

A first principles theoretical determination of the rate constant for the dissociation of singlet ketene

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State-of-the-art *ab initio* quantum chemical techniques have been employed in the determination of the reaction path and attendant energetics for the singlet dissociation of CH₂CO. Variational RRKM calculations implementing these results provide first principles predictions for the dissociation kinetics which are in quantitative agreement with the corresponding experimental data.

Rice–Ramsperger–Kassel–Marcus (RRKM) theory has been and continues to be widely used in the chemical kinetics community as a means of interpolating and extrapolating the temperature and/or pressure dependence of unimolecular reactions.¹ Accordingly, it is of fundamental importance to understand its limits of validity and to enhance the accuracy of its implementations. The singlet dissociation of ketene provides an excellent opportunity for a quantitative assessment of the validity of RRKM theory, or more precisely of its form which constitutes variational transition state theory.² Recent groundbreaking energy-resolved experimental studies of the product state distributions^{3–9} and of the rate constants in real time¹⁰ have provided data which are among the most detailed, accurate, and wide ranging for any dissociation, thereby placing stringent limits on any RRKM modeling. Furthermore, the relatively small size of ketene facilitates accurate quantum chemical determinations of the reaction energetics. Finally, the singlet dissociation of ketene is exemplary of the class of unimolecular reactions for which there is no reverse barrier. For such reactions quantitative, nonempirical tests of the validity of RRKM theory have been very limited.¹¹

An earlier theoretical study¹² has demonstrated that RRKM models can simultaneously provide a quantitative description of the energy dependence of the rate constants and the product rovibrational distributions for the singlet dissociation of ketene. However, this investigation employed a simple model potential energy surface and thus, as in most RRKM studies, could not be taken as definitive evidence for the quantitative validity of the theory. Furthermore, subsequent variational RRKM calculations implementing a potential based on second-order Møller–Plesset perturbation theory (MP2)¹³ with a 6-31G* basis set¹⁴ yielded rate constants which were in error by as much as a factor of 4.¹⁵ Such discrepancies in the rate constant suggest corresponding errors in the product state distributions, which were not explicitly calculated, however.

This communication describes a definitive, first principles RRKM calculation of the dissociation kinetics for the CH₂CO → ¹CH₂ + CO reaction. Within RRKM theory, the microcanonical rate constant, k_{EJ} , for dissociation at energy E and total angular momentum J , is given by¹

$$k_{EJ} = \frac{N_{EJ}^{\ddagger}}{h\rho_{EJ}} \quad (1)$$

In this study, the evaluation of the reactant density of states, ρ_{EJ} , is based on a high-level *ab initio* quartic force field,¹⁶ while the enumeration of the number of accessible states (N_{EJ}^{\ddagger}) at the transition state is based on a bond-length reaction coordinate variational RRKM formalism directly implementing high-level *ab initio* predictions for the CH₂⋯CO interaction potential.¹⁷

The scheme employed in the determination of the quartic force field for the reactants is described in more detail in a forthcoming publication.¹⁶ The quadratic force field was determined at the coupled-cluster singles and doubles (CCSD)¹⁸ level of theory with a basis set nominally of quadruple-zeta quality including 2 sets of correlation-optimized polarization functions on all atoms. This basis set, which is denoted QZ(2*d*, 2*p*) here, was also augmented for various applications by higher-order polarization manifolds on all atoms to give a QZ(2*d*1*f*, 2*p*1*d*) set.¹⁹ The reference geometry employed in these CCSD/QZ(2*d*, 2*p*) computations was obtained from structural optimizations at the CCSD(T)/QZ(2*d*1*f*, 2*p*1*d*) level, which includes a perturbative contribution from connected triple excitations.²⁰ The cubic and quartic force constants were then determined via finite differences of analytic MP2/QZ(2*d*, 2*p*) second derivatives²¹ around the CCSD(T)/QZ(2*d*1*f*, 2*p*1*d*) optimized geometry. The resulting reference quartic force field was then employed in the computation of anharmonic fundamental vibrational frequencies by means of standard spectroscopic perturbation theory.²² A fitting procedure involving very *minor* adjustments to the reference geometry (i.e., coordinate shifts of less than 0.007 Å and 0.11°) and to the quadratic part of the force field (variations typically less than 1%) then yielded agreement to within 3 cm⁻¹ between the calculated and experimental fundamentals of the isotopomers of ketene.

The reactant number of available states was obtained through the direct summation over each of the vibrational quantum numbers of a step function in the total energy minus the state-dependent vibrational energy, i.e.,

$$N_{\text{vib,reactants}}(E) = \sum_{i_1, \dots, i_9}^{N_{i_{\text{max}}}} \Theta(E - E_{i_1, \dots, i_9}), \quad (2)$$

TABLE I. Transitional mode force constants.^a

ij^b	$R_{CC}=2.2$	$R_{CC}=2.5$	$R_{CC}=2.8$	$R_{CC}=3.1$
55	0.1437(0.14) ^c	0.0676(0.061)	0.0375(0.035)	0.0233(0.023)
65	0.1451(0.14)	0.0801(0.080)	0.0437(0.045)	0.0251(0.026)
66	0.5704(0.60)	0.3604(0.37)	0.2019(0.20)	0.1075(0.11)
88	0.4324(0.44)	0.2345(0.24)	0.1113(0.11)	0.0499(0.051)
98	-0.0194(-0.019)	-0.0083(-0.0085)	-0.0036(-0.0034)	-0.0017(-0.0017)
99	0.0058(0.0078)	0.0024(0.0039)	0.0012(0.0019)	0.00069(0.00091)

^aForce constants in units of $\text{mdyn } \text{\AA}/\text{rad}^2$.

^bModes 5, 6, 8, and 9 correspond to the CCO bending angle, the symmetric and antisymmetric HCC bending angles, and the symmetric HCCO torsional angle, respectively. The complementary conserved mode coordinates employed in these force constant evaluations are the symmetric CH stretch, the CO stretch, the HCH bend, the fixed CC stretch, and the antisymmetric CH stretch.

^cThe principal entries are CCSD/QZ(2*d*, 2*p*) values, and those in parentheses are MP2/6-31G* results.

with E_{i_1, \dots, i_9} determined via perturbation theory²² from the aforementioned adjusted anharmonic force field. The density of states was then obtained by analytic differentiation of a functional form which smoothly fits $N_{\text{vib, reactants}}$.¹⁷ At high vibrational energies, some uncertainty exists regarding the contribution to the off-diagonal anharmonicities arising from Coriolis interactions and a particular Fermi resonance. The present calculations of the rate constants employ the state density which we consider to be most accurate, viz., that entailing the neglect of Coriolis contributions to the anharmonicities. Interestingly, at the threshold for the *triplet* dissociation this density is 1.34×10^4 states per cm^{-1} , in comparison with an estimate by Moore and co-workers of 4.5×10^4 states per cm^{-1} .²³ However, the explicit determination of this density of states from the triplet rate constant data is highly uncertain and warrants further investigation.

The first step in evaluating N_{EJ}^\dagger involves the determination of the minimum energies along the reaction path. Here, the CC bond length (R_{CC}) is assumed to provide an accurate parametrization of the reaction path in the neighborhood of the variational transition states. The present calculations have focused on the determination of the minimum energies and geometries for the four specific, fixed CC bond lengths of 2.2, 2.5, 2.8, and 3.1 \AA , covering the range of transition state locations determined in our prior study.¹⁵ First, fully optimized structures and energies at each R_{CC} were obtained at the CCSD(T)/QZ(2*d*1*f*, 2*p*1*d*) level of theory. To these energies, R_{CC} -dependent correction factors were appended to account for the incompleteness of the basis set and higher-order electron correlation terms. The basis set correction factor was obtained as the difference between MP2/QZ(2*d*1*f*, 2*p*1*d*) interaction energies and corresponding predictions with an extended (13*s*8*p*6*d*4*f*, 8*s*6*p*4*d*) set.²⁴ The correction factor for higher-order electron correlation effects was obtained with the aid of Brueckner doubles calculations including perturbative corrections for connected triple and quadruple excitations [BD(TQ)],²⁵ as given by the standard 6-31G* basis set.¹⁴ Finally, an exponentially decaying bond additivity correction (BAC)^{17,26} was incorporated to bring the asymptotes of the potential curve into exact coincidence with the precisely known experimental dissociation energy.⁴ At the four R_{CC} values of 3.1, 2.8, 2.5, and 2.2 \AA , this BAC takes on the values -1, -17, -57, and -156 cm^{-1} , yielding

final estimates for the optimized interaction energy of -861, -1409, -2454, and -4818 cm^{-1} , respectively.

The next step in the present evaluation of N_{EJ}^\dagger involved the determination of CCSD/QZ(2*d*, 2*p*) force fields at the same values of R_{CC} . Corresponding vibrational frequencies were then obtained via a standard FG matrix analysis²⁷ in which the CC stretching motion was projected out.²⁸ In interpreting these force constants and/or vibrational frequencies it is useful to introduce an approximate separation of modes which provides the basis for the variational RRKM calculations presented here. In particular, the vibrational modes are partitioned into the internal CH_2 and CO modes, which exhibit little change in character during the reaction process and are thus termed conserved modes, and the remaining relative $\text{CH}_2 \cdots \text{CO}$ motions, which transform from vibrations to free rotations and are thus termed transitional modes. The motion in the conserved modes is expected to be nearly adiabatic from the transition state region on to products, and thus an important indication of its effect is provided by the total conserved-mode zero-point energy, which is found to be 4737, 4744, 4746, 4746, and 4738 cm^{-1} at $R_{CC}=2.2, 2.5, 2.8, 3.1 \text{ \AA}$, and infinite separation, respectively. In contrast, the transitional modes vary quite substantially, as indicated in Table I, wherein the transitional mode frequencies are given for both the CCSD/QZ(2*d*, 2*p*) and MP2/6-31G* levels of theory at the four R_{CC} distances. Importantly, the MP2/6-31G* force constants are all within 10% of their CCSD/QZ(2*d*, 2*p*) counterparts for each R_{CC} value, except for the diagonal symmetric HCCO torsion element, which differs by roughly a factor of 1.5 for each distance.

The number of available states at the transition state is evaluated using the variational RRKM formalism described in Ref. 29 with one important modification. In particular, instead of employing an analytic potential in the evaluation of the phase space integral for the transitional modes, the configuration-dependent interaction energies are evaluated directly from additional *ab initio* calculations at the MP2/6-31G* level. In doing so, the MP2/6-31G* energies are used solely to determine the $\text{CH}_2 \cdots \text{CO}$ orientational dependence, with the reference $E(R_{CC})$ interaction energies for the optimum geometry taken from the more extensive *ab initio* analyses described above. In this "direct" Monte Carlo

evaluation of the phase space integral, 1000 configurations were sampled over for each R_{CC} . Furthermore, as a means to improve the accuracy, the momentum portion of the integral was sampled separately with 500 Monte Carlo points for each individual configuration. Efficiency was also enhanced by analyzing preliminary sets of *ab initio* conformational data, which made it possible to establish *a priori* when an interaction energy exceeds the maximum available energy according to whether the smallest interfragment separation of the configuration lies below a certain cutoff. Such configurations make no contribution to the phase space integral and thus can be rejected prior to any explicit energetic determination. A more detailed description of the motivation, validity, and procedural aspects of this direct statistics approach will be provided in Refs. 17 and 30. This procedure then provides an estimate for N_{EJ}^\dagger via a quadratic fitting of the number of states determined at each R_{CC} value and each E . The specific calculations reported here were for $J=0$ and had estimated Monte Carlo uncertainties between 10 and 20%, with uncertainties from the quadratic fit for N_{EJ}^\dagger also being at most about 10%. Finally, the estimates for N_{EJ}^\dagger were corrected for the difference in force constants evaluated at the CCSD/QZ(2d, 2p) and MP2/6-31G* levels via calculations of the ratio of the number of available states for the two force fields when implementing potentials similar to those of Ref. 15, but based on the new minimum energies. These corrections result in a 0 to 20% increase in N_{EJ}^\dagger for the E and J values considered here.

In addition to the inner transition state determined in these variational RRKM calculations, a minimum in the reactive flux also arises at much larger separations (greater than 10 Å). For these large separations simple evaluations of the number of states based on quantum mechanical expressions for free rotational energy levels have been implemented. At low energies (i.e., below 100 cm^{-1}) this outer transition state determined by "phase space theory" (PST)³¹ provides more of a bottleneck to the reactive flux than does the inner transition state. A first estimate for N_{EJ}^\dagger is then given by the minimum of these two separate evaluations for the inner and outer transition states.

The final theoretical rate constants are plotted in Fig. 1, together with the real time experimental measurements of Potter, Gruebele, Khundkar, and Zewail¹⁰ for excess energies ranging from 450 to 5600 cm^{-1} as well as those estimated for the lower energies by Kim, Choi, Pibel, Zheng, and Moore⁵ on the basis of interpolations of experimentally observed triplet rate constants and singlet-triplet branching ratios. The experiments of Ref. 10 observed the total dissociation rate constant, so these results have been adjusted here by the singlet/triplet branching ratio measured in Ref. 5, assuming an estimated value of 0.75 for energies above 2500 cm^{-1} . An expanded view of the threshold region is given in Fig. 2. The experiments were performed with cold molecular beams ($T \approx 3-4$ K). Thus, for completeness here an appropriate thermal averaging over the rate constants has been performed for the PST calculations. Meanwhile, such an averaging is expected to have little to no effect on the inner transition state calculations due to the diminished energy dependence

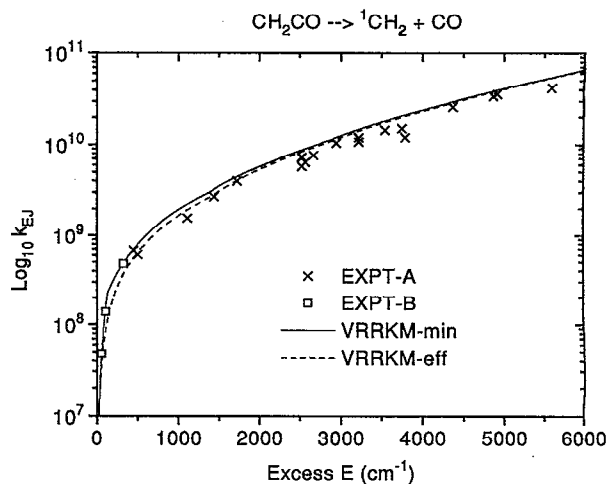


FIG. 1. Plot of the logarithm of the rate constant versus energy for the singlet dissociation of ketene. The solid line denotes the present variational RRKM results while the crosses and squares represent the experimental data of Potter *et al.* (Ref. 10) and of Kim *et al.* (Ref. 5), respectively.

arising from the substantially greater available energy in the transitional modes.

The solid line in Figs. 1 and 2 is seen to be in excellent agreement with the experimental results, with the maximum discrepancy being only about 35%, thereby verifying the quantitative validity of variational RRKM theory for this reaction. This level of agreement is well within the limits of accuracy of the present calculations, particularly since there has been no optimization of the form of the reaction coordinate²⁹ and since the present estimate of the density of states might well be expected to gradually degrade in accuracy as the energy increases.

Finally, it is interesting to consider the expanded view given in Fig. 2. At an energy of about 110 cm^{-1} , there is seen to be an abrupt change in the slope of the rate versus energy plot, indicating a change from a transition state at essentially infinite separation to the inner transition state between 2.2 and 3.1 Å. At energies near this transition, there are really

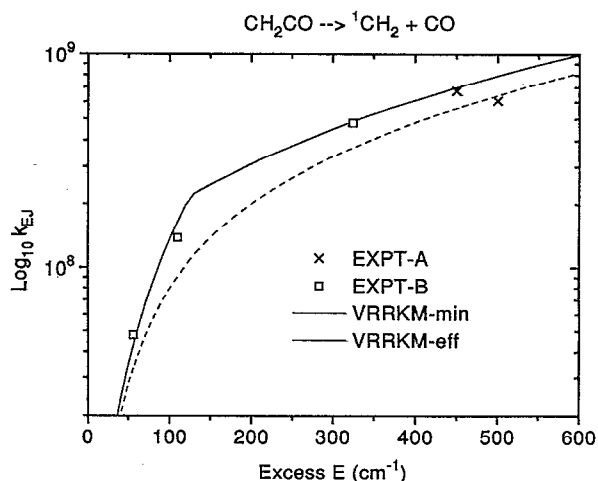


FIG. 2. An expanded view of the plot given in Fig. 1.

two transition states^{2(b),12} acting in series, and a rough estimate of the *maximum* effect that this combination of transition states might have is provided by an effective number of states N_{eff} given by^{12,32}

$$\frac{1}{N_{\text{eff}}} = \frac{1}{N_{\text{inner}}} + \frac{1}{N_{\text{outer}}} \quad (3)$$

The dotted line in Figs. 1 and 2 corresponds to the rate constants evaluated from this effective number of states; it not only smooths out the transition but also provides an explanation for the minor overestimate in the 100 cm⁻¹ region. The fact that this transition from the outer to the inner transition state occurs at about 110 cm⁻¹ suggests that the product vibrational distributions and vibrational PHOFEX spectra^{6,7} would be very accurately modeled by the present variational RRKM theory calculations, as in Ref. 12, thus providing further verification for the quantitative validity of variational RRKM theory for this system.

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- ¹R. A. Marcus and O. K. Rice, *J. Phys. Colloid, Chem.* **55**, 894 (1951); R. A. Marcus, *J. Chem. Phys.* **20**, 359 (1952); R. G. Gilbert and S. C. Smith, *Theory of Unimolecular and Recombination Reactions* (Blackwell Scientific, Boston, 1990).
- ²(a) B. C. Garrett and D. G. Truhlar, *J. Chem. Phys.* **70**, 1593 (1979); (b) S. N. Rai and D. G. Truhlar, *ibid.* **79**, 6046 (1983).
- ³W. H. Green, Jr., I.-C. Chen, and C. B. Moore, *Ber. Bunsenges. Phys. Chem.* **92**, 389 (1988).
- ⁴I.-C. Chen, W. H. Green, Jr., and C. B. Moore, *J. Chem. Phys.* **89**, 314 (1988).
- ⁵S. K. Kim, Y. S. Choi, C. D. Pibel, Q.-K. Zheng, and C. B. Moore, *J. Chem. Phys.* **94**, 1954 (1991).
- ⁶W. H. Green, Jr., A. J. Mahoney, Q.-K. Zheng, and C. B. Moore, *J. Chem. Phys.* **94**, 1961 (1991).
- ⁷W. H. Green, Jr., C. B. Moore, and W. F. Polik, *Annu. Rev. Phys. Chem.* **43**, 591 (1992).
- ⁸I. Garcia-Moreno, E. R. Lovejoy, and C. B. Moore, *J. Chem. Phys.* **100**, 8890 (1994).
- ⁹I. Garcia-Moreno, E. R. Lovejoy, and C. B. Moore, *J. Chem. Phys.* **100**, 8902 (1994).
- ¹⁰E. D. Potter, M. Gruebele, L. R. Khundkar, and A. H. Zewail, *Chem. Phys. Lett.* **164**, 463 (1989).
- ¹¹W. L. Hase and D. M. Wardlaw, in *Bimolecular Collisions*, edited by J. E. Baggott and M. N. Ashfold (Burlington House, London, 1989), p. 171; E. E. Aubanel, D. M. Wardlaw, L. Zhu, and W. L. Hase, *Int. Rev. Phys. Chem.* **10**, 249 (1991).
- ¹²S. J. Klippenstein and R. A. Marcus, *J. Chem. Phys.* **91**, 2280 (1989); **93**, 2418 (1990).
- ¹³C. Möller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934); J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.* **10**, 1 (1976); R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.* **14**, 91 (1978); R. Krish-

- nan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980);
- ¹⁴W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley-Interscience, New York, 1986); P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.* **28**, 213 (1973).
- ¹⁵J. Yu and S. J. Klippenstein, *J. Phys. Chem.* **95**, 9882 (1991).
- ¹⁶A. L. L. East, W. D. Allen, and S. J. Klippenstein, *J. Chem. Phys.* (submitted).
- ¹⁷S. J. Klippenstein, A. L. L. East, and W. D. Allen (in preparation).
- ¹⁸R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981); G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982); J. Paldus, in *New Horizons of Quantum Chemistry*, edited by P.-O. Löwdin and B. Pullman (Reidel, Dordrecht, 1983), p. 31; R. J. Bartlett, C. E. Dykstra, and J. Paldus, in *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, edited by C. E. Dykstra (Reidel, Dordrecht, 1984), p. 127; G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice, and H. F. Schaefer III, *J. Chem. Phys.* **86**, 2881 (1987); A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer III, *ibid.* **87**, 5361 (1987).
- ¹⁹A. L. L. East, C. S. Johnson, and W. D. Allen, *J. Chem. Phys.* **98**, 1299 (1993).
- ²⁰K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989); G. E. Scuseria and T. J. Lee, *J. Chem. Phys.* **93**, 5851 (1990).
- ²¹N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice, and E. D. Simandiras, *Chem. Phys. Lett.* **120**, 151 (1985).
- ²²D. Papoušek and M. R. Aliev, *Molecular Vibrational-Rotational Spectra* (Elsevier, Amsterdam, 1982); D. A. Clabo, Jr., W. D. Allen, R. B. Remington, Y. Yamaguchi, and H. F. Schaefer III, *Chem. Phys.* **123**, 187 (1988). The E_0 term described in [D. G. Truhlar and A. D. Isaacson, *J. Chem. Phys.* **94**, 357 (1991)] is negligible at the energies of interest here and has been neglected.
- ²³E. R. Lovejoy, S. K. Kim, and C. B. Moore, *Science* **256**, 1541 (1992); E. R. Lovejoy, S. K. Kim, R. A. Alvarez, and C. B. Moore, *J. Chem. Phys.* **98**, 7846 (1993).
- ²⁴A. L. L. East and W. D. Allen, *J. Chem. Phys.* **99**, 3865 (1993).
- ²⁵K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *J. Phys. Chem.* **94**, 5579 (1990); T. J. Lee, R. Kobayashi, N. C. Handy, and R. D. Amos, *J. Chem. Phys.* **96**, 8931 (1992).
- ²⁶The precise form of this BAC (in cm⁻¹) was chosen as $f(R)=1116.3$

$$\times \frac{\{\Delta E_e[R; \text{CCSD(T)/QZ}(2d1f, 2p1d)] - \Delta E_e[R; \text{CCSD(T)/QZ}(2d, 2p)]\}}{\{\Delta E_e[eq; \text{CCSD(T)/QZ}(2d1f, 2p1d)] - \Delta E_e[eq; \text{CCSD(T)/QZ}(2d, 2p)]\}}$$
- where ΔE_e is the electronic energy at the given separation R relative to that at infinite separation.
- ²⁷E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (Dover, New York, 1955).
- ²⁸D.-H. Lu and D. G. Truhlar, *J. Chem. Phys.* **99**, 2723 (1993).
- ²⁹S. J. Klippenstein, *J. Phys. Chem.* (in press); this article describes an efficient approach for implementing the variable reaction coordinate RRKM formalism described in S. J. Klippenstein, *J. Chem. Phys.* **96**, 367 (1992); **94**, 6469 (1991); *Chem. Phys. Lett.* **170**, 71 (1990).
- ³⁰S. J. Klippenstein (unpublished).
- ³¹P. Pechukas and J. C. Light, *J. Chem. Phys.* **42**, 3281 (1965); P. Pechukas, R. Rankin, and J. C. Light, *ibid.* **44**, 794 (1966); E. E. Nikitin, *Teor. Eksp. Khim. Acad. Nauk Ukr. SSR* **1**, 135, 428 (1965); C. E. Klots, *J. Phys. Chem.* **75**, 1526 (1971).
- ³²J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.* **7**, 616 (1939); W. H. Miller, *ibid.* **65**, 2216 (1976); W. J. Chesnavich, L. Bass, T. Su, and M. T. Bowers, *ibid.* **74**, 2228 (1981).