Quantal study of the exchange reaction for $N + N_2$ using an *ab initio* potential energy surface

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Abstract

The $N + N_2$ exchange rate is calculated using a time-dependent quantum dynamics method on a newly determined *ab initio* potential energy surface (PES) for the ground $^4A''$ state. This *ab initio* PES shows a double barrier feature in the interaction region with the barrier height at 47.2 kcal/mol, and a shallow well between these two barriers, with the minimum at 43.7 kcal/mol. A quantum dynamics wave packet calculation has been carried out using the fitted PES to compute the cumulative reaction probability for the exchange reaction of $N + N_2(J{=}0)$. The $J - K$ shift method is then employed to obtain the rate constant for this reaction. The calculated rate constant is compared with experimental data and a recent quasi-classical calculation using a LEPS PES. Significant differences are found between the present and quasiclassical results. The present rate calculation is the first accurate 3D quantal dynamics study for $N + N_2$ reaction system and the *ab initio* PES reported here is the first such surface for N_3.

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The high-speed entry of a spacecraft into the Earth's atmosphere imparts a large amount of heat to the ambient gas. This large heat load excites, dissociates and ionizes the atoms and molecules in the atmosphere. The radicals and ions so formed are chemically reactive and the reactions can proceed rapidly under the high temperature conditions. Both the heat load, and the reactivity of the species produced are important data for heat shield design. Since the major component of the Earth's atmosphere is N_2, the exchange and dissociation reactions of nitrogen play primary roles in flow-field modeling and in determining the heat load on spacecraft surfaces. Thus the rate constants of these reactions are part of the necessary database for heat shield design. The nitrogen reactions are also important in other high temperature environments involving N_2 gas, such as shock tube experiments and comet/meteor entry into Titan's atmosphere. Experimental measurements for these high temperature ($\backsim$ 20,000 K) reactions are difficult and extrapolations from lower temperature data are generally unreliable. Consequently theoretical calculations become the only available means to determine these high temperature rate constants.

It has been shown in recent years that the time-dependent quantum dynamics scattering method can provide reliable rates for atom-diatom and diatom-diatom reactions[1]. However, most of the studies so far have been for relatively light systems, involving one or more hydrogen atoms[1], as a result of the relatively low computational cost for light-atom systems. In contrast, heavy-atom systems are seldom studied due to the large amount of computational resources required. Up to now no accurate quantum dynamics study has been applied to the $N + N_2$ reaction system,although several classical trajectory and quasi-classical calculations [2–8] have been reported based on an empirical LEPS PES by Laganà et al.[2].

Another bottleneck in solving the $N + N_2$ problem is the lack of a reliable PES. Up to now only the empirical LEPS surface[2] has been available. This PES has a linear transition state, with a barrier height at 36 kcal/mol, which is the lower limit of the activation energy deduced from the results of a nuclear radiation experiment[9]. Apparently the choice of transition state geometry and barrier height for the LEPS surface is not based on any *ab initio* calculations. Later studies[10, 11] indicate a non-linear transition state to be likely; a change of transition state geometry from linear to bent would make it more efficient to transfer collision energy into effective motion along the reaction path. Nevertheless, the original LEPS surface was still used in recent studies of vibrational excitation[7] and

exchange and dissociation reactions[8] of the $N + N_2$ system.

In this communication, we report the first *ab initio* calculation of the full surface of the N_3 system. An analytical PES is then derived by fitting the 3326 *ab initio* points using 68 parameters. A time-dependent wave packet study of the exchange reaction

$$N + N_2(\nu, j) \rightarrow N_2(\nu', j') + N \tag{1}$$

is then carried out using the fitted surface. We believe this is the first accurate 3D quantum dynamics study for this reaction. As seen below, the *ab initio* surface has entirely different characteristics from the LEPS surface. In particular, the *ab initio* surface has double barriers in the transition state region. Only a quantal treatment can describe the quantum interference effect between the two barriers.

The lowest N_3 state is a $^4A''$ state. The global minimum of the surface corresponds to the van der Waals minimum at large N-N_2 separation. Because the bonding nature changes at different N_3 geometries, different quantum chemical treatments and different Gaussian basis sets are used in different regions of the surface. A detailed description of the *ab initio* calculation and the fitting of the PES will be presented elsewhere[12]. Briefly, the region with large $N + N_2$ separation distance is calculated using the open shell CCSD(T) method (spin-unrestricted couple-cluster singles and doubles with perturbation-correction of triples) as formulated by Watts et al.[13] using Dunning's cc-pVQZ Gaussian basis[14, 15] plus bond functions placed midway between the N atom and the center-of-mass of the N_2 molecule. Basis set superposition error is important in this region and corrections for BSSE have been carried out[16]. For the region with one N-N bond distance less than 4 a.u., the potential energies are determined using the CCSD(T) method as formulated by Knowles et al.[17] using Dunning's aug-cc-pVTZ Gaussian basis[14, 15]. The validity of the use of the CCSD(T) method has been confirmed by selected calculations using the ICMRCI (internally contracted multi-reference configuration-interaction) method[18, 19]. In the region where all three N-N bonds are large, the ICMRCI method is used in the calculations. All calculations used the computer code MOLPRO[20].

The N_3 energy is specified by the three Jacobi coordinates [16]; i.e., the separation distance r of a diatomic molecule, the separation distance R from the center of the atom to the center of mass of the diatomic molecule, and the angle θ between r and R. The N_3 energy is determined using a many-body expansion[21]; the three-particle contribution to

the short-range N_3 energy is constructed from an expansion of the form

$$V_3(r,R,\theta) = \exp(-\alpha r^2 - \beta R^2)\sum A_{lmn} r^l R^m P_{2n}(\cos\theta) \quad (2)$$

where $P_{2n}(\cos\theta)$ is a Legendre polynomial. The coefficients A_{lmn} are chosen to conform to the symmetry of the N_3 molecule and and the values of l, m, and n are selected to satisfy the convergence criterion stated in Ref. 21. The values of A_{lmn} and the Gaussian cut-off coefficients[22] α and β are determined from the *ab initio* data using a nonlinear least-squares fitting program LDER1 from the MINPACK package[23]. The 3-particle contribution to the long-range N_3 energy is adapted from the results of Ref. 16.

The present *ab initio* PES for N_3 is drastically different from the LEPS surface. Not only is the lowest-lying transition state on the *ab initio* PES nonlinear, but the PES actually has double barriers, i.e., two transition states connected by a shallow well. The two barriers are symmetric with respect to interchange of two N atoms. Thus one is located in the entrance channel and the other in the exit channel of the exchange reaction. Based on the fitted PES, the lengths for the two $N-N$ bonds of the two barriers are 2.23 a.u. and 2.80 a.u. respectively and the bond angle is 119°. The shallow well between the two barriers, corresponding to a metastable N_3 state, has C_{2v} symmetry with both bond lengths at 2.40 a.u. and the bond angle is 120°. Fig. 1 shows a contour plot of the fitted *ab initio* PES in term of two $N-N$ bonds with the angle fixed at the transition state angle (119°). The height of the two barriers is 47.2 kcal/mol and the shallow minimum is 3.5 kcal/mol below the barrier.

Geometry optimizations and harmonic frequency analysis were performed at the Knowles formulated CCSD(T) and the CASSCF(15 electrons in 12 orbitals) levels of theory using the aug-cc-pVTZ basis set to confirm the existence of the double barrier and shallow well features. Vibrational analyses show that the two barrier tops are true transition states with one imaginary frequency and the shallow well is a true minimum with all real frequencies. The geometries of the transition state and the well, determined using the geometry search approach with the CCSD(T) method and the results of the fitted *ab initio* PES, are tabulated in Table 1. Good agreement is obtained in a comparison between the fitted results and the geometry search. The CASSCF search gives the transition state geometry as $r_a(r_b) = 2.28$ a.u., $r_b(r_a) = 2.64$ a.u., and $\theta = 117°$ and the well geometry as $r_a = r_b = 2.41$ a.u. and $\theta = 118°$. The CASSCF geometry is somewhat different from the RCCSD(T) values, a result

of the different treatment of electron correlation. Nevertheless, the three sets of results are sufficiently close that we consider the nature of the transition states and the well to be confirmed.

The characteristics of the transition state region are further confirmed by ICMRCI calculations at the transition state and metastable minimum geometries as determined by the CCSD(T) geometry search. At the shallow well geometry, the Hartree-Fock function in the ICMRCI wave function has a coefficient of 0.90, and at the transition state geometry its coefficient is 0.91. Also, the energy order for these two points are maintained in the ICMRCI calculation. Thus the ICMRCI result justifies the use of CCSD(T) method to characterize the transition state region.

A time-dependent wave-packet method[24] is employed to carry out a three dimensional calculation for the initial state selected probability for $J = 0$ in the Jacobi coordinates. The parameters for this calculation are: 280 sine functions to expand the translational coordinate,160 DVR vibrational basis for the $N - N$ coordinate and 70 even(j_{max}=140) or odd(j_{max}=141) Legendre functions for the angular part. For total energy up to 4.0 eV, 10 vibrational open channels, and a total of 771 open vibrational-rotational initial states need to be considered for the cumulative reaction probability for $J = 0$. Then the $J - K$ shifting method[25] is applied to calculate the total cumulative reaction probability for the rate constant calculation. Each initial state reaction probability calculation is performed with 32 CPU on an SGI Origin 3000 system. In total about 10,000 CPU hours have been used for the quantum dynamics rate constant calculation.

Fig. 2 shows the cumulative reaction probability, for J=0, as a function of total energy. It clearly shows the reaction resonances caused by the well in the potential energy surface, especially at the lower scattering energies. Detailed analysis will be pursued in future studies.

Fig. 3 compares the present 3D quantum dynamics rate based on our *ab initio* PES and the quasi-classical results calculated by Capitelli et al.[8] based on the LEPS with available experimental data[9, 26, 27]. The error for data from Ref. [26] is estimated based on the spread of their data in their Fig. 6. Note that Lyon[9] and Back and Mui's[27] experiments only give the upper limits for the rate constant at 1273 K. The comparison shows differences of the rate constants from the present results and the quasi-classical results. This is attributable mainly due to the different characteristics of our *ab initio* PES and the LEPS, as well as the difference between the dynamics treatment. All these quoted experimental

measurements have large uncertainties and cannot be used to differentiate between the two sets of the theoretical results. Based on the quality of our *ab initio* PES and the established reliability of our quantum dynamics treatment, we consider the present set of rate constants to be suitable for flowfield modeling purposes.

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Table 1. Parameters of the two transition states and well.

	RCCSD(T) Search	fitted PES
transition state	$r_a(r_b)$=2.21 a.u.	$r_a(r_b)$=2.23 a.u.
	$r_b(r_a)$=2.84 a.u.	$r_b(r_a)$=2.80 a.u.
	θ = 117°	θ= 119°
	ΔE=47.1 kcal/mol[a]	ΔE= 47.2 kcal/mol[a]
well	r_a=2.39 a.u.	r_a=2.40 a.u.
	r_b=2.39 a.u.	r_b=2.40 a.u.
	θ=120°	θ=120°
	ΔE=44.7 kcal/mol[a]	ΔE=43.7 kcal/mol[a]

[a] With respect to the reactant energy $N + N_2$.

Fig. 1 Contour plot of the fitted potential energy surface based on 3326 *ab initio* points in terms of the two $N - N$ bond distances r_a and r_b. The bond angle is fixed at the transition state 119°.

Fig. 2 Cumulative Reaction Probability for $J = 0$ as a function of the total energy.

Fig. 3 Comparison of the present quantal rate on our *ab initio* PES and quasi-classical rate[8] on LEPS with experimental data: Lyon[9], Bar-Nun and Lifshitz[26], Back and Mui[27].

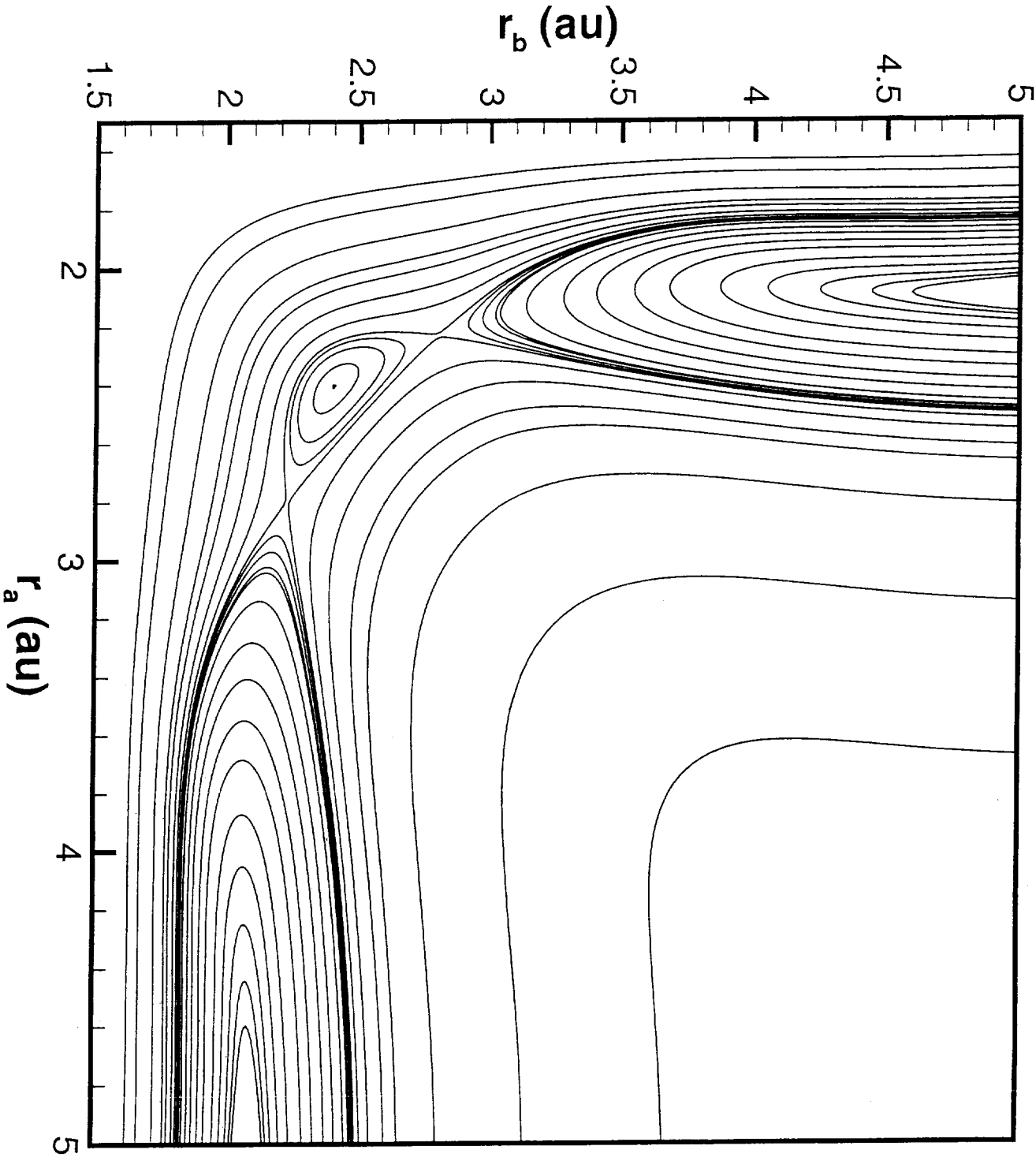

Fig. 1

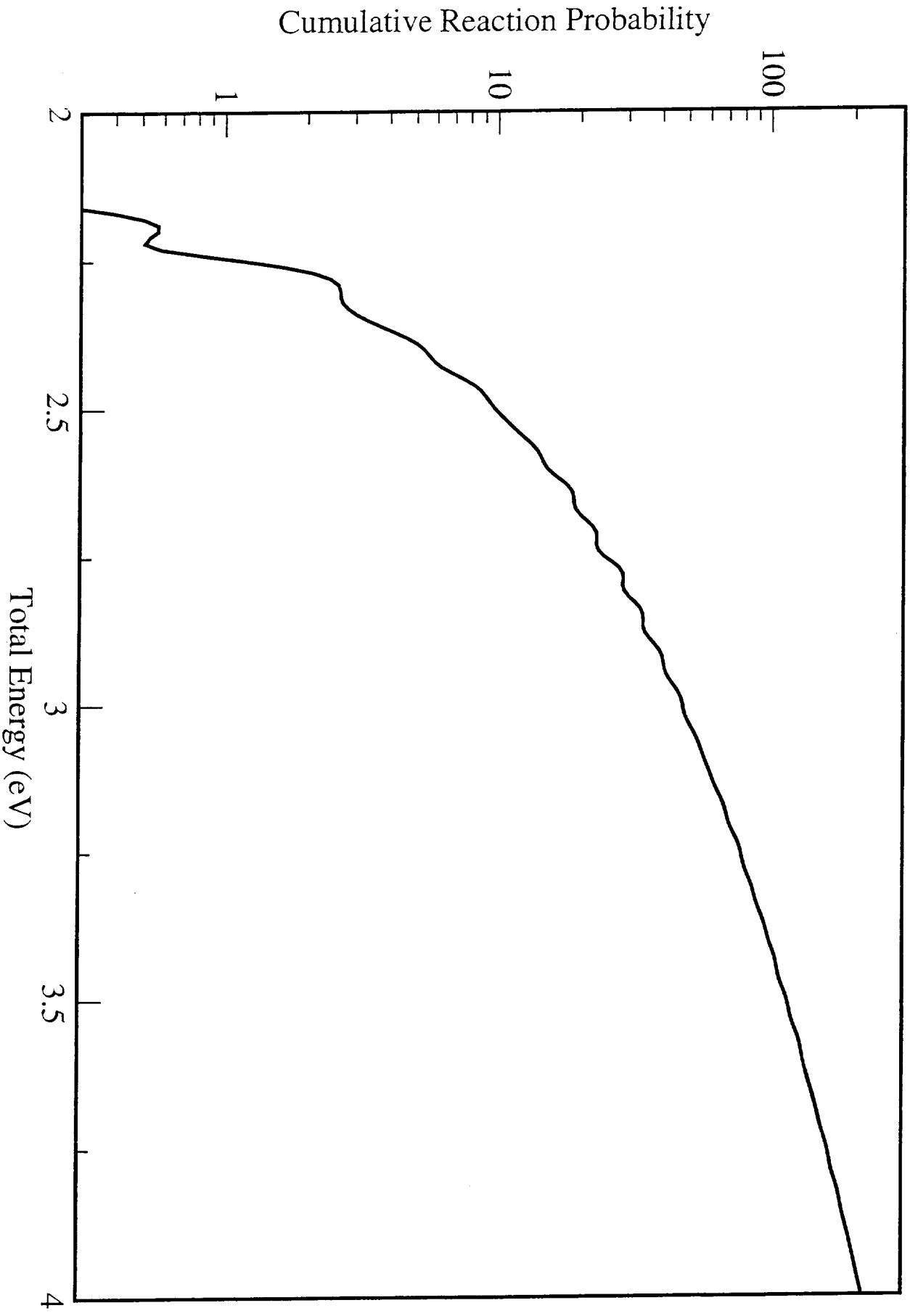
Cumulative Reaction Probability
1
10
100
2
2.5
3
3.5
4
Total Energy (eV)

Fig. 2

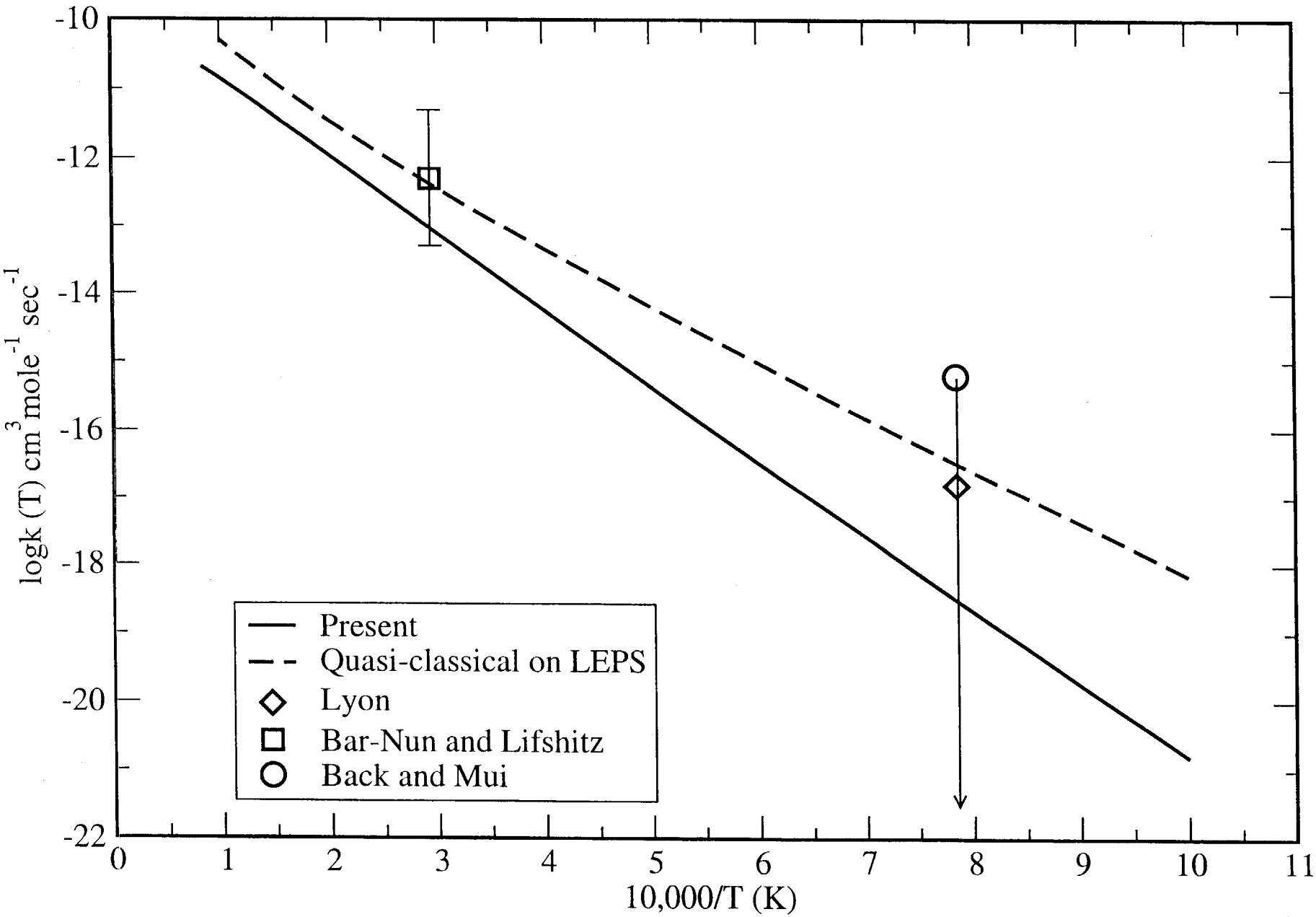
-10
-12
-14
-16
-18
-20
-22
0
1
2
3
4
5
6
7
8
9
10
11
logk (T) cm^{3}mole^{-1} sec^{-1}
10,000/T (K)
Present
Quasi-classical on LEPS
Lyon
Bar-Nun and Lifshitz
Back and Mui

Fig. 3