua. Therefore such extension allows us to examine various low-energy collision processes between the electron and the ion. To calculate dissociative recombination of diatomic molecular ions with low-energy electrons is the main subject of the present paper.

Dissociative recombination of diatomic molecular ions with electrons is of high interest because of the importance of the processes in many regions of Earth's ionosphere² (i.e., the so-called *D*, *E*, and *F* regions). In this paper, we will apply the multichannel treatment to dissociative recombination of NO^+ ions with electrons since some recent theoretical calculations³⁻⁵ have yielded rather dif-

ferent predictions, and some recent experimental measurements⁶⁻⁸ (an afterglow measurement⁷ and a measurement by the stored-ion technique⁸) have also given quite different electron temperature dependences of the recombination rate.

In Sec. II, we will first present the multichannel treatment, specifically applied to the dissociative recombination process. We will then present, in Sec. III, our calculations of dissociative recombination of NO⁺ ions in X¹Σ⁺ ($\bar{\nu}=0$ and 1) with low-energy electrons. Our calculations are carried out by utilizing the wealth of spectroscopic data on NO systems which have been studied extensively by Miesher and his colleagues.⁹⁻¹⁵ In our calculations, we perform partial-wave expansions up to the d wave of the incident electron and include the effect of the four dissociative states, i.e., B'²Δ, B²Π, I²Σ⁺, and A'²Σ⁺. The dissociative state L²Π is neglected here, but may become important for dissociative recombination of NO⁺ ions in higher vibrational states with higher-energy electrons. We also make comparisons with the previous theoretical predictions³⁻⁵ and the experimental data.^{7,8} A possible reconciliation of the apparent discrepancy in the afterglow and stored-ion measurements⁸ is suggested. Based on the calculations, we also estimate the branching ratio leading to the excited nitrogen atoms N(²D) by dissociative recombination of NO⁺ ions with thermal electrons. Finally, in Sec. IV, we make some concluding remarks.

II. MULTICHANNEL TREATMENT

We consider a low-energy electron colliding with a diatomic molecular ion in a state $\bar{x}\bar{\nu}\bar{K}(\bar{\Lambda}\bar{\eta}\bar{S})$. The angular momentum coupling of the molecular ion is described in Hund's coupling case (b),¹⁶ which is usually appropriate for light molecules because of negligible spin-orbital coupling interactions. Here $\bar{\Lambda}$ represents the absolute value of the component of the electronic orbital angular momentum along the internuclear axis of the molecular ion, \bar{S} the total electron spin, $\bar{\eta}$ the parity quantum number,¹⁷ \bar{K} the total orbital angular momentum, $\bar{\nu}$ the vibrational quantum number, and \bar{x} refers to the electronic state of the molecular ion (e.g., X¹Σ⁺, a³Σ⁺, . . . , etc. for NO⁺). First let us examine some characteristics of this "electron+molecular ion" system; as the incident electron penetrates the molecular ion, i.e., within the reaction zone, the incident electron and the molecular ion form an excited molecular complex as a whole, and many-body interactions prevail, such as electron-electron correlations and interactions between various internal degrees of freedom (e.g., vibronic). The size of the reaction zone may be esti-

mated as $r \leq r_0 = 20-30$ a.u., where r is the distance between the incident electron and the molecular ion (incidently, the r_0 for atomic systems is usually smaller¹⁸ and the r_0 for negative-ion complexes may be much larger). Moreover, any specific estimation of the reaction-zone size here will not affect all the later arguments because the asymptotic boundary conditions are imposed analytically at infinity (as discussed later) in terms of the physically meaningful eigenchannel parameters, which lump all dynamics within the reaction zone. The exact size of the reaction zone would only be relevant to the calculational efforts in any first-principles determination of these eigenchannel parameters.

Here we will first discuss the excited complex without taking into account the effect of dissociation of the complex into two neutral atoms, and we will return to consider the effect later. As the incident electron is outside the reaction zone, the interactions between the electron and the ion can be adequately described by the corresponding Coulombic potential. Such an "electron+molecular ion" system is characterized asymptotically by various combinations of the electron of an orbital energy and the ion in a specified energy level, specifying the angular momenta of the electron and the ion, and their coupling. Each of the combinations identifies one possible mode of dissociation of the systems into the electron and the molecular ion, and is therefore called a *dissociation channel* (to prevent confusion with dissociation of the molecule into two neutral atoms, we will refer to them as *i channels* later). A stationary *i*-channel wave function in the laboratory frame, *outside the reaction zone* and with a total angular momentum K and a total electron spin S , can then be written as an antisymmetrized-product-type function of the molecular ion in the state $\bar{x}\bar{\nu}\bar{K}(\bar{\Lambda}\bar{\eta}\bar{S})$ and the electron with an orbital angular momentum l and an orbital energy $\epsilon_{\bar{x}\bar{\nu}\bar{K}}$:

$$\psi_{KM}^i = \mathcal{Q} \phi_{KM}^i [c_i f_i(r, \epsilon_{\bar{x}\bar{\nu}\bar{K}}) - d_i g_i(r, \epsilon_{\bar{x}\bar{\nu}\bar{K}})], \quad (1)$$

outside the reaction zone and with

$$\begin{aligned} \phi_{KM}^i &= \phi_{KM}^{\bar{x}\bar{\nu}\bar{K}(\bar{\Lambda}\bar{\eta}\bar{S})S l} \\ &= \sum_m Y_{lm}(\theta, \phi) [\omega_{\bar{\Lambda}}^{\bar{x}\bar{\nu}\bar{S}, S} D_{\bar{\Lambda}, M-m}^{\bar{K}}(\theta, \Phi) \\ &\quad + \bar{\eta} \omega_{-\bar{\Lambda}}^{\bar{x}\bar{\nu}\bar{S}, S} D_{-\bar{\Lambda}, M-m}^{\bar{K}}(\theta, \Phi)] \\ &\quad \times \left(\frac{2K+1}{8(1+\delta_{\bar{\Lambda}0})} \right)^{1/2} (lm, \bar{K}M - m | l\bar{K}KM), \quad (2) \end{aligned}$$

where \mathcal{Q} refers to antisymmetrization, $\delta_{\bar{\Lambda}0}$ the Kronecker delta, and $(lm, \bar{K}M - m | l\bar{K}KM)$ the Clebsch-Gordan coefficient. Here ϕ_{KM}^i is a combined wave function of the electronic vibrational rota-

tional wave function of the molecular ion and the spin, angular wave function of the electron, $Y_{lm}(\theta, \phi)$ is the angular component of the incident-electron wave function in the laboratory frame, $\bar{\omega}$ is a combined wave function of the electronic vibrational wave function of the molecular ion and the incident-electron spin function together with a total electron spin S (with the convention $\omega_{\bar{S}} = \eta\omega_{-\bar{S}}$ for $\bar{\Lambda} = 0$), and D is the rotational wave function of the molecular ion. Outside the reaction zone, the radial component of the incident-electron wave function in the i channel can be expressed analytically as a linear combination of the regular and irregular stationary Coulombic wave functions f and g as shown in Eq. (1). The regular and irregular stationary Coulombic wave functions, $f_i(r, \epsilon_{\bar{x}\bar{v}\bar{K}})$ and $g_i(r, \epsilon_{\bar{x}\bar{v}\bar{K}})$, have known analytical properties^{19,20} and are smooth functions of the orbital energy $\epsilon_{\bar{x}\bar{v}\bar{K}}$ across the threshold $\epsilon_{\bar{x}\bar{v}\bar{K}} = 0$. We will adopt atomic units throughout this paper and will take the total energy of the molecular ion in its ground state [e.g., $X^1\Sigma^+(\bar{v}=0, \bar{K}=0)$, for NO^+] as a reference zero energy. Thus a total energy ϵ of the "electron+molecular ion" system is

$$\epsilon = E_{\bar{x}\bar{v}\bar{K}} + \epsilon_{\bar{x}\bar{v}\bar{K}}, \quad (3)$$

with

$$\epsilon_{\bar{x}\bar{v}\bar{K}} = -1/2\nu_{\bar{x}\bar{v}\bar{K}}^2. \quad (4)$$

Here $E_{\bar{x}\bar{v}\bar{K}}$ is the excitation energy of the molecular ion from its ground state to a state $\bar{x}\bar{v}\bar{K}$, and $\epsilon_{\bar{x}\bar{v}\bar{K}}$ is the orbital energy of the electron in the i channel with the molecular ion in the state $\bar{x}\bar{v}\bar{K}$. The energy parameter $\nu_{\bar{x}\bar{v}\bar{K}}$ is a positive real number for a closed i channel, and it is a pure imaginary number (i.e., $\nu_{\bar{x}\bar{v}\bar{K}} = i/k_{\bar{x}\bar{v}\bar{K}}$) for an open i channel.

With a total orbital angular momentum K and a total electron spin S , a stationary wave function of the "electron+molecular ion" system, outside the reaction zone, can generally be expressed as superpositions of these i -channel functions. Applying the multichannel quantum-defect theory,²⁰ one can define and construct eigenchannels α which serve as an appropriate basis to describe the dynamical characteristics of the "electron+molecular ion" complex within the reaction zone. These eigenchannel wave functions, *within the reaction zone*, vary only weakly with the total energy ϵ . Outside the reaction zone, the eigenchannel wave functions, $\psi_{\alpha, KM}$ with the total angular momentum K and the total electron spin S , can be written analytically as particular superpositions of the i -channel wave functions,

$$\psi_{\alpha, KM} = \mathcal{G} \sum_i \phi_{KM}^i U_{i\alpha} (f_i \cos \pi \mu_\alpha - g_i \sin \pi \mu_\alpha), \quad (5)$$

with the eigenchannel parameters, transformation

matrix $U_{i\alpha}$, and eigen-quantum-defects μ_α . These eigenchannel parameters serve as boundary-condition parameters over the reaction zone boundary¹⁸ and also vary smoothly with the total energy ϵ . So far, we have deliberately not discussed the effects of dissociation of the molecular complex into atoms simply for convenience; we will return to treat such effects later. At any total energy ϵ of the "electron+molecular ion" system, the energy eigenfunction is then constructed as a linear combination of the α -channel wave functions

$$\begin{aligned} \Psi_{KM} &= \sum_\alpha \psi_{\alpha, KM} A_\alpha \\ &= \mathcal{G} \sum_\alpha \sum_i \phi_{KM}^i U_{i\alpha} (f_i \cos \pi \mu_\alpha - g_i \sin \pi \mu_\alpha) A_\alpha, \end{aligned} \quad (6)$$

outside the reaction zone and with the mixing coefficients A_α independent of M , which are determined analytically by imposing various appropriate asymptotic boundary conditions at $r = \infty$.^{18,20} These asymptotic boundary conditions are different in various regions of the spectrum, i.e., discrete, autoionization, and continuum regions. We will discuss in detail how to impose these asymptotic boundary conditions for the purpose of the calculation of the "indirect" and "direct" dissociative recombination cross sections, which correspond to the autoionization and the open-continuum regions of the spectrum.

We adopt here the laboratory-frame representation in Eq. (1). It is known¹⁷ that there exists an orthogonal transformation between the laboratory-frame representation and the molecular-body-frame representation, i.e.,

$$\begin{aligned} \phi_{KM}^i &\equiv \phi_{KM}^{\bar{x}\bar{v}\bar{K}(\bar{\Lambda}\bar{\eta}\bar{S})S^i} \\ &= \sum_{\lambda\lambda'} U_{(\Lambda\lambda)}^{\bar{K}\bar{\eta}} X_{KM}^{\bar{x}\bar{v}\bar{K}(\Lambda\lambda)\bar{\eta}\bar{S}S^i} \end{aligned} \quad (7)$$

with

$$\bar{U}_{(\Lambda\lambda)}^{\bar{K}\bar{\eta}} = (-)^{K+\lambda-\bar{K}} (l-\lambda, K\lambda+\bar{\Lambda} | lK\bar{K}) [1 + \eta\bar{\eta}(-)^{K-l-\bar{K}}] / 2. \quad (8)$$

Here $X_{KM}^{\bar{\alpha}} \equiv X_{\bar{x}\bar{v}\bar{K}(\Lambda\lambda)\bar{\eta}\bar{S}S^i}^{\bar{x}\bar{v}\bar{K}(\Lambda\lambda)\bar{\eta}\bar{S}S^i}$ is a combined wave function¹⁷ in the molecular-body frame, which is defined in a similar manner as the wave function ϕ_{KM}^i ; $\Lambda = |\bar{\Lambda} + \lambda|$ and $\eta = \bar{\eta}(-)^{K-l-\bar{K}}$ are the corresponding quantum number of the "electron+molecular ion" as a whole. The λ is the projection of the incident-electron orbital angular momentum along the molecular axis. Let us adopt the collective indices, $i \equiv \{\bar{x}\bar{v}\bar{K}(\bar{\Lambda}\bar{\eta}\bar{S})S^i\}$ and $\alpha \equiv \{\bar{x}'\bar{v}'\bar{\Lambda}'(\Lambda\lambda)\bar{\eta}\bar{S}'S'^i\}$, and we can define the transformation matrix \bar{U} from the laboratory frame to the molecular-body frame as $\bar{U}_{\alpha}^i = \bar{U}_{(\Lambda\lambda)\bar{\eta}}^{\bar{K}\bar{\eta}} \delta_{\bar{x}\bar{x}'} \delta_{\bar{v}\bar{v}'} \delta_{\bar{\Lambda}\bar{\Lambda}'} \delta_{\bar{\eta}\bar{\eta}'} \delta_{\bar{S}\bar{S}'} \delta_{\bar{S}\bar{S}'} \delta_{i i'}$, which is diagonal with respect to the quantum numbers

\bar{x} , \bar{v} , \bar{A} , \bar{S} , S , and l . Thus, Eq. (6) can also be written in the molecular-body-frame representation,

$$\Psi_{KM} = G \sum_{\alpha} \sum_{\bar{\alpha}} \sum_i X_{KM}^{\bar{\alpha}} \bar{U}_{\bar{\alpha}}^i U_{i\alpha} \times (f_i \cos \pi \mu_{\alpha} - g_i \sin \pi \mu_{\alpha}) A_{\alpha}, \quad (9)$$

outside the reaction zone.

If we are only interested in the overall structures due to vibrations, and we will ignore the rotational structures (equivalent to having insufficient energy resolution to distinguish the rotational structures), the radial component of the electron wave function in Eq. (9), $(f_i \cos \pi \mu_{\alpha} - g_i \sin \pi \mu_{\alpha})$, is the same for the molecular ion in the state $\bar{x}\bar{v}$ (with different \bar{K} 's) and then can be factored out in the summation of Eq. (9). Therefore, Eq. (9) reduces to

$$\Psi_{KM} = G \sum_{\alpha} \sum_{\bar{\alpha}} X_{KM}^{\bar{\alpha}} U_{\bar{\alpha}\alpha}^m \times [f_{\bar{\alpha}}(\bar{r}) \cos \pi \mu_{\alpha} - g_{\bar{\alpha}} \sin \pi \mu_{\alpha}] A_{\alpha}, \quad (10)$$

outside the reaction zone and with

$$U_{\bar{\alpha}\alpha}^m = \sum_i \bar{U}_{\bar{\alpha}}^i U_{i\alpha}. \quad (11)$$

The eigenchannel parameters, $U_{\bar{\alpha}\alpha}^m$ and μ_{α} , then serve as a concise quantitative representation of vibronic interactions of the "electron+molecular ion" complex within the reaction zone. These parameters are generally smoothly varying functions of energy and have negligible K dependence for our present purpose (i.e., to ignore the rotational structure). Therefore we will omit the subscript K later on.

A. Eigenchannels including the effects of the molecular dissociative channels

After we have introduced the eigenchannels α which characterize the dynamics of the "electron + molecular ion" complex within the reaction zone, we will then return to the effects of additional channels of dissociation of the molecular complex into atoms. These molecular dissociative states are usually non-Rydberg states of the molecule. The molecular dissociative wave function is written, in the Born-Oppenheimer separation, as a product of electronic and nuclear terms:

$$\Phi_d = \Phi_d F_d(R). \quad (12)$$

The Φ_d is the combined wave function of the electronic wave function of the molecular dissociative state and the angular wave function of the nuclear term. $F_d(R)$ is the corresponding radial wave func-

tion of the relative motion of the atomic nuclei, which is normalized per unit energy range (in a.u.), i.e.,

$$F_d(R) \overset{R \rightarrow \infty}{\sim} (M/2K_d)^{1/2} \sin(K_d R + \delta_d) \quad (13)$$

with

$$K_d^2/2M = \epsilon + E_d. \quad (14)$$

M is the reduced mass of the atomic nuclei in atomic units and E_d is the energy difference between the ground state of the molecular ion and the molecular dissociation limit. δ_d is a phase shift including the phase shift due to the centrifugal potential. If the molecular dissociative state has a repulsive potential curve, the molecular dissociative channel consists only of the continuum spectrum. If the molecular dissociative potential curve can support the existence of vibration states, the molecular dissociative channel then consists of the continuum and the discrete spectrum. In this paper, we will neglect the couplings among the nuclear wave functions in the various dissociative electronic states during dissociation, which will greatly affect predictions of the branching ratios. However, to neglect the couplings will not affect the result of the total cross section, since the effect of the couplings during dissociation can be regarded as a unitary transformation of the amplitude vector of the relevant nuclear wave functions, and then results in only a redistribution of the partial contributions to the total cross section. We will return to discuss it in Sec. III when we attempt to estimate the branching ratio leading to the excited nitrogen atoms $N(^2D)$ by dissociative recombination of the NO^+ ions with thermal electrons. In this paper, we will treat a nontrivial simple case in which, with a specific symmetry, all the eigenchannels α mix individually with only one molecular dissociative channel (it is adequate for our later application in Sec. III). Such mixings result from interchannel interactions which can be classified as one type of configuration interaction.²¹ An important domain in the configuration space for the interchannel interaction matrix elements is within the reaction zone, where the definition of the reaction zone is implicitly extending to include the space for the relative motion of the atomic nuclei. In a perturbation treatment as shown in the Appendix, the eigenchannel wave functions, after taking into account the effect of the molecular dissociation, have the following forms:

$$\psi_{\alpha}^1 = \frac{1}{(1 + \xi_{\alpha,d}^2)^{1/2}} G \sum_{\bar{\alpha}} X_{\bar{\alpha}} U_{\bar{\alpha}\alpha}^m (f_{\bar{\alpha}} \cos \pi \mu_{\alpha} - g_{\bar{\alpha}} \sin \pi \mu_{\alpha}) + \frac{\xi_{\alpha,d}}{(1 + \xi_{\alpha,d}^2)^{1/2}} \phi_d G_d(R), \quad (15a)$$

$$\begin{aligned} \psi_\alpha^2 &= \frac{\xi_{\alpha,d}}{(1+\xi_{\alpha,d}^2)^{1/2}} \mathcal{Q} \\ &\times \sum_{\bar{\alpha}} X_{\bar{\alpha}} U_{\alpha\bar{\alpha}}^m (g_{\bar{\alpha}} \cos \pi \mu_\alpha - f_{\bar{\alpha}} \sin \pi \mu_\alpha) \\ &+ \frac{1}{(1+\xi_{\alpha,d}^2)^{1/2}} \phi_d F_d(R), \end{aligned} \quad (15b)$$

outside the reaction zone, where the radial wave functions, $G_d(R)$ and $F_d(R)$, have the following asymptotic forms $-(2M/\pi K)^{1/2} \cos(\dots)$ and $(2M/\pi K)^{1/2} \sin(\dots)$, respectively. The mixing parameter $\xi_{\alpha,d}$ is

$$\begin{aligned} \xi_{\alpha,d} &\approx \pi \langle \psi_\alpha(\epsilon) | V_{\text{int}} | \Phi_d(\epsilon) \rangle \\ &\approx \pi H_{\alpha,d}^{\text{el}} f_{\alpha,d}. \end{aligned} \quad (16)$$

$H_{\alpha,d}^{\text{el}}$ is the electronic interaction matrix element which varies smoothly with the energy ϵ , and $f_{\alpha,d}$ is the Frank-Condon factor which can be calculated approximately as the overlap integral between the molecular-ion vibrational wave function and the molecular dissociative radial wave function $F_d(R)$. The energy eigenfunction of the "electron + molecular ion" system at an energy ϵ is then constructed as a linear combination of the eigenchannel wave functions,

$$\begin{aligned} \Psi(\epsilon) &= \sum_{\alpha} \psi_\alpha^1 A_{\alpha,1} + \sum_{\alpha} \psi_\alpha^2 A_{\alpha,2} \\ &= \sum_{\alpha} \sum_{\bar{\alpha}} \frac{1}{(1+\xi_{\alpha,d}^2)^{1/2}} \{ [\mathcal{Q} X_{\bar{\alpha}} U_{\alpha\bar{\alpha}}^m (f_{\bar{\alpha}} \cos \pi \mu_\alpha - g_{\bar{\alpha}} \sin \pi \mu_\alpha) + \xi_{\alpha,d} \phi_d G_d] A_{\alpha,1} \\ &\quad + [\xi_{\alpha,d} \mathcal{Q} X_{\bar{\alpha}} U_{\alpha\bar{\alpha}}^m (g_{\bar{\alpha}} \cos \pi \mu_\alpha + f_{\bar{\alpha}} \sin \pi \mu_\alpha) + \phi_d F_d] A_{\alpha,2} \}, \end{aligned} \quad (17)$$

outside the reaction zone. The mixing coefficients, $A_{\alpha,1}$ and $A_{\alpha,2}$, are determined analytically by imposing the appropriate asymptotic boundary conditions at $r \rightarrow \infty$. We will discuss this in detail later.

B. How to determine the eigenchannel parameters

The eigenchannel parameters may be obtained by first-principles calculations, formulating the Schrödinger equation in a finite volume as an eigenvalue problem for the boundary values of the wave function.²² So far, a pilot eigenchannel calculation directly aiming at the eigenchannel parameters has been carried out only for the "electron + atomic ion" system.¹⁸ Such an eigenchannel calculation for the molecular system remains to be demonstrated. On the other hand, these eigenchannel parameters can be extracted semiempirically by fitting to the spectroscopic data. These two methods complement each other; either may be pursued, but their judicious combination might prove most effective. For our application in Sec. III, the eigenchannel parameters are determined by the semiempirical method.

From absorption and emission spectra, bound states of the "electron + molecular ion" system can be identified. The excited states of the diatomic molecule may be classified as Rydberg states and non-Rydberg states. Rydberg series usually converge to various ionization thresholds corresponding to various states of the molecular ion and perturb each other. Rydberg series may also be perturbed by non-Rydberg states, which may lead to the molecular dissociations into atoms. We will

first utilize the data of the "deperturbed" energy levels⁹⁻¹³ of Rydberg series to determine the eigenchannel parameters, $U_{\bar{\alpha}\alpha}^m$ and μ_α . For a Rydberg state [e.g., $A^2\Sigma^+(\nu=0)$ for NO], the "deperturbed" level energy, with reference to the energy of the ground state of the molecular ion, is parametrized by Eq. (3) which reduces to

$$\epsilon_n = E_{\bar{\alpha}} - 1/2\nu_{\bar{\alpha},n}^2 \quad \text{for all } \bar{\alpha}, \quad (18)$$

since we here ignore rotational structures. The $E_{\bar{\alpha}} = E_{\bar{x}\bar{v}}$ is the excitation energy of the molecular ion in the electronic state \bar{x} and the vibrational state \bar{v} for the $\bar{\alpha}$ channel. Thus, each energy ϵ_n is represented by a set of numbers $\{\nu_{\bar{\alpha},n}\}$, where the number of the different $\nu_{\bar{\alpha},n}$ in each set equals the number of molecular ion states $\bar{x}\bar{v}$ involved. The asymptotic boundary conditions of the energy eigenfunction of the "deperturbed" Rydberg state, that is, $\Psi_n \rightarrow 0$ as $r \rightarrow \infty$, leads to¹⁸

$$F(\{\nu_{\bar{\alpha},n}\}, \{\mu_\alpha, U_{\bar{\alpha}\alpha}^m\}) = \det | U_{\bar{\alpha}\alpha}^m \sin(\nu_{\bar{\alpha},n} + \mu_\alpha) | = 0. \quad (19)$$

For a set of the available "deperturbed" Rydberg-level energies $\{\epsilon_n; n=1, \dots, N\}$, the eigenchannel parameters, μ_α and $U_{\bar{\alpha}\alpha}^m$, are then determined by numerical fitting such that the sum

$$S = \sum_{n=1}^N [F(\{\nu_{\bar{\alpha},n}\}, \{U_{\bar{\alpha}\alpha}^m, \mu_\alpha\})]^2 \quad (20)$$

is minimized.

For the mixing parameters $\xi_{\alpha,d} = H_{\alpha,d}^{\text{el}} f_{\alpha,d}$, the electronic term $H_{\alpha,d}^{\text{el}}$ can be obtained by spectroscopic analysis of the Rydberg-non-Rydberg per-

turbations. The Frank-Condon factors $f_{\alpha,d}$ are then calculated based on the potential curves for the molecular-ion electronic state and the non-Rydberg dissociative states of the molecule, which are usually determined either by spectroscopic analysis or by first-principles calculations.

C. Dissociative recombination cross section

We will calculate the dissociative recombination cross sections in terms of these eigenchannel parameters.

1. Direct dissociative recombination

The direct dissociative recombination in conventional language³ refers to the process in which the incident electron is captured by the molecular ion directly to form an autoionizing dissociative state of the molecule. However, in the multichannel treatment, it is a matter of the energy range of interest; specifically, the conventional direct dissociative recombination corresponds to the energy range in which all the relevant $\bar{\alpha}$ channels are open, namely,

$$\epsilon = E_{\bar{\alpha}} + \frac{1}{2}k_{\bar{\alpha}}^2 \quad \text{for all } \bar{\alpha}. \quad (21)$$

In order to calculate the reaction cross section from any specified incoming channel $\bar{\beta}$, the mixing coefficients $A_{\alpha,1}^{(\bar{\beta}+)}$ and $A_{\alpha,2}^{(\bar{\beta}+)}$ in Eq. (17) are determined by requiring that the amplitudes of all the incoming electron waves vanish in all channels $\bar{\alpha} \neq \bar{\beta}$ and that the amplitude of the incoming wave in the molecular dissociative state also vanish:

$$\sum_{\alpha} \left(\frac{1}{(1+\xi_{\alpha,d}^2)^{1/2}} U_{\alpha\alpha}^m A_{\alpha,1}^{(\bar{\beta}+)} + \frac{i\xi_{\alpha,d}}{(1+\xi_{\alpha,d}^2)^{1/2}} U_{\alpha\alpha}^m A_{\alpha,2}^{(\bar{\beta}+)} \right) = \delta_{\bar{\alpha}\bar{\beta}} e^{i\sigma_{\bar{\beta}}}, \quad (22)$$

$$\sum_{\alpha} \left(\frac{i\xi_{\alpha,d}}{(1+\xi_{\alpha,d}^2)^{1/2}} A_{\alpha,1}^{(\bar{\beta}+)} + \frac{1}{(1+\xi_{\alpha,d}^2)^{1/2}} A_{\alpha,2}^{(\bar{\beta}+)} \right) = 0 \quad \text{for all } \bar{\beta}, \quad (23)$$

where $\sigma_{\bar{\beta}}$ is the Coulomb phase shift in the $\bar{\beta}$ channel, i.e., $\sigma_{\bar{\beta}} = \arg[\tau(l_{\bar{\beta}} + 1 - i/k_{\bar{\beta}})]$. The desired mixing coefficients are

$$A_{\alpha,1}^{(\bar{\beta}+)} = \frac{e^{i\sigma_{\bar{\beta}}} U_{\bar{\beta}\alpha}^m e^{i\pi\mu_{\alpha}}}{(1+\xi_{\alpha,d}^2)^{1/2}}$$

and

$$A_{\alpha,2}^{(\bar{\beta}+)} = (-i) \frac{e^{i\sigma_{\bar{\beta}}} U_{\bar{\beta}\alpha}^m \xi_{\alpha,d} e^{i\pi\mu_{\alpha}}}{(1+\xi_{\alpha,d}^2)^{1/2}}. \quad (24)$$

Thus, the scattering matrix for dissociative recombination from the $\bar{\beta}$ channel is

$$S_{\bar{\beta},d} = (-i) \sum_{\alpha} \frac{\xi_{\alpha,d}}{(1+\xi_{\alpha,d}^2)^{1/2}} A_{\alpha,1}^{(\bar{\beta}+)} e^{i\theta_{\alpha}} + \sum_{\alpha} \frac{1}{(1+\xi_{\alpha,d}^2)^{1/2}} A_{\alpha,2}^{(\bar{\beta}+)} e^{i\theta_{\alpha}} = -e^{i\sigma_{\bar{\beta}}} \left(\sum_{\alpha} \frac{2i\xi_{\alpha,d}}{(1+\xi_{\alpha,d}^2)} U_{\bar{\beta}\alpha}^m e^{i\pi\mu_{\alpha}} \right) e^{i\theta_{\alpha}}. \quad (25)$$

Let $P_{\bar{x}\bar{v}}$ denote a set of the relevant channels $\bar{\beta}$ corresponding to a specific state $\bar{x}\bar{v}$ of the molecular ion [e.g., $X^1\Sigma^+(\bar{v}=0)$ for NO^+]. The dissociative recombination cross section for the molecular ion in the state $\bar{x}\bar{v}$ then is

$$\sigma_{\bar{x}\bar{v}}^d = \frac{\pi}{k_{\bar{x}\bar{v}}^2} \sum_{\bar{\beta} \in P_{\bar{x}\bar{v}}} \frac{(2 - \delta_{\Lambda_{\bar{\beta},d}})(2S+1)}{2(2S+1)} |S_{\bar{\beta},d}|^2, \quad (26)$$

with the quantum numbers $\Lambda_{\bar{\beta}}$, S , and \bar{S} defined before.

2. Dissociative recombination in resonance region

The indirect dissociative recombination in the conventional language,³ refers to the process in which the incident electron is first captured via an autoionizing, vibrationally excited Rydberg state which predissociates. In the multichannel treatment, it is again a matter of the energy range of interest, i.e., the energy range in which some of the relevant $\bar{\alpha}$ channels are open and some are closed. We here treat the two mechanisms, viz., "direct" and "indirect" mechanisms, simultaneously as they should be in the energy range of interest. The sets of the open and closed channels will be denoted as P and Q , respectively. The energy ϵ of the "electron+molecular ion" system is then parametrized as

$$\begin{aligned} \epsilon &= E_{\bar{\alpha}} - 1/2\nu_{\bar{\alpha}}^2, \quad \bar{\alpha} \in Q \\ &= E_{\bar{\alpha}} + \frac{1}{2}k_{\bar{\alpha}}^2, \quad \bar{\alpha} \in P. \end{aligned} \quad (27)$$

We will first impose asymptotic boundary conditions for autoionization states, namely, that the components of an energy eigenfunction vanish at $r = \infty$ for the closed channels and that the components consist of Coulombic waves with a common phase shift $\pi\tau$ asymptotically for the open channels, and will obtain the collision eigenchannel functions, $\psi(\tau_1, \epsilon)$ and $\psi(\tau_2, \epsilon)$, which will be given in the following. For the collisional eigenchannel $\psi(\tau_1, \epsilon) = \sum_{\alpha} \psi_{\alpha}^1 A_{\alpha,1}$, the asymptotic boundary conditions lead to

$$\begin{aligned} \sum_{\alpha} \frac{U_{\bar{\alpha}\alpha}^m \sin\pi(-\tau_1 + \mu_{\alpha}) A_{\alpha,1}}{(1+\xi_{\alpha,d}^2)^{1/2}} &= 0, \quad \bar{\alpha} \in P, \\ \sum_{\alpha} \frac{U_{\bar{\alpha}\alpha}^m \sin\pi(\nu_{\bar{\alpha}} + \mu_{\alpha}) A_{\alpha,1}}{(1+\xi_{\alpha,d}^2)^{1/2}} &= 0, \quad \bar{\alpha} \in Q. \end{aligned} \quad (28)$$

Equation (28) has the compatibility condition for

the existence of nontrivial solutions, which is

$$F(\tau_1, \epsilon) = \det|F_{\bar{\alpha}\alpha}| = 0, \quad (29)$$

with

$$F_{\bar{\alpha}\alpha} = \begin{cases} U_{\bar{\alpha}\alpha}^m \sin\pi(-\tau_1 + \mu_\alpha), & \bar{\alpha} \in P \\ U_{\bar{\alpha}\alpha}^m \sin\pi(\nu_{\bar{\alpha}} + \mu_\alpha), & \bar{\alpha} \in Q. \end{cases} \quad (30)$$

At any specified energy ϵ , Eq. (29) has the roots denoted as $\{\tau_{\rho_1}\}$ where the number of roots exactly equals the number of all the open channels α in P . The corresponding solutions $A_{\alpha,1}^{\rho_1}$ of Eq. (28) for the τ_{ρ_1} are

$$\bar{A}_{\alpha,1}^{\rho_1} = \frac{A_{\alpha,1}^{\rho_1}}{(1 + X_{\alpha,d}^2)^{1/2}} = \frac{C_{\bar{\alpha}\alpha}(\tau_{\rho_1}, \epsilon)}{C_{\bar{\alpha}}}, \quad (31)$$

with

$$C_{\bar{\alpha}}^2 = \sum_{\alpha} [C_{\bar{\alpha}\alpha}(\tau_{\rho_1}, \epsilon)]^2. \quad (32)$$

The $C_{\bar{\alpha}\alpha}$ is the cofactor of the element $F_{\bar{\alpha}\alpha}$ of the determinant $\det|F_{\bar{\alpha}\alpha}|$, and the choice of $\bar{\alpha}$ is arbitrary. The collisional eigenchannel functions $\psi(\tau_{\rho_1}, \epsilon)$, after an appropriate normalization, then have the form

$$\begin{aligned} \psi(\tau_{\rho_1}, \epsilon) &= \frac{1}{(1 + X_{\rho_1,d}^2)^{1/2}} \mathcal{G} \\ &\times \sum_{\alpha \in P} X_{\bar{\alpha}} T_{\bar{\alpha}}^{\rho_1} f_{\bar{\alpha}} (\cos\pi\tau_{\rho_1} - g_{\bar{\alpha}} \sin\pi\tau_{\rho_1}) \\ &+ \frac{X_{\rho_1,d}}{(1 + X_{\rho_1,d}^2)^{1/2}} \phi_d G_d, \end{aligned} \quad (33)$$

outside the reaction zone with

$$T_{\bar{\alpha}}^{\rho_1} = \left(\sum_{\alpha} U_{\bar{\alpha}\alpha}^m \cos\pi(-\tau_{\rho_1} + \mu_\alpha) \bar{A}_{\alpha,1}^{\rho_1} \right) N_{\rho_1}^{-1}, \quad (34)$$

$$X_{\rho_1,d} = \left(\sum_{\alpha} \xi_{\alpha,d} \bar{A}_{\alpha,1}^{\rho_1} \right) N_{\rho_1}^{-1}, \quad (35)$$

$$N_{\rho_1}^2 = \sum_{\alpha \in P} \left(\sum_{\alpha} U_{\bar{\alpha}\alpha}^m \cos\pi(-\tau_{\rho_1} + \mu_\alpha) \bar{A}_{\alpha,1}^{\rho_1} \right)^2. \quad (36)$$

In a similar manner, for the collision eigenchannels $\psi(\tau_2, \epsilon) = \sum_{\alpha} \psi_{\bar{\alpha}}^2 A_{\alpha,2}$, the asymptotic boundary condition leads to

$$\sum_{\alpha} \frac{U_{\bar{\alpha}\alpha}^m \cos\pi(-\tau_2 + \mu_\alpha) \xi_{\alpha,d} A_{\alpha,2}}{(1 + \xi_{\alpha,d}^2)^{1/2}} = 0, \quad \bar{\alpha} \in P, \quad (37)$$

$$\sum_{\alpha} \frac{U_{\bar{\alpha}\alpha}^m \cos\pi(\nu_{\bar{\alpha}} + \mu_\alpha) \xi_{\alpha,d} A_{\alpha,2}}{(1 + \xi_{\alpha,d}^2)^{1/2}} = 0, \quad \bar{\alpha} \in Q.$$

We then have the compatibility condition

$$\bar{F}(\tau_2, \epsilon) = \det|\bar{F}_{\bar{\alpha}\alpha}| = 0, \quad (38)$$

with

$$\bar{F}_{\bar{\alpha}\alpha} = \begin{cases} U_{\bar{\alpha}\alpha}^m \cos\pi(-\tau_2 + \mu_\alpha), & \bar{\alpha} \in P \\ U_{\bar{\alpha}\alpha}^m \cos\pi(\nu_{\bar{\alpha}} + \mu_\alpha), & \bar{\alpha} \in Q. \end{cases} \quad (39)$$

Equation (38) has the roots denoted as $\{\tau_{\rho_2}\}$. The corresponding solutions $A_{\alpha,2}^{\rho_2}$ are

$$\bar{A}_{\alpha,2}^{\rho_2} = \frac{\xi_{\alpha,d} \bar{A}_{\alpha,2}^{\rho_2}}{(1 + \xi_{\alpha,d}^2)^{1/2}} = \frac{\bar{C}_{\bar{\alpha}\alpha}(\tau_{\rho_2}, \epsilon)}{C_{\bar{\alpha}}}, \quad (40)$$

with

$$\bar{C}_{\bar{\alpha}}^2 = \sum_{\alpha} [\bar{C}_{\bar{\alpha}\alpha}(\tau_{\rho_2}, \epsilon)]^2. \quad (41)$$

The $\bar{C}_{\bar{\alpha}\alpha}$ is the cofactor of the element $\bar{F}_{\bar{\alpha}\alpha}$ of $\det|\bar{F}_{\bar{\alpha}\alpha}|$. The renormalized collision eigenchannel functions $\psi(\tau_{\rho_2}, \epsilon)$ then are

$$\begin{aligned} \psi(\tau_{\rho_2}, \epsilon) &= \frac{1}{(1 + X_{\rho_2,d}^2)^{1/2}} \mathcal{G} \\ &\times \sum_{\alpha \in P} X_{\bar{\alpha}} \bar{T}_{\bar{\alpha}}^{\rho_2} (f_{\bar{\alpha}} \cos\pi\tau_{\rho_2} - g_{\bar{\alpha}} \sin\pi\tau_{\rho_2}) \\ &+ \frac{X_{\rho_2,d}}{(1 + X_{\rho_2,d}^2)^{1/2}} \phi_d F_d, \end{aligned} \quad (42)$$

outside the reaction zone and with

$$\bar{T}_{\bar{\alpha}}^{\rho_2} = \left(\sum_{\alpha} U_{\bar{\alpha}\alpha}^m \sin\pi(-\tau_{\rho_2} + \mu_\alpha) \bar{A}_{\alpha,2}^{\rho_2} \right) \bar{N}_{\rho_2}^{-1}, \quad (43)$$

$$X_{\rho_2,d} = \left(\sum_{\alpha} \frac{\bar{A}_{\alpha,d}^{\rho_2}}{\xi_{\alpha,d}} \right) \bar{N}_{\rho_2}^{-1}, \quad (44)$$

$$N_{\rho_2}^2 = \sum_{\alpha \in P} \left(\sum_{\alpha} U_{\bar{\alpha}\alpha}^m \sin\pi(-\tau_{\rho_2} + \mu_\alpha) \bar{A}_{\alpha,2}^{\rho_2} \right)^2. \quad (45)$$

The energy eigenfunction $\Psi^{(\bar{\beta}+)}$ is then constructed as a linear combination of the collision eigenchannel functions,

$$\Psi^{(\bar{\beta}+)} = \sum_{\rho_1} \psi(\tau_{\rho_1}, \epsilon) C_{\rho_1}^{(\bar{\beta}+)} + \sum_{\rho_2} \psi(\tau_{\rho_2}, \epsilon) C_{\rho_2}^{(\bar{\beta}+)}. \quad (46)$$

The coefficients $C_{\rho_1}^{(\bar{\beta}+)}$ and $C_{\rho_2}^{(\bar{\beta}+)}$ are determined by requiring that the amplitudes of all the incoming electron waves vanish in all channels $\bar{\alpha} \neq \bar{\beta}$ ($\bar{\alpha}, \bar{\beta} \in P$) and that the amplitude of the incoming wave in the molecular dissociative state also vanish, namely,

$$\sum_{\rho_1} \frac{T_{\bar{\alpha}}^1 C_{\rho_1}^{(\bar{\beta}+)}}{(1 + X_{\rho_1,d}^2)^{1/2}} + \sum_{\rho_2} \frac{\bar{T}_{\bar{\alpha}}^{\rho_2} C_{\rho_2}^{(\bar{\beta}+)}}{(1 + X_{\rho_2,d}^2)^{1/2}} = \delta_{\bar{\alpha}, \bar{\beta}} e^{i\sigma_{\bar{\beta}}}, \quad (47)$$

$$\sum_{\rho_1} \frac{iX_{\rho_1,d}}{(1 + X_{\rho_1,d}^2)^{1/2}} C_{\rho_1}^{(\bar{\beta}+)} + \sum_{\rho_2} \frac{X_{\rho_2,d}}{(1 + X_{\rho_2,d}^2)^{1/2}} C_{\rho_2}^{(\bar{\beta}+)} = 0 \quad \text{for all } \bar{\beta}. \quad (48)$$

The desired coefficients $C_{\rho_1}^{(\bar{\beta}+)}$ and $C_{\rho_2}^{(\bar{\beta}+)}$ are

$$\begin{aligned} C_{\rho_1}^{(\bar{\beta}+)} &= e^{i\sigma_{\bar{\beta}}} T_{\bar{\beta}}^{\rho_1} Y_{\rho_1} (1 + X_{\rho_1,d}^2)^{1/2} e^{i\pi\tau_{\rho_1}}, \\ C_{\rho_2}^{(\bar{\beta}+)} &= e^{i\sigma_{\bar{\beta}}} \bar{T}_{\bar{\beta}}^{\rho_2} Y_{\rho_2} (1 + X_{\rho_2,d}^2)^{1/2} e^{i\pi\tau_{\rho_2}}, \end{aligned} \quad (49)$$

where

$$Y_{\rho_2} = \sum_{\rho_1} (N^{-1})_{\rho_2\rho_1} X_{\rho_1,d} e^{i\pi\tau\rho_1}, \quad (50)$$

$$Y_{\rho_1} = 1 - \sum_{\rho_2} M_{\rho_1\rho_2} M_{\rho_1\rho_2} Y_{\rho_2},$$

with

$$M_{\rho_1\rho_2} = \sum_{\alpha \in P} T_{\alpha}^{\rho_1} \bar{T}_{\alpha}^{\rho_2}, \quad (51)$$

$$N_{\rho_1\rho_2} = iM_{\rho_1\rho_2} X_{\rho_2,d} e^{i\pi\tau\rho_2} + M_{\rho_1\rho_2} M_{\rho_1\rho_2} X_{\rho_2,d} e^{i\pi\tau\rho_1}. \quad (52)$$

Thus, the scattering matrix for dissociative recombination from the $\bar{\beta}$ channel is

$$\begin{aligned} S_{\bar{\beta},d} &= \left(-i \sum_{\rho_1} \frac{X_{\rho_1,d}}{(1+X_{\rho_1,d}^2)^{1/2}} C_{\rho_1}^{(\bar{\beta}+)} \right. \\ &\quad \left. + \sum_{\rho} \frac{X_{\rho_2,d}}{(1+X_{\rho_2,d}^2)^{1/2}} C_{\rho_2}^{(\bar{\beta}+)} \right) e^{i\delta d} \\ &= e^{i\sigma_{\bar{\beta}}} \left(\sum_{\rho_1} (-i) X_{\rho_1,d} T_{\bar{\beta}}^{\rho_1} e^{i\pi\tau\rho_1} Y_{\rho_1} \right. \\ &\quad \left. + \sum_{\rho_2} X_{\rho_2,d} \bar{T}_{\bar{\beta}}^{\rho_2} e^{i\pi\tau\rho_2} Y_{\rho_2} \right) e^{i\delta d}. \quad (53) \end{aligned}$$

The dissociative recombination cross section for the molecular ion in the state $\bar{x}\bar{v}$ then is

$$\sigma_{\bar{x}\bar{v}}^d = \frac{\pi}{k_{\bar{x}\bar{v}}^2} \sum_{\beta \in P_{\bar{x}\bar{v}}} \frac{(2 - \delta_{\Lambda, \beta^0})(2S+1)}{2(2S+1)} |S_{\bar{\beta},d}|^2. \quad (54)$$

III. ELECTRON-NO⁺-ION DISSOCIATIVE RECOMBINATION

Here we will apply the multichannel treatment to the dissociative recombination process between an electron with kinetic energy 0–2 eV and a NO⁺ ion in the electronic ground states $X^1\Sigma^+$ ($\bar{v}=0$ and 1) characterized by the electron configuration $(1s\sigma)^2(1s\bar{\sigma})^2(2s\sigma)^2(2s\bar{\sigma})^2(2p\sigma)^2(2p\pi)^4$. The energy of the NO⁺ in the next electronic excited state $a^3\Sigma^+$ is about 5 eV above the ground state $X^1\Sigma^+$.²³ Thus, in the energy range of our interest, we only consider the relevant channels $\bar{\alpha}$ characterized by various couplings between the NO⁺ ion in $X^1\Sigma^+$ and the incident electron. The relevant eigenchannel parameters in the multichannel theory will be extracted from the many spectroscopic data.

Fortunately, Miesher and his colleagues^{9–15} have conducted extensive studies on the spectra of the NO molecule. A clear interpretation of all the excited states of the NO molecule known from absorption and emission spectra was given in their papers.^{9–15} These states separate into two classes: Rydberg states forming nl complexes and characterized by electron configurations (core $^1\Sigma^+$)($nl\lambda$)

and, on the other hand, non-Rydberg states with the configurations,

$(1s\sigma)^2(1s\bar{\sigma})^2(2s\sigma)^2(2s\bar{\sigma})^2(2p\sigma)(2p\pi)^4(2p\bar{\pi})^2$, $(1s\sigma)^2(1s\bar{\sigma})^2(2s\sigma)^2(2s\bar{\sigma})^2(2p\sigma)^2(2p\pi)^3(2p\bar{\pi})^2$, and $(1s\sigma)^2(1s\bar{\sigma})^2(2s\sigma)^2(2s\bar{\sigma})^2(2p\sigma)^2(2p\pi)^4(2p\bar{\sigma})$. These Rydberg states appear in the form of l complexes involving the l electron coupled to the NO⁺ ion in the $X^1\Sigma^+$ states with coupling conditions intermediate between Hund's case (b) to case (c). Such intermediate coupling of the Rydberg states due to l uncoupling can be adequately treated in the multichannel theory as transformations from the molecular-body frame to the laboratory frame.²⁰

In this paper, the rotational structures escape our detection because of inadequate energy resolution, and because we are only interested in the overall vibrational structures. Therefore, the eigenchannels are constructed as superpositions of the $\bar{\alpha}$ channels defined in the molecular-body frame as discussed in Sec. II. The $\bar{\alpha}$ channels are then characterized by $(\bar{v}\bar{\Lambda}\bar{S})(l\lambda s)\Lambda S$ with $\Lambda = |\lambda|$ and $S = s = \frac{1}{2}$ (because $\bar{\Lambda} = 0$ and $\bar{S} = 0$). In the multichannel treatment for the collisions between the electron and the NO⁺ ions in the states $X^1\Sigma^+$ ($\bar{v}=0$ and $\bar{v}=1$), the relevant $\bar{\alpha}$ channels only with $\bar{v} \leq 2$ will be taken into account since the molecular potential curves for the Rydberg states and the state $X^1\Sigma^+$ of NO⁺ are all similar in first approximation, and consequently, there exists quasiorthogonality between the vibrational wave functions for the NO⁺ and the NO complex.

Homogeneous perturbations^{13,24} between states with an equal symmetry (i.e., same Λ and S) result from Rydberg–non-Rydberg configuration interactions, and it is these non-Rydberg states which may lead to dissociations of the NO molecule. We also note that the Rydberg f complexes detected in the NO spectrum, in contrast to all the complexes with $l < 3$, are apparently not exposed to perturbations involving non-Rydberg states and are not predissociated.^{9,10,14,15} Therefore, we perform a partial-wave analysis for the dissociative recombination process only up to the d waves, namely, $l \leq 2$.

A. d waves

The structure of d complex has three components, i.e., $d\sigma$, $d\pi$, and $d\delta$. The δ component of the nd Rydberg states is far separated from the σ, π components and is strongly perturbed due to the Rydberg–non-Rydberg interaction.^{9,12,13} However, no such strong perturbations are observed in the σ, π components.^{9,12,14} Thus, for the d waves, we only consider the contribution from the $d\delta$ wave.

In the $d\delta$ component, we have three $\bar{\alpha}$ channels, $\bar{\alpha} = 1, 2, 3$, corresponding to the couplings of

TABLE I. Eigenchannel parameters (eigen-quantum-defect $\mu_\alpha = \mu_\alpha^0 + \mu_\alpha^1 \epsilon$ transformation matrix $U_{\alpha\alpha}^m$ and mixing parameter H_α^{e1}).

Symmetry	$(X^1\Sigma^+)d\delta^2\Delta$			$(X^1\Sigma^+)p\pi^2\Pi$			$(X^1\Sigma^+)p\sigma^2\Sigma^+$			$(X^1\Sigma^+)s\sigma^2\Sigma^+$		
α	1	2	3	1	2	3	1	2	3	1	2	3
μ_α^0	0.075	0.078	0.080	0.742	0.750	0.754	0.669	0.690	0.707	1.2269	1.2271	1.2273
μ_α^1	0.128	0.120	0.122	-0.495	-0.328	-0.434	-0.428	-0.413	-0.437	0.9403	0.9580	0.9529
$U_{\alpha\alpha}^m$	$\begin{bmatrix} 0.975 & -0.211 & 0.072 \\ 0.221 & 0.954 & -0.203 \\ -0.026 & 0.213 & 0.977 \end{bmatrix}$			$\begin{bmatrix} 0.890 & -0.387 & 0.242 \\ 0.456 & 0.787 & -0.416 \\ -0.030 & 0.480 & 0.877 \end{bmatrix}$			$\begin{bmatrix} 0.959 & -0.246 & 0.142 \\ 0.274 & 0.933 & -0.234 \\ -0.075 & 0.263 & 0.962 \end{bmatrix}$			$\begin{bmatrix} 0.927 & -0.361 & 0.106 \\ 0.376 & 0.895 & -0.241 \\ -0.008 & 0.263 & 0.965 \end{bmatrix}$		
H_α^{e1}	Rydberg ${}^2\Delta$ - $B'{}^2\Delta$ 0.018+0.116 ϵ			Rydberg ${}^2\Pi$ - $B^2\Pi$ 0.025+0.087 ϵ			Rydberg ${}^2\Sigma^+$ - $A'{}^2\Sigma^+$ 0.019			Rydberg ${}^2\Sigma^+$ - $I^2\Sigma^+$ 0.017		

$[X^1\Sigma^+(\bar{v}=0)]d\delta$, $[X^1\Sigma^+(\bar{v}=1)]d\delta$, and $[X^1\Sigma^+(\bar{v}=2)]d\delta$, with the molecular symmetry ${}^2\Delta$ (i.e., $\Lambda=2, S=\frac{1}{2}$). The corresponding eigenchannels α represent the superexcited molecular complex with ${}^2\Delta$ symmetry and vibrational quanta 0, 1, 2, respectively. The eigen-quantum-defects μ_α and the transformation matrix $U_{\alpha\alpha}^m$ are determined by fitting the nine "deperturbed" energy-level positions of the Rydberg states,^{9,12,13} $F^2\Delta, N^2\Delta, U^2\Delta$, with $v \leq 2$. Here the "deperturbed" energy-level positions which have been obtained^{9,12,13} by rotational analyses of the NO spectroscopic data are adopted. More specifically, we minimize the sum in Eq. (20) with $N=9$. The electronic term H_α^{e1} of the mixing parameter $\xi_{\alpha d}$ in Eq. (16) is then ob-

tained from the analysis¹³ of the perturbation between the Rydberg states $F^2\Delta, N^2\Delta$ and the non-Rydberg state $B'{}^2\Delta$. These adopted eigenchannel parameters are listed in Table I. The Frank-Condon factors $f_{\alpha, \epsilon}$ are calculated based on the potential curves of the state $X^1\Sigma^+$ of NO^+ and the state $B'{}^2\Delta$ of NO as shown in Fig. 1. With these physically meaningful parameters, the $d\delta$ contribution of dissociative recombination of NO^+ ions [$X^1\Sigma^+(\bar{v}=0$ and 1)] with 0–2-eV electrons is then calculated by formula (26) and Eq. (54) for the conventional "direct" and "indirect" processes, respectively, as shown in Figs. 2 and 3. The cross sections have been convoluted with the incident-electron beam of a half width 0.025 eV.

Let us examine in detail the feature of the dissociative recombination cross sections through the $B'{}^2\Delta$ state. Since the Frank-Condon overlap fac-

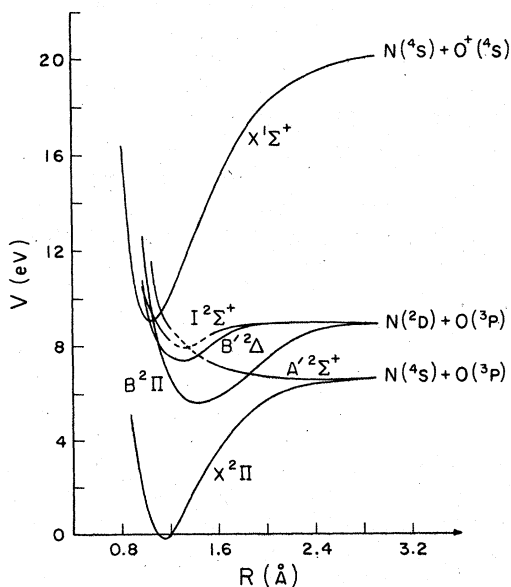


FIG. 1. Relevant potential curves for NO and NO^+ systems.

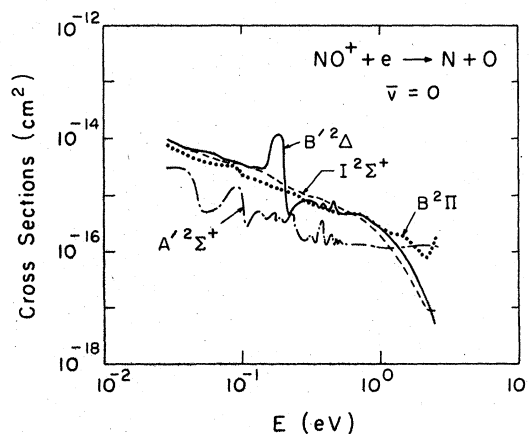


FIG. 2. Partial dissociative recombination cross sections of NO^+ ions in the state $X^1\Sigma^+(\bar{v}=0)$ with electrons. The theoretical curves have been convoluted with the incident electron beam of a half width of 0.025 eV.

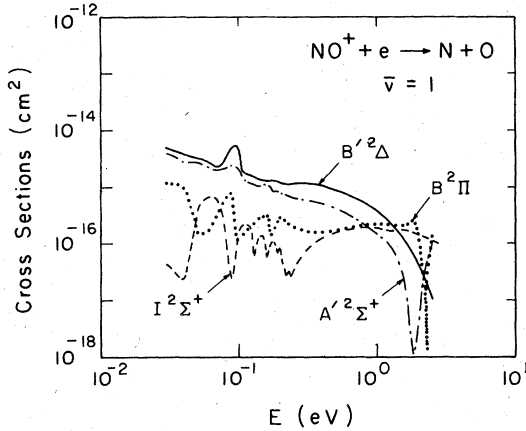


FIG. 3. Partial dissociative recombination cross sections of NO^+ ions in the state, $X^1\Sigma^+(\bar{v}=1)$ with electrons. The theoretical curves have been convoluted with the incident electron beam of a half width of 0.025 eV.

tor is very small for $v=1$ at electron energies below about 0.15 eV, the cross section for NO^+ in $\bar{v}=1$ is smaller than that for NO^+ in $\bar{v}=0$. However, at about 0.1 eV, the cross section through $B'^2\Delta$ state for NO^+ in $\bar{v}=1$ is larger than that for NO^+ in $\bar{v}=0$. Such an enhancement peak, for $\bar{v}=1$, at about 0.1 eV is due to the resonance via the $9d\delta^2\Delta(v=2)$ Rydberg state, which is identified by examining the behavior of the mixing coefficients $\bar{A}_{\alpha,1}^{\rho_1}$ at the resonance $9d\delta^2\Delta$ (the value of $\bar{A}_{\alpha,1}^{\rho_1}$ in one of the collisional eigenchannel ρ_1 equals 1). We can also trace all the other resonances in the $B'^2\Delta$ channel for NO^+ in $X^1\Sigma^+(\bar{v}=1)$: the first resonance via $7d\delta^2\Delta(v=2)$ at 0.006 eV is out of the scale of Fig. 3; the second resonance via $8d\delta^2\Delta(v=2)$ at 0.074 eV is smeared out by the energy convolution of the incident electron beam with a half width 0.025 eV, and therefore only a tiny trace remained; the third one is the resonance via $9d\delta^2\Delta(v=2)$ discussed above; and the rest, resonance structures via $nd\delta^2\Delta(v=2)$, $n \geq 10$, are smeared out by the energy convolution because they are within a half width of the electron beam. Very interestingly, in Fig. 2 for the dissociative recombination of NO^+ [$X^1\Sigma^+(\bar{v}=0)$] and electron, the resonance structures via $nd\delta^2\Delta(v=1)$ Rydberg states are not noticeable because the Frank-Condon overlap factor is very small for $v=1$. However, the resonance at about 0.18 eV, in Fig. 2, is due to the resonance via the $6d\delta^2\Delta(v=2)$ Rydberg state.

B. p wave

The p complexes consist of $p\sigma$ and $p\pi$ components.⁹⁻¹² Both of the $p\sigma$ and the $p\pi$ Rydberg states have a diffuse, perturbed structure due to homo-

geneous Rydberg-non-Rydberg interactions. Thus, the contributions from the $p\sigma$ and the $p\pi$ waves should be included.

For the $p\pi$ wave, we have again three $\bar{\alpha}$ channels corresponding to the couplings of [$X^1\Sigma^+(\bar{v}=0)$] $p\pi$, [$X^1\Sigma^+(\bar{v}=1)$] $p\pi$, and [$X^1\Sigma^+(\bar{v}=2)$] $p\pi$ with the symmetry $^2\Pi(\Lambda=1, S=\frac{1}{2})$. The corresponding eigen-quantum-defects μ_α and transformation matrix $U_{\alpha\alpha}^m$ are determined by fitting to the eight "deperturbed" energy-level positions of the Rydberg state^{10,11} $C^2\Pi$, $K^2\Pi$, $I^2\Pi$, and $W^2\Pi$ with $v \leq 2$. The electronic term of the mixing parameter $\xi_{\alpha,d}$ is determined from the analysis of the perturbation between Rydberg state $C^2\Pi$, $K^2\Pi$, and the non-Rydberg state $B^2\Pi$. We here ignore the effect of another non-Rydberg state $L^2\Pi$ which may become important for dissociative recombination of NO^+ ions in higher vibrational states with higher-energy electrons.⁵ The adopted eigenchannel parameters for $^2\Pi$ symmetry are listed in Table I. The Frank-Condon factors $f_{\alpha,d}$ are calculated based on the potential curves shown in Fig. 1. With these eigenchannel parameters, the dissociative recombination cross section via $B^2\Pi$ is calculated by the formula, Eq. (26) and Eq. (56), as shown in Figs. 2 and 3. All the resonance structures can be traced out in detail by examining the behavior of the mixing coefficients $\bar{A}_{\alpha,1}^{\rho_1}$ as in the case of the $d\delta$ wave discussed above, and we will not repeat similar discussions for the other λ waves.

For the $p\sigma$ wave (i.e., $^2\Sigma^+$ symmetry), the eigen-quantum-defect μ_α and transformation matrix $U_{\alpha\alpha}^m$ are determined by fitting to the nine "deperturbed" energy-level positions of the Rydberg states^{9,10} $D^2\Sigma^+$, $M^2\Sigma^+$, $R^2\Sigma^+$, and $Y^2\Sigma^+$ with $v \leq 2$. The electronic term of the mixing parameters is estimated from the perturbation⁹⁻¹¹ between the Rydberg states $D^2\Sigma^+$, $M^2\Sigma^+$, and the non-Rydberg state $A'^2\Sigma^+$. Table I lists the adopted eigenchannel parameters. The Frank-Condon factors $f_{\alpha,d}$ are calculated based on the potential curves shown in Fig. 1. In Figs. 2 and 3 we present the recombination cross sections via $A'^2\Sigma^+$ for NO^+ ion in $\bar{v}=0$ and $\bar{v}=1$, respectively.

C. s wave

The ($s\sigma$) $^2\Sigma^+$ Rydberg states are perturbed strongly by the non-Rydberg state $I^2\Sigma^+$.^{9,10} Thus, the s wave should make some contribution to dissociative recombination process. In the ($s\sigma$) $^2\Sigma^+$ symmetry, the eigen-quantum-defects μ_α and transformation matrix $U_{\alpha\alpha}^m$ are determined by fitting to the 14 "deperturbed" energy-level positions of the Rydberg states⁹⁻¹¹ $A^2\Sigma^+$, $E^2\Sigma^+$, $S^2\Sigma^+$, $T^2\Sigma^+$, and $Z^2\Sigma^+$ with $v \leq 2$. The electronic term of $\xi_{\alpha,d}$ is estimated from the perturbation between

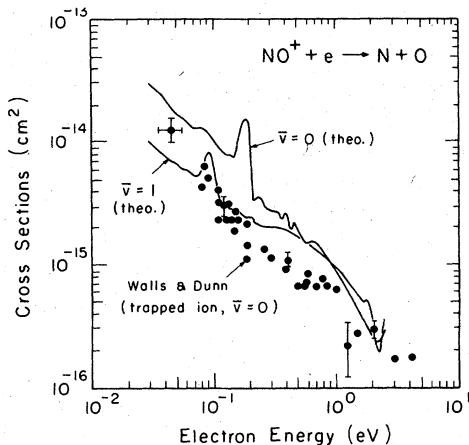


FIG. 4. Dissociative recombination cross sections of NO^+ ions in the states $X^1\Sigma^+(\bar{v}=0)$ and $\bar{v}=1$ with electrons. The theoretical curves have been convoluted with the incident electron beam of a half width of 0.025 eV.

the Rydberg state $E^2\Sigma^+$ and the non-Rydberg state $I^2\Sigma^+$. The Frank-Condon factors $f_{\alpha,d}$ are again calculated based on the potential curves shown in Fig. 1. With the adopted eigenchannel parameters listed in Table I, the dissociative recombination cross sections via $I^2\Sigma^+$ are calculated and are shown in Figs. 2 and 3.

Figure 2 presents the decomposition of the dissociative recombination cross section for $\text{NO}^+(\bar{v}=0)$ into the contributions from the states $B'^2\Delta$, $B^2\Pi$, $A'^2\Sigma^+$, and $I^2\Sigma^+$. The theoretical cross sections here have been convoluted with the incident electron beam of a half width 0.025 eV. The resonance features below about 0.58 eV, the excitation energy of NO^+ ions from $\bar{v}=0$ and $\bar{v}=2$, result from dissociative recombination via the Rydberg states in either $v=1$ or 2. The features above 0.58 eV reflect mainly the energy dependence of the Frank-Condon factors. Similarly, Fig. 3 presents the decomposition of the dissociative recombination cross section for NO^+ ions in $\bar{v}=1$ into the contributions from the states $B'^2\Delta$, $B^2\Pi$, $A'^2\Sigma^+$, and $I^2\Sigma^+$. The resonance features below about 0.28 eV, the excitation energy of NO^+ ions from $\bar{v}=1$ to $\bar{v}=2$, arise from dissociative recombination via the $\bar{v}=2$ Rydberg states, and the features above 0.28 eV reflect the energy dependence and the interference of the Frank-Condon factors in the multichannel treatment. In Fig. 4, we present the total dissociative recombinations for NO^+ ions in $\bar{v}=0$ and 1. To compare with experimental data, the present theoretical result for $\text{NO}^+(\bar{v}=0)$ may be consistent with the "stored-ion" measurement by Walls and Dunn⁸ except for the overall normalization factor and some fine-detail features. The present theoretical result is larger than the stored-ion data by

an overall factor 2, although the present theoretical data may have an uncertainty of about 50% and the stored-ion data may also be subject to a change of the overall normalization as well as the insufficient energy resolution, particularly at low incident-electron energies. Regarding the fine-detail features in the cross sections, let us first examine the features in the "indirect dissociative recombination region." Although the experimental data may have some indications for the resonance features at about 0.2 and 0.4 eV, the appreciable resonance at about 0.18 eV, as our theoretical results indicate, seems to escape from detection. Such resonance features will certainly have significant effects on the recombination rate at electron temperatures $T_3=300$ to 3000 K; we will discuss this point later as we examine the afterglow measurement by Huang, Biondi, and Johnsen.⁷ Therefore, it would be very enlightening to have some high-resolution merged-beam measurements of the ($e-\text{NO}^+$) recombination similar to the recent merged electron-ion beam measurement of the ($e+\text{H}_3^+$) recombination by the McGowan group.²⁵ Concerning the experimental minimum at about 1.2 eV compared with the theoretical minimum at about 2 eV, this feature results mainly from the energy dependence of the Frank-Condon factors, which are sensitive to the positions of the crossing point between the potential curves of the $\text{NO}^+(X^1\Sigma^+)$ and the $\text{NO}(B^2\Pi)$. The mismatch between the experimental 1.2 eV and the theoretical 2 eV may indicate that the adopted potential curves, $X^1\Sigma^+$ and $B^2\Pi$ shown in Fig. 1, have the crossing point at somewhat larger distance than it should be.

The electron-temperature dependence of the dissociative recombination of NO^+ ions was studied by Huang, Biondi, and Johnsen⁷ by means of a microwave-afterglow-mass-spectrometer apparatus employing microwave heating of the electrons. If we assume the electron energy distribution to be Maxwellian, we can obtain the recombination rate

$$\alpha_{\bar{v}} = \frac{4\pi\sqrt{m}}{(2kT)^{3/2}} \int v^2 \sigma_{\bar{v}}^d \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon, \quad (55)$$

where $\sigma_{\bar{v}}^d$ is the cross section for dissociative recombination of NO^+ ions in the state $X^1\Sigma^+(\bar{v})$ with electrons. In Fig. 5, we present the calculated reaction rates along with the experimental data^{7,8} and some other theoretical results.³⁻⁵ Regarding the experimental conditions of the afterglow measurement⁷ [i.e., the gas temperature $T_n \approx 380$ K, the buffer-gas (Ar) pressure $P(\text{Ar}) \approx 12.5$ Torr, and the NO pressure $P(\text{NO}) = 1.3$ mTorr], it may be reasonable to consider that the measured recombination is dominantly due to NO^+ ions in the state $X^1\Sigma^+(\bar{v}=0)$, although there are some un-

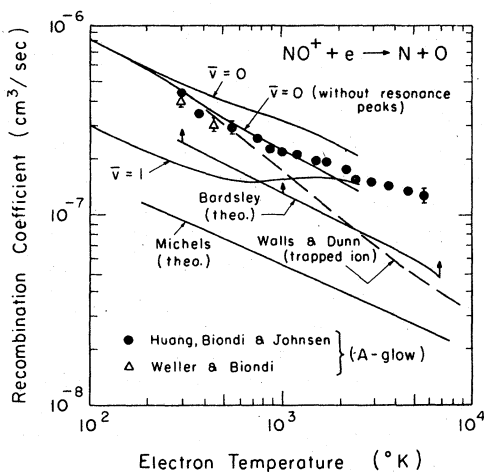


FIG. 5. Dissociative recombination coefficient of NO^+ ions in the states $X^1\Sigma^+(\bar{v}=0$ and $\bar{v}=1$).

certainties concerning the vibrational population of the NO^+ ions (probably in $\bar{v}=0$ or 1).⁷ The present theoretical reaction rate for the $\bar{v}=0$ state seems to be consistent with the afterglow measurement regarding the electron-temperature dependence and the absolute magnitude since the present theoretical data may have an uncertainty of about 50%. For NO^+ ions in the $\bar{v}=1$ state, the recombination rate, shown in Fig. 5, has a smaller magnitude and a much flatter electron-temperature dependence. There is something interesting, if we take off the resonance peaks from the recombination cross section, as shown in Fig. 4, and then perform Maxwellian folding, Eq. (55), to obtain the reaction rate which has much steeper electron-temperature dependence, as shown in Fig. 5 by the curve indicated as " $\bar{v}=0$ without resonance peaks." Interestingly, this may suggest one possible reconciliation of the discrepancy of the electron-temperature dependences between the afterglow measurement and the stored-ion measurement since some resonance structures at low energies may escape from detection in the stored-ion measurement.

In Fig. 1, there are four dissociative electronic states $B'^2\Delta$, $B^2\Pi$, $I^2\Sigma^+$, and $A'^2\Sigma^+$. We will neglect the couplings among the dissociative electronic states $^2\Delta$, $^2\Pi$, and $^2\Sigma$ via heterogeneous perturbations which are due to finer rotation-electronic interactions and which are not noticeable in the NO spectroscopic data.²⁶ We only consider the coupling between $I^2\Sigma^+$ and $A'^2\Sigma^+$ via homogeneous perturbation.²⁶ We then estimate the branching ratio in the two extreme cases, namely diabatically and adiabatically. Following the potential curves diabatically in Fig. 1, the dissociative electronic states $B'^2\Delta$, $B^2\Pi$, and $I^2\Sigma^+$ will lead to the dis-

sociation into the excited nitrogen atom $\text{N}(^2D)$ and the ground-state oxygen atom $\text{O}(^3P)$, and the $A'^2\Sigma^+$ will lead to the dissociation into the ground-state nitrogen atom $\text{N}(^4S)$ and the ground-state oxygen atom $\text{O}(^3P)$. However, following the potential curves adiabatically, the $B'^2\Delta$, $B^2\Pi$, and $A'^2\Sigma^+$ will lead to $\text{N}(^2D)$ and $\text{O}(^3P)$, and the $I^2\Sigma^+$ will lead to $\text{N}(^4S)$ and $\text{O}(^3P)$. At $T_e=300$ K for NO^+ ions in the state $X^1\Sigma^+(\bar{v}=0)$ there is then a percentage of about 67 to 94% of the dissociative recombination leading to $\text{N}(^2D)$ according to the adiabatic and the diabatic pictures, respectively. For NO^+ ions in the state $X^1\Sigma^+(\bar{v}=1)$, there is some dependence on the vibrational state, i.e., a percentage of about 98 to 58% of the dissociative recombination leading to $\text{N}(^2D)$ according to the adiabatic and diabatic pictures, respectively. To summarize, the dissociative recombination of NO^+ ions in the states $X^1\Sigma^+(\bar{v}=0$ and 1) leads preferentially to the excited nitrogen atoms $\text{N}(^2D)$ at thermal electron temperature.

IV. DISCUSSION

The "electron+molecular ion" complex here is described as superpositions of the various channels in terms of the eigenchannel parameters; transformation matrix $U_{\alpha\alpha}^m$, eigen-quantum-defects μ_α , and mixing parameters $\xi_\alpha = H_\alpha^{\text{el}} f_{\alpha,a}$. Such eigenchannel parameters lump all dynamics of the complex within the reaction zone, and the electronic parts of the parameters, U , μ , and H_α^{el} , vary very smoothly with the degree of excitations. The molecular complex may break either into the electron and the molecular ion or into the two neutral atoms according to various dissociation channels. Thus, the present multichannel treatment serves as a quantitative description of such an "electron+molecular ion" complex in "super-excited" states²⁷ of the molecule. Since the eigenchannel parameters can be regarded as boundary parameters over the reaction zone boundary, to treat the relevant physical process then becomes an exercise of imposing the appropriate boundary conditions at infinity as demonstrated in Sec. II, where we have treated dissociative recombination process. The conventional "indirect" and "direct" dissociative recombinations are thus handled together on the same footing since the "indirect" dissociative recombination is a resonance process via Rydberg states, which have been taken into account by the multichannel treatment.

Finally, we would like to comment on how to obtain such vitally important eigenchannel parameters. The parameters can be obtained either by fitting to the available experimental data, as demonstrated in the present paper, or by first-princi-

ples calculations, which have been demonstrated only for an atomic system.²² Thus, a practical first-principles calculation scheme for a molecular system, aiming directly at such eigenchannel parameters, remains to be developed. The compact set of the physically meaningful eigenchannel parameters here represents a vast set of apparently different experimental measurements, such as spectroscopic data and electron-ion collision data. Therefore, such physically meaningful parameters should merit much attention. We hope that such parameters would be a target of both first-principles theoretical calculations and experimental data analysis in the future.

ACKNOWLEDGMENT

The author would like to express his gratitude to Dr. C. M. Huang and Dr. R. Johnsen for interesting discussions about afterglow measurements. He would also like to thank Dr. J. N. Bardsley for informing him of the recent theoretical work on the ($e + \text{NO}^+$) recombination in Ref. 5.

APPENDIX^{21,28}

Traditional treatment of dissociation of the molecular complex via configuration mixing with the dissociative states here is handled by channel interactions between the α channels and the dissociative channels. Here for simplicity we only consider one α channel ψ_α interacting with one dissociative channel Φ_d via an interaction matrix element $\langle \psi_\alpha | V_{\text{int}} | \Phi_d \rangle$ which, in Born-Oppenheimer approximation, can be written as

$$\langle \psi_\alpha | V_{\text{int}} | \Phi_d \rangle \simeq H_{\alpha,d}^{\text{el}} f_{\alpha,d}, \quad (\text{A1})$$

with $H_{\alpha,d}^{\text{el}}$ the electronic matrix element and $f_{\alpha,d}$ the Frank-Condon factors. Taking into account the channel interaction, the eigenchannel functions become

$$\psi_\alpha^1(\epsilon) = \int d\bar{\epsilon} \psi_\alpha(\bar{\epsilon}) A_{\alpha\bar{\epsilon},\alpha\epsilon} + \int d\bar{\epsilon} \Phi_d(\bar{\epsilon}) A_{d\bar{\epsilon},\alpha\epsilon}, \quad (\text{A2})$$

$$\psi_\alpha^2(\epsilon) = \int d\bar{\epsilon} \psi_\alpha(\bar{\epsilon}) A_{\alpha\bar{\epsilon},d\epsilon} + \int d\bar{\epsilon} \Phi_d(\bar{\epsilon}) A_{d\bar{\epsilon},d\epsilon}, \quad (\text{A3})$$

$$\psi_\alpha^1(\epsilon) = B_\alpha(\epsilon) \left[\mathcal{Q} \sum_{\bar{\alpha}} X_{\bar{\alpha}} U_{\bar{\alpha}\alpha}^m (f_{\bar{\alpha}} \cos \pi \mu_{\bar{\alpha}} - g_{\bar{\alpha}} \sin \pi \mu_{\bar{\alpha}}) + \pi K_{\alpha\alpha} \mathcal{Q} \sum_{\bar{\alpha}} X_{\bar{\alpha}} U_{\bar{\alpha}\alpha}^m (g_{\bar{\alpha}} \cos \pi \mu_{\bar{\alpha}} - f_{\bar{\alpha}} \sin \pi \mu_{\bar{\alpha}}) + K_{d\alpha} \phi_d G_\alpha(R) \right], \quad (\text{A15})$$

and

$$\psi_\alpha^2(\epsilon) = B_d(\epsilon) \left(\pi K_{\alpha d} \mathcal{Q} \sum_{\bar{\alpha}} X_{\bar{\alpha}} U_{\bar{\alpha}\alpha}^m (g_{\bar{\alpha}} \cos \pi \mu_{\bar{\alpha}} - f_{\bar{\alpha}} \sin \pi \mu_{\bar{\alpha}}) + \phi_d F_d(R) + \pi K_{dd} \phi_d G_d(R) \right). \quad (\text{A16})$$

In a perturbation treatment of Eq. (12), we have

$$K_{\alpha d} = K_{d\alpha} \simeq \langle \psi_\alpha(\epsilon) | V_{\text{int}} | \Phi_d(\epsilon) \rangle, \quad (\text{A17})$$

$$K_{\alpha\alpha} = K_{dd} \simeq 0. \quad (\text{A18})$$

Therefore, we are led to Eq. (15).

with

$$A_{\alpha\bar{\epsilon},\alpha\epsilon} = \{ [P/(\epsilon - \bar{\epsilon})] K_{\alpha\bar{\epsilon}\alpha\epsilon} + \delta(\epsilon - \bar{\epsilon}) \} B_\alpha(\epsilon), \quad (\text{A4})$$

$$A_{d\bar{\epsilon},\alpha\epsilon} = [P/(\epsilon - \bar{\epsilon})] K_{d\bar{\epsilon},\alpha\epsilon} B_\alpha(\epsilon), \quad (\text{A5})$$

$$A_{\alpha\bar{\epsilon},d\epsilon} = [P/(\epsilon - \bar{\epsilon})] K_{\alpha\bar{\epsilon},d\epsilon} B_d(\epsilon), \quad (\text{A6})$$

$$A_{d\bar{\epsilon},d\epsilon} = \{ [P/(\epsilon - \bar{\epsilon})] K_{d\bar{\epsilon},d\epsilon} + \delta(\epsilon - \bar{\epsilon}) \} B_d(\epsilon), \quad (\text{A7})$$

where P refers to taking the Cauchy principal value in integrations. The K matrix satisfies the following integral equations:

$$K_{\alpha\bar{\epsilon},\alpha\epsilon} = \int d\epsilon' V_{\alpha\bar{\epsilon},d\epsilon'} \frac{P}{\epsilon - \epsilon'} K_{d\epsilon',\alpha\epsilon}, \quad (\text{A8})$$

$$K_{d\bar{\epsilon},\alpha\epsilon} = V_{d\bar{\epsilon},d\epsilon} + \int d\epsilon' V_{d\bar{\epsilon},\alpha\epsilon'} \frac{P}{\epsilon - \epsilon'} K_{\alpha\epsilon',\alpha\epsilon}, \quad (\text{A9})$$

$$K_{\alpha\bar{\epsilon},d\epsilon} = V_{\alpha\bar{\epsilon},d\epsilon} + \int d\epsilon' V_{\alpha\bar{\epsilon},d\epsilon'} \frac{P}{\epsilon - \epsilon'} K_{d\epsilon',d\epsilon}, \quad (\text{A10})$$

$$K_{d\bar{\epsilon},d\epsilon} = \int d\epsilon' V_{d\bar{\epsilon},\alpha\epsilon'} \frac{P}{\epsilon - \epsilon'} K_{\alpha\epsilon',d\epsilon}, \quad (\text{A11})$$

with

$$V_{\alpha\bar{\epsilon},d\epsilon'} = \langle \psi_\alpha(\bar{\epsilon}) | V_{\text{int}} | \Phi_\alpha(\epsilon') \rangle$$

and

$$V_{\alpha\bar{\epsilon},\alpha\epsilon'} = \langle \Phi_d(\bar{\epsilon}) | V_{\text{int}} | \psi_\alpha(\epsilon') \rangle.$$

The integral equations can be written symbolically as

$$K = V + \int d\epsilon' V \frac{P}{\epsilon - \epsilon'} K. \quad (\text{A12})$$

The normalization factors, $B_\alpha(\epsilon)$ and $B_d(\epsilon)$, are given by

$$B_\alpha(\epsilon) = 1/(1 + \pi^2 K_{\alpha\alpha}^2 + \pi^2 K_{d\alpha}^2)^{1/2}, \quad (\text{A13})$$

$$B_d(\epsilon) = 1/(1 + \pi^2 K_{\alpha d}^2 + \pi^2 K_{dd}^2)^{1/2}, \quad (\text{A14})$$

where $K_{\alpha\alpha}$, $K_{d\alpha}$, K_{dd} , and $K_{\alpha d}$ denote the values of the K -matrix elements on the energy shell (i.e., $K_{\alpha\alpha} \equiv K_{\alpha\epsilon,\alpha\epsilon}$, etc.). Outside the reaction zone, the eigenchannel wave functions are obtained by performing the Cauchy principal-value integrations in Eqs. (A2) and (A3) and are expressed, in terms of the K -matrix elements on the energy shell, as follows:

*Supported in part by the NSF under Grant No. MPS74-03531.

†Present address: Laboratory for Laser Energetics, University of Rochester, Rochester, N. Y. 14627.

¹U. Fano, *J. Opt. Soc. Am.* **65**, 979 (1975).

²T. M. Donahue, *Science* **159**, 489 (1968).

³J. N. Bardsley, *J. Phys. B* **1**, 365 (1968).

⁴H. H. Michaels, "Theoretical studies of dissociative recombination kinetics," Air Force Cambridge Research Lab. Report No. AFWL-TR-73-288, 1974 (unpublished).

⁵H. H. Michaels, "Theoretical Study of Dissociative-Recombination of $e + NO^+$," Air Force Cambridge Research Lab. Report No. AFCRL-TR-75-0509, 1975 (unpublished).

⁶C. S. Weller and M. A. Biondi, *Phys. Rev.* **172**, 198 (1968); R. C. Gunton and T. M. Shaw, *ibid.* **140**, A756 (1965); R. A. Young and G. S. John, *ibid.* **152**, 25 (1966); J. P. Doering and B. H. Mahan, *J. Chem. Phys.* **36**, 669 (1962); M. Mentzoni and J. Donohoe, *Can. J. Phys.* **45**, 1505 (1967).

⁷C. M. Huang, M. A. Biondi, and R. Johnsen, *Phys. Rev. A* **11**, 901 (1975).

⁸F. L. Walls and G. H. Dunn, *J. Geophys. Res.* **79**, 1911 (1974).

⁹E. Miescher, *J. Mol. Spectrosc.* **20**, 130 (1966).

¹⁰K. Dressler and E. Miescher, *Astrophys. J.* **141**, 1266 (1965).

¹¹A. Lagerquist and E. Miescher, *Can. J. Phys.* **44**, 1525 (1966).

¹²E. Miescher, *Can. J. Phys.* **49**, 2350 (1971).

¹³Ch. Jungen, *Can. J. Phys.* **44**, 3197 (1966).

¹⁴Ch. Jungen and E. Miescher, *Can. J. Phys.* **47**, 1769 (1969).

¹⁵R. Suter, *Can. J. Phys.* **47**, 881 (1969).

¹⁶G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, 2nd. ed. (Van Nostrand, Princeton, N.J., 1965), p. 221.

¹⁷E. Chang and U. Fano, *Phys. Rev. A* **6**, 173 (1972).

¹⁸C. M. Lee, *Phys. Rev. A* **10**, 584 (1974).

¹⁹M. M. J. Seaton, *Proc. Phys. Soc. Lond.* **88**, 801 (1966).

²⁰U. Fano, *Phys. Rev. A* **2**, 353 (1970).

²¹U. Fano, lecture notes at the University of Chicago.

²²U. Fano and C. M. Lee, *Phys. Rev. Lett.* **31**, 1573 (1973), and Ref. 18.

²³F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer* **5**, 369 (1965).

²⁴P. Felenbok and H. Lefebvre-Brion, *Can. J. Phys.* **44**, 1677 (1966).

²⁵R. Caudano, S. F. J. Wild, and J. W. McGowan, in *Electronic and Atomic Collisions*, edited by J. S. Risley and G. Geballe (University of Washington Press, Seattle, 1975) p. 389.

²⁶Ch. Jungen and E. Miescher, *Can. J. Phys.* **46**, 987 (1969).

²⁷R. L. Platzman, *Vortex* **23**, 372 (1962); *Radiat. Res.* **17**, 419 (1962).

²⁸M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1967), p. 215.