

# From the Absorption Profile to the Potential by a Time-dependent Inversion Method

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Received August 7, 1997

The time-dependent tracking inversion method is developed to extract the potential of the excited state from frequency-domain measurements, such as the absorption profile. Based on the relay of the regularized inversion procedure and time-dependent wave-packet propagation, the algorithm extract the underlying potential piece by piece by tracking the time-dependent data which can be synthesized from frequency-domain measurements. We have demonstrated the algorithm to extract the potential of excited state for a model diatomic molecule. Finally, we describe the merits of the time-dependent tracking inversion method compared to the time-independent inversion method and discuss several extensions of the algorithm.

## Introduction

The exact information of the inter- and intramolecular potential energy surfaces (PES) is important for understanding molecular dynamics and chemical reactions.<sup>1</sup> Thus, the determination of PES has been studied for many years by two different approaches.<sup>2-4</sup> One is to perform *ab initio* calculation within the Born-Oppenheimer approximation,<sup>5</sup> which is a forward method, and the other, which is an inverse method,<sup>6,7</sup> is to perform inversion of experimental data.

In recent years, *ab initio* calculation for this task are very advanced but still limited to relatively small systems and still lack the accuracy demanded by quantitative dynamical calculation. On the other hand, existing numerical procedures to extract PES from laboratory data are almost use a traditional least-squares fitting methods,<sup>8</sup> but these methods have the drawback of constraining PES to follow a fixed function form; thus good fits are hard to obtain. Without assuming any PES form, a direct inversion methods exist for the simple case of diatomic molecules, known as the semi-classical Rydberg-Klein-Rees (RKR) method.<sup>9</sup> Although the RKR method has been a great success in the determination of one-dimensional PES, it cannot be applied to multi-dimensional PES and to PES with more than one minimum.<sup>10</sup>

Recently, a regularized inversion method has been developed within the framework of the functional sensitivity analysis and the Tikhonov regularization procedure.<sup>11</sup> The method is related to the iterative inversion algorithm which makes successive corrections to a trial PES, based on the functional derivatives of the experimental data with respect to the PES.<sup>7</sup> One of the important aspects of this method is that it allows the value of the PES at every point in space to vary independently compared with the parameter-fitting methods. Because there are more discretization points for PES than data points (*i.e.*, ill-posedness of the inversion<sup>11-13</sup>), a reasonable regularization constraints have to be included for the stability of the solution, *e.g.*, smoothness of the potential.

In general, the experimental data can be obtained from either stationary (frequency-domain)<sup>7</sup> or time-dependent ex-

periments. The latter just recently becomes available as exciting real-time dynamical experiments, such as femtosecond transition-state spectroscopy (FTS).<sup>14-19</sup> Gruebele *et al.*<sup>18</sup> have reported on the use of FTS to yield accurate spectral information (vibrational and rotational) *via* the Fourier transformation and to invert directly to the PES using the semiclassical RKR method. (*i.e.*, frequency-domain inversion)<sup>20</sup>

In this paper, we present the time-dependent inversion method to extract PES of the excited state from tracking the time-dependent data<sup>21</sup> (*i.e.* the correlation function) which can be synthesized from frequency-domain measurements. For example the correlation function can be synthesized from the absorption profile to invert an excited-state PES with bound vibrational levels and from the Raman excitation profile (REP) to invert one with only continuous state (as in photodissociation). The merits of the time-dependent tracking inversion method<sup>21</sup> are following. First, there is no need to assign quantum numbers or, more generally, energy level labels. In many situations, it is notoriously difficult in frequency-domain inversion approach. However, the assignment problem is completely avoided in the tracking algorithm, since the time ordering of data does the assigning. Secondly, compared with the iterative inversion method in frequency domain the proposed inversion algorithm is direct and computationally efficient due to solving the inversion problem at each time step to extract PES piece by piece.

In the following section, we formulate the time-dependent inversion method based on the Tikhonov regularization procedure to extract PES from the correlation function. Next, we simulate the inversion of the potential of a diatomic molecule. This is followed by discussions on possible application of the inversion method to problems involving dipole function and REP.

## Theory

In this section, we develop the time-dependent inversion algorithm to extract PES of the excited state from frequency-domain measurements, such as the absorption profile. We consider the case of diatomic molecule where two elec-

tronic PES, a ground state and an excited state, and its vibrational coordinate are only relevant to the dynamics.

In the limit of the Condon approximation (to ignore dependence of the transition moments on internal nuclear coordinates), the initial nonstationary wave packet  $|\Psi_j(0)\rangle$  on the excited PES in the Frank-Condon (FC) region<sup>22</sup> can be prepared as

$$|\Psi_j(0)\rangle = \mu |\Phi_j\rangle \quad (1)$$

Then, these wave packet can be expressed as a coherent superposition of eigenstates  $|\phi_k\rangle$

$$|\Psi_j(0)\rangle = \sum_k a_{jk} |\phi_k\rangle, \quad a_{jk} = \langle \phi_k | \mu | \Phi_j \rangle \quad (2)$$

where  $\mu$  is the transition dipole moment and  $|\Phi_j\rangle$  is a known  $j$ -th vibrational wave function of ground electronic state from which the absorption initiated. Then the initial wave packets are propagated on the excited PES according to the time-dependent Schrödinger equation and the solution can be expressed as

$$i\hbar \frac{d}{dt} |\Psi_j(t)\rangle = H_e |\Psi_j(t)\rangle \quad (3)$$

$$|\Psi_j(t)\rangle = e^{-\frac{i}{\hbar} H_e t} |\Psi_j(0)\rangle \quad (4)$$

where  $H_e$  is the Hamiltonian for the excited electronic states.

Let us define the correlation function  $C_j(t)$  as

$$\begin{aligned} C_j(t) &= \langle \Phi_j | \mu e^{-\frac{i}{\hbar} H_e t} \mu | \Phi_j \rangle = \langle \Psi_j(0) | \Psi_j(t) \rangle \\ &= \sum_k |a_{jk}|^2 e^{-\frac{i}{\hbar} E_k t} \end{aligned} \quad (5)$$

where FC factor  $|a_{jk}|^2$  and energy  $E_k$  can be calculated from the absorption profile, so  $C_j(t)$  is known data term.

Also, it can be obtained from the fact that the absorption coefficient  $\epsilon_j(\omega)$  can be expressed as the Fourier transform of the correlation function  $C_j(t)$  as

$$\epsilon_j(\omega) = k \omega \int_{-\infty}^{\infty} e^{i\omega t} C_j(t) dt \quad (6)$$

where  $k$  is a collection of physical constants. With the known initial wave packet and the correlation function which can be obtained from the absorption profile, we want to extract PES of the excited state on which the wave packet is propagated. For this, we may rewrite Eq. (5) as

$$C_j(\Delta t) = \langle \Psi_j(0) | \Psi_j(\Delta t) \rangle = \langle \Psi_j(\tau) | \Psi_j(\tau + \Delta t) \rangle \quad (7)$$

Then one may notice that  $C_j(\Delta t)$  in the FC region give the same correlation data for any  $\tau$  outside the FC region. It is the key point of the time-dependent inversion algorithm. Further differentiating  $C_j(\Delta t)$  with respect to  $\Delta t$ , PES of the excited state can be related with it as

$$\begin{aligned} i\hbar \frac{dC_j(\Delta t)}{d\Delta t} &= \langle \Psi_j(\tau) | i\hbar \frac{d}{d\Delta t} | \Psi_j(\tau + \Delta t) \rangle \\ &= \langle \Psi_j(\tau) | T | \Psi_j(\tau + \Delta t) \rangle + \langle \Psi_j(\tau) | V | \Psi_j(\tau + \Delta t) \rangle \end{aligned} \quad (8)$$

where the Hamiltonian of the excited state is partitioned between kinetic and potential operators  $H_e = T + V$ . The time derivative of correlation function and the kinetic energy operator  $T$  is known and the potential  $V$  is what we want to

extract. Rearranging Eq. (8) gives the Fredholm integral equation of the first kind as

$$\int_0^{\infty} dR K_j(R, \Delta t) V(R) = g_j(\Delta t) \quad (9)$$

where the known term  $g_j(\Delta t)$  and the kernel  $K_j(R, \Delta t)$  in Eq. (9) are

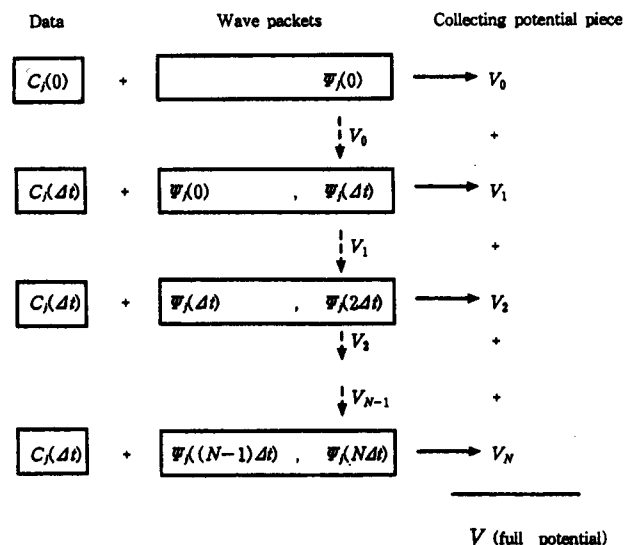
$$g_j(\Delta t) = i\hbar \frac{dC_j(\Delta t)}{d\Delta t} = \langle \Psi_j(\tau) | T | \Psi_j(\tau + \Delta t) \rangle \quad (10)$$

$$K_j(R, \Delta t) = \Psi_j^*(R, \tau) \Psi_j(R, \tau + \Delta t) \quad (11)$$

If we put  $\tau = \Delta t = 0$  (i.e., using the autocorrelation function  $C_j(0)$ ) in Eq. (9), the solution of the integral equation gives the local excited potential  $V_0$  where the initial nonstationary states  $\Psi_j(0)$  are localized in the FC region. Then, this piece of potential  $V_0$  are used to propagate the wave function  $\Psi_j(0)$  to the next time  $\Psi_j(\Delta t)$  according to the time-dependent Schrödinger equation by the split operator method of Feit and Fleck.<sup>23</sup> The wave function at the next time step can be expressed as

$$\begin{aligned} |\Psi_j(\tau + \Delta t)\rangle &= \exp\left[\frac{-i}{\hbar} H_e \Delta t\right] |\Psi_j(\tau)\rangle \\ &\approx \exp\left(\frac{-i}{2\hbar} T \Delta t\right) \exp\left(\frac{-i}{\hbar} V_\tau \Delta t\right) \exp\left(\frac{-i}{2\hbar} T \Delta t\right) |\Psi_j(\tau)\rangle \end{aligned} \quad (12)$$

With the known  $\Psi_j(0)$  and  $\Psi_j(\Delta t)$  (i.e., using the correlation function  $C_j(\Delta t)$ , Eq. (9) gives the next piece of the potential  $V_1$ . With  $V_1$ , the wave function at the next time step  $\Psi_j(2\Delta t)$  can be obtained by propagation and wave functions  $\Psi_j(\Delta t)$  and  $\Psi_j(2\Delta t)$  allow to get  $V_2$  from Eq. (9), etc. The process of inversion plus propagation continues until the wave functions have sampled all dynamically accessible regions of the PES as shown in Figure 1. Finally the potential is the sum of these pieces  $V_i$ . We should point out that the known data term (the time derivative of correlation function) are the same at any time  $\tau$ , so once the known data term is calculated in the FC region, it can be used at any time  $\tau$  for



**Figure 1.** Time-dependent tracking inversion method algorithm, where the solid line is the inversion by  $\Psi_j((i-1)\Delta t)$  and  $\Psi_j(i\Delta t)$ , and the dash line is the propagation by  $V_i$ ,  $i=1, 2, \dots, N$ .

all PES regions.

In general, with the known PES, the correlation function can be calculated from Eq. (3), because this forward problem is usually well-posed problem and it has a unique solution. However, the inverse problem to extract PES from experiments data, is ill-posed problem because it corresponds to the determination of the continuous PES from given a set of discrete data (observable measurements). Thus, a reasonable regularization constraint, e.g. smoothness of PES, is needed to solve Eq. (9). For this, Eq. (9) can be transformed, via integration by parts as:

$$g_j = \int_0^\infty dR K_j^{[2]}(R) V^{(2)}(R) \quad (13)$$

where

$$\int_0^R K_j^{[n]}(R') dR' V^{(n)}(R) \Big|_{R=0}^0 = 0, \quad n=0, 1, \dots \quad (14)$$

$$K_j^{[2]}(R) = - \int_0^R dR' K_j^{[1]}(R') \quad (15)$$

$$V^{(2)}(R) = \frac{d^2 V(R)}{dR^2} \quad (16)$$

Here we have taken into account the fact that the potential, as well as its derivative  $V^{(n)}(R)$  usually approach zero quickly as the internuclear distance  $R \rightarrow \infty$ . Then, the regularized solution in Eq. (13) is achieved by minimizing the following functional<sup>7</sup>:

$$J[V^{(2)}, g_j] = \sum_j \left| \int_0^\infty dR K_j^{[2]}(R) V^{(2)}(R) - g_j \right|^2 + \alpha \int_0^\infty dR [V^{(2)}(R)]^2 \quad (17)$$

The regularization parameter  $\alpha$  denotes the tradeoff between reproducing the data and the solution being smooth. If we choose too small an  $\alpha$  value, PES overfitted with the data and lose the smoothness. On the other hand, the resolution of PES may be very poor if we try to oversuppress the smoothness of PES by choosing too large an  $\alpha$  value. Consequently, it is necessary to properly choose an  $\alpha$  value for Eq. (17) to yield an adequate PES.

Taking the variation of the functional with respect to  $V^{(2)}(R)$ , we obtain

$$\int_0^\infty dR' K(R, R') V^{(2)}(R') + \alpha V^{(2)}(R) = \sum_j K_j^{[2]}(R) g_j \quad (18)$$

where

$$K(R, R') = \sum_j K_j^{[2]}(R) K_j^{[2]}(R') \quad (19)$$

The solution of Eq. (18) is

$$V_\alpha^{(2)} = \sum_j \frac{(u_j^T g_j)}{w_j^2 + \alpha} w_j v_j(R) \quad (20)$$

where  $u_j, v_j(R)$  are the singular function for the kernel  $K_j^T$  and  $K_j$  with singular values  $w_j$

$$\sum_j K_j^{[2]}(R) u_{j,p} = w_p v_p(R) \quad (21)$$

and

$$\int_0^\infty dR K_j^{[2]}(R) v_p(R) = w_p u_{j,p} \quad (22)$$

For more detailed derivation, see refs. 7.

The inversion is actually achieved through the 2nd derivative  $V^{(2)}(R)$  instead of  $V(R)$  itself, which imposed a smoothness condition on  $V(R)$ , we need to integrate 2 times from  $V^{(2)}(R)$  to get  $V(R)$  as

$$V^{(k-1)}(R) = - \int_R^\infty V^{(k)}(R') dR' \quad (23)$$

## Calculations

To test the time-dependent inversion algorithm, we simulate the inversion of PES of a diatomic molecule. For the simplicity, the ground state and the excited state are taken as a harmonic and Morse oscillator, respectively. Here, we adopt a fully dimensionless representation through scale transformation. Hence, the dimensionless Hamiltonian, momentum, internuclear distance are defined in terms of their dimensional counterparts with a hat by<sup>21</sup>

$$H = \frac{\hat{H}}{2D_e}; \quad p = \frac{\hat{p}}{\sqrt{2\mu D_e}}; \quad x = \alpha r. \quad (24)$$

where  $D_e, \mu$  and  $\alpha$  denote the dissociation energy, the reduced mass and the range parameter of the Morse potential, respectively. Thus, the scaled excited state Hamiltonian can be expressed as

$$H_e = \frac{\hat{H}_e}{2D_e} = T + V = \frac{\hat{p}^2}{2} + \frac{1}{2} (1 - e^{-\alpha x})^2 - \frac{1}{2} \quad (25)$$

and the effective Plank constant can be written as

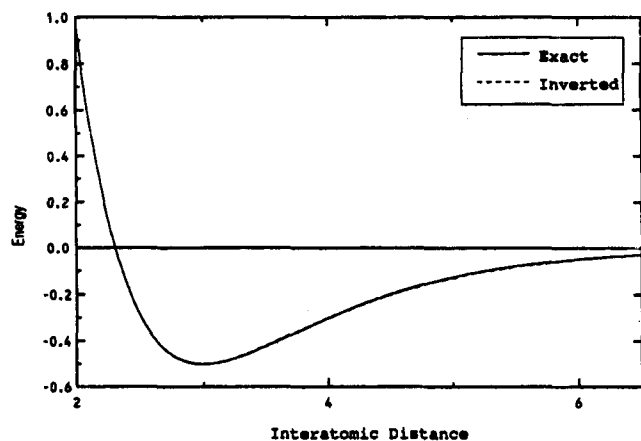
$$\hbar_{eff} = -i [x, p] = -i \left[ \alpha r, \frac{\hat{p}}{\sqrt{2\mu D_e}} \right] = \frac{\alpha \hbar}{\sqrt{2\mu D_e}} = \left[ N_B + \frac{1}{2} \right]^{-1} \quad (26)$$

where  $N_B$  is the number of bound states that the excited potential  $V$  supports. Within the Condon approximation, at time  $t=0$  the laser transfer initial ground state wave functions  $|\Phi\rangle$  to the excited state as  $|\Psi_f(0)\rangle$ .  $|\Psi_f(0)\rangle$  is not eigenstates of the excited state Hamiltonian  $H_e$  and become moving wave packets  $|\Psi_f(t)\rangle$  on the excited state.

In the simulation, the initial wave packets  $|\Psi_f(0)\rangle$  are taken as 4 harmonic oscillators of ground state and  $\hbar_{eff}=0.05$ , which means that the Morse potential supports 20 bound states. From these initial condition, one may generate the correlation function  $C_f(t)$  by propagating initial wave packets on the exact PES. We use the second derivative of the potential for smooth constraint and the numerical grid contained 1024 points with  $\Delta x=0.01$ . We certify that the result has no essential difference between propagation time step  $\Delta t=0.01$  and  $\Delta t=0.005$ , so  $\Delta t=0.005$  is adopted in inversion calculation. In a dimensionless unit, the propagation time and a dimensionless constant are

$$\Delta t = \omega_0 \hat{\Delta t}, \quad \omega_0 = \alpha \left( \frac{2D_e}{\mu} \right)^{1/2}. \quad (28)$$

If we may choose  $D_e \approx 0.1$  au,  $\mu \approx 2000$  au and  $\alpha \approx 1$  ( $\text{au}^{-1}$ ), then  $\omega_0 \approx 0.01$  au and  $\hat{\Delta t} \approx 0.5$  au. From these in-

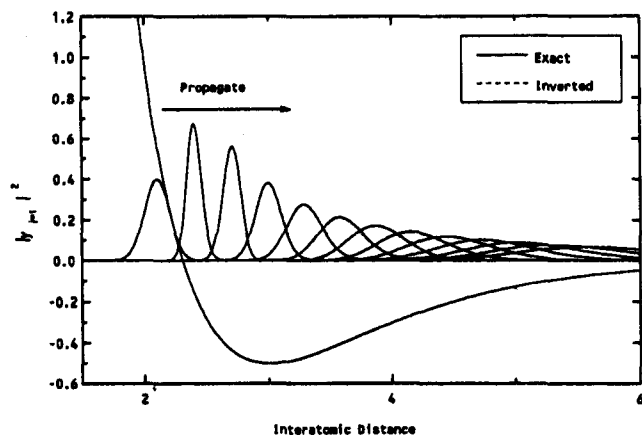


**Figure 2.** The solid line is exact PES and the dash line is inverted PES.

initial conditions, we have performed the relay of the regularized inversion procedure and time-dependent wave-packet propagation to extract the underlying potential piece by piece. Figure 2. shows the comparison of the inverted potential with the exact one. It is found that the inverted potential closely resembles the exact one over the whole region, but is slightly lower than the dissociation threshold of the exact one. The discrepancy at the large distance can be attributed to the error accumulated by propagating the wave packet. For more detail analysis, the wave function on the inverted potential at fixed time intervals is compared to those obtained by the propagation on the exact potential in Figure 3. The wave functions propagated on the inverted potential have no essential difference from the exact ones, except that a small fluctuation is visible at the large distance, which results from the finite size of the chosen numerical grid.

### Discussion

The time-dependent inversion method have been developed to extract the excited-state PES from tracking the time-dependent data, *i.e.*, the correlation function, which



**Figure 3.** The wave function  $|\Psi_{j,t}|^2$  at successive intervals of time is obtained by the propagation on the inverted potential and the exact one.

can be synthesized from the absorption profile. Using the inversion of the local PES and wave-packet propagation by turns, we have demonstrated this algorithm extract underlying PES piece by piece for a model diatomic molecule.

Compared to the time-independent inversion methods, the time-dependent tracking inversion approach has several advantages. Quantum number assignments are needed in time-independent method in order to compare the experimental data to the corresponding data generated from the trial potential. The assignment process is very difficult in many situation, for example, when the potential is multidimensional and spectra are nonseparable. However, in the tracking approach, the assignment is completely avoided, since the time does the assigning.

Also, the proposed tracking inversion method is computationally efficient. The timeindependent inversion method usually require time consuming iterative calculation for convergence. However, in the tracking approach, the inversion problem is direct and is solved just once at each time step. Furthermore, the size of the inversion problem is much smaller than that in the time-independent methods because the potential is inverted piece by piece where the wave-packet is localized. Also, once the correlation function is determined in the FC region it can be used to extract the PES out of the FC region because Eq. (6) holds for any time  $\tau$ .

Finally, we note that the proposed approach can be extended to extract the dipole function from the same type of data, and to extract PES from the correlation function synthesized from the Raman Excitation profile.

**Acknowledgment.** This research was supported by the Basic Science Research Institute Program, Ministry of Education of Korea (BSRI-96-3428).

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## Collisional Excitation using Metastable Helium Jet Produced in a Graphite Tube Nozzle

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Received August 22, 1997

The graphite tube nozzle has been developed for the generation of metastable He jet by which the nitrogen molecules initially excited in a jet with Engelking type nozzle have been further excited in a corona excited supersonic expansion. The excitation process of nitrogen molecules in the jet collision has been discussed in detail by observing the emission intensity from the vibronic emission spectra of nitrogen molecules and nitrogen molecular ions upon helium jet collision.

### Introduction

The transient molecules are of considerable interest in chemistry because they are believed to play important roles in chemical reaction as reaction intermediates.<sup>1</sup> So far, many experimental techniques have been developed to produce these short lived molecules because they only exist under abnormal conditions. One of the most popular methods obtaining these molecules is to decompose the stable precursor by providing the molecules with the external energy using the methods such as microwave discharge, electric discharge, chemical reaction, photolysis, etc.<sup>2</sup>

As one of the most convenient devices, Engelking has recently developed the supersonic nozzle system using an electric discharge, which is called a corona excited supersonic expansion.<sup>3,4</sup> This has been widely used for the observation of the vibronic emission spectra of rotationally cooled transient molecules in the gas phase because it gives enough continuous photon intensity for the high resolution studies of weak transitions in a jet.<sup>5-8</sup> Nevertheless, this method is only suitable for the transitions of large Franck-Condon factor as well as of small excitation energy. In addition to these limitation in this scheme, the excitation is only possible to the energy states with long lifetime because of the rapid collisional relaxation process occurring at the high pressure region after excitation by electron impact.<sup>7</sup>

A technique using a jet collision in an expansion chamber has been devised as another method for the effective energy transfer. Cossart and Cossart-Magos<sup>9</sup> have succeeded the observation of the emission spectra of highly excited CO<sup>+</sup> in the gas phase employing jet collision between metastable Ne atom and CO molecule generated from Geissler type electric discharge. The same technique has been ap-

plied for the generation of CS<sup>+</sup> by collision of the metastable He atom with long-lived CS radical.<sup>10</sup> Li and coworkers have applied the jet collision process to the energy transfer reaction between rare gas atom and small precursor molecules for observation of the dissociative excitation of small molecules.<sup>11-13</sup> This method was also used for the collision between small molecules under molecular beam conditions.<sup>14</sup> Recently, Tokeshi *et al.* employed the ion-molecule collisions to generate the unstable molecular ion for observing the emission spectra of CH produced in collisions of Ar<sup>+</sup> with aliphatic compounds.<sup>15</sup>

Very recently, we have reported the development of excitation technique using jet collision in a corona excited supersonic expansion.<sup>16</sup> In this scheme, two identical Engelking type nozzles were employed for the excitation of both target and colliding jets. The nitrogen molecules initially excited by the electron impact were further excited by the collision of metastable He atomic jet, leading to produce the nitrogen molecular ions at the excited state. Although this method has been turned out to be very effective for highly excitation process, there exists a technical difficulty in maintaining the electrical discharge at both nozzles.

In this work we have modified the excitation scheme using the graphite tube nozzle instead of Engelking type nozzle for the colliding atomic jet. The target nitrogen molecules initially excited using Engelking type nozzle in a corona excited supersonic expansion are further excited to nitrogen molecular ions *via* jet collision with metastable He atoms.

### Experimental Details

Figure 1 illustrates the schematic diagram of the jet col-