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Vibrational predissociation of $\text{Ar} \cdot \text{BCl}_3$: A Monte Carlo-RRKM study

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Experiments have shown that absorption of a single photon by the high-frequency asymmetric stretching mode of boron trichloride will lead to dissociation of the $\text{Ar} \cdot \text{BCl}_3$ van der Waals molecule in 1–3 ps. Since it appears unlikely that a direct dynamical coupling of the excited mode to the weak van der Waals bond occurs, it is somewhat difficult to understand why the observed lifetime of the metastable complex is so short. One finds, however, that an RRKM calculation (performed within a Monte Carlo framework) correctly predicts that a short lifetime will be observed, suggesting that energy randomization amongst the low-frequency modes of oscillation may play an important role in the predissociation dynamics.

INTRODUCTION

A number of workers have, in recent years, pointed out the advantages of using the vibrational predissociation of small van der Waals molecules as a probe of intermolecular forces and intramolecular energy redistribution.^{1,2} The basic procedure here is conceptually quite simple: the weakly bound van der Waals molecules are, typically, produced by the supersonic expansion of a gas mixture, thereby yielding internally cold (and hence stable) clusters. These clusters are then irradiated in the infrared at a frequency near one of the absorption lines of the isolated strongly bound moiety, the result being the transmission to the molecule of more energy than is required for the breaking of the comparatively weak van der Waals bond. By determining the predissociation lifetime (in practice, the width of the photodissociation spectral line) of the vibrationally excited metastable species, one then has a measure of the rate at which the vibrational energy is exchanged among the available internal modes of the molecule, since dissociation quickly follows the flow of that energy into the van der Waals bond.

To date, most of these investigations of van der Waals complexes have examined fairly small complexes, with rare gas- I_2 systems being the most intensively studied.³ However, a number of more recent papers have addressed the intramolecular processes occurring in somewhat larger molecules.^{2,4} Janda,⁵ Gentry,⁶ and their respective co-workers have, e.g., looked at the vibrational predissociation of ethylene dimers as well as ethylene bound to rare gas atoms, tetrafluoroethylene, and larger ethylene clusters. A study has also been made of the photolysis of the $\text{Ar} \cdot \text{BCl}_3$ cluster,⁷ and it is this system which provides the subject of the present paper. In that experiment a supersonic beam of $\text{Ar} \cdot \text{BCl}_3$ was uniformly irradiated with a low-power cw CO_2 laser tuned near the ν_3 fundamental (doubly degenerate, high-frequency asymmetric stretch) of the isolated BCl_3 molecule, with the photodissociation spectrum being found by monitoring the intensity of a particular mass spectrometer signal (due to $\text{Ar}^{35}\text{Cl}^+$) as the CO_2 laser frequency was scanned. The strongest peak in the resulting spectrum could be attributed to the predissociation of $\text{Ar} \cdot ^{11}\text{BCl}_3$, its width yielding a

value for the predissociation lifetime of between one and three ps. [Unfortunately, the analysis of the experimental findings may not be quite as straightforward as had been thought. Results of a recent re-examination⁸ of the problem have suggested that even at very low BCl_3 concentrations appreciable numbers of dimeric and trimeric species are formed in the molecular beam. The observed $\text{Ar}^{35}\text{Cl}^+$ mass peak, thus, might also include photolysis products coming from the breakup of larger clusters of the form $\text{Ar}_n(\text{BCl}_3)_m$. We note, however, that similar experiments involving ethylene clusters have revealed that the predissociation rate can be remarkably insensitive to a variation in van der Waals partner.⁵ Consequently, it appears reasonable to assume that the reported lifetime represents at least a good estimate of the true value, since if larger clusters do indeed form, their photodissociation rates are not likely to differ greatly from that obtained for the simple $\text{Ar} \cdot \text{BCl}_3$ cluster.]

One should recognize that the determined predissociation lifetime is really quite short, being on the order of a few tens of vibrational periods of the excited ν_3 mode. This point is of particular importance when combined with the observation by Janda *et al.*⁹ of a "perpendicular" equilibrium geometry for the analogous $\text{Ar} \cdot \text{BF}_3$ molecule, i.e., the rare gas atom is located directly above the boron atom. The direct coupling between the van der Waals bond and the in-plane ν_3 asymmetric stretch of BCl_3 presumably should therefore be small, implying that a prior step in the dissociation must be the transfer of energy from the ν_3 mode to the out-of-plane bending mode ν_2 and that it is probably the excited ν_2 mode which directly couples to the dissociative channel. This analysis suggests that a theoretical model incorporating a fast energy redistribution assumption (e.g., RRKM theory) might provide a quite adequate description of the dissociation process.

The bulk of the theoretical work on van der Waals molecule predissociation proceeds from a quantum mechanical viewpoint and is attributable either to Beswick and Jortner¹⁰ or to Ewing.¹¹ These workers base their arguments on a low-dimensional, coupled-channel description within which the excited energy level of the cluster represents a resonant scattering state. Prob-

ably the most important conclusions drawn from that work are embodied in the "energy-gap" and "momentum-gap" principles, which correctly predict the qualitative dependence of the computed decay widths upon the degree of excitation and the extent of vibrational frequency commensurability. One anticipates, however, that the extension of quantum mechanical analyses to larger, more complex systems will be exceedingly difficult. In an attempt to avoid this practical restriction, Woodruff and Thompson¹² have adopted a quasiclassical trajectory approach to the predissociation problem, and in doing so have demonstrated that classical mechanics can provide answers comparable in accuracy to those deriving from the corresponding quantum formalism. The Monte Carlo-RRKM procedure employed in the present work is very much in the same spirit as the full trajectory study, except, of course, for the energy randomization supposition. While one cannot rule out the possibility that quantum effects may play a role in the predissociation, it is useful to have at hand some model (the quasiclassical case constituting the only tractable one¹³) for use in discussing the observed energy transfer.

REVIEW OF THE THEORY

In this section only a very brief description of the theoretical foundations of the present calculations will be given. For more details the reader is referred to a number of recent papers¹⁴ as well as to several standard treatments of the RRKM formalism.¹⁵ We simply recall here that RRKM theory becomes formally equivalent to unimolecular transition state theory when the appropriate statistical averages appearing in the transition state development are evaluated within the microcanonical ensemble. Specifically, if the function $r(t)$ describes a process (assumed to be stationary¹⁶) corresponding to motion along the dissociation coordinate and if the dissociation is presumed to occur whenever $r(t)$ takes on some critical value r_d , then the (energy dependent) unimolecular dissociation rate constant is given for a system of N degrees of freedom by

$$k(E) = \left\langle \delta(r(t) - r_d) \frac{|\dot{r}|}{2} \right\rangle = \frac{h^{-N} \int d\mathbf{x} \int d\mathbf{p} \delta(E - H(\mathbf{x}, \mathbf{p})) \delta(r - r_d) \frac{|\dot{r}|}{2}}{h^{-N} \int d\mathbf{x} \int d\mathbf{p} \delta(E - H(\mathbf{x}, \mathbf{p}))}, \quad (1)$$

where $H(\mathbf{x}, \mathbf{p})$ is the complete system Hamiltonian and $r = r(\mathbf{x})$. (This expression can be easily shown to reduce to the familiar RRKM form written in terms of numbers of energetically available states.)

One could now perform a series of quasiclassical trajectories after the fashion of Woodruff and Thompson¹² and obtain a value for $k(E)$, however it is particularly convenient, in light of that fact that only an equilibrium average is required, to attempt a Monte Carlo evaluation of the expression.¹⁷ In such a case one replaces Eq. (1) by a summation over M permitted configurations (i.e., those arrangements consistent with allowed partitionings of kinetic and potential energy, the total en-

ergy being fixed) of the system,

$$k(E) \cong \frac{1}{M} \sum_{i=1}^M \delta(r_i - r_d) \frac{|\dot{r}|}{2}.$$

It is a quite simple matter to generate the required configurations by means of a Metropolis sampling procedure "on the energy shell," i.e., one involving a random walk which samples phase space uniformly in accordance with an energy delta function probability density. (A particularly good description of this sampling method is found in Ref. 18.) When using delta functions in computational schemes, one normally replaces them with their prelimit forms, the Lorentzian forms being used herein. Thus, e.g.,

$$\delta(r_i - r_d) \cong \frac{1}{\pi} \frac{\epsilon_r}{\epsilon_r^2 + (r_i - r_d)^2}, \quad (2)$$

where ϵ_r is a conveniently chosen small parameter (the limit $\epsilon_r \rightarrow 0$ yields the exact equality; in practice a value of 0.001 a.u. works well). A similar form is adopted for the Metropolis sampling transition probabilities, namely $\delta(E - H(\mathbf{x}, \mathbf{p}))$, where in addition to a parameter ϵ [in this case having units of energy rather than length as in Eq. (2)] one also specifies an energy width ΔE such that if a configuration has a total energy which does not fall within ΔE of the desired fixed energy, then that configuration will be automatically rejected.

It is useful, at this point, to recall the general advantages of the above method as compared with what might be termed the "conventional" approach to RRKM calculations.^{14(b),15} Most notably, one finds that the present formalism avoids any assumptions concerning the character of the potential interactions, e.g., that the potentials are harmonic or separable. Monte Carlo techniques can consequently be extended to the treatment of large, complex systems for which the usual state counting schemes can be of questionable accuracy. (This advantage may well be of importance for the case of van der Waals molecule predissociation, inasmuch as the weak van der Waals bond is surely quite anharmonic.) Admittedly, for particular simple systems the desire for efficiency may dictate that one adopt the more conventional approaches; however, in analyzing an arbitrary dissociative system, one may instead opt for a method the accuracy of which does not rest upon the appropriateness of simple potential forms. [We should also note that Monte Carlo methods can be employed in RRKM calculations in ways other than through the evaluation of Eq. (1). Farantos and co-workers¹⁹ have recently described what amounts to a Monte Carlo method of state counting which is valid for an arbitrary potential form.]

NUMERICAL APPLICATION TO $\text{Ar} \cdot {}^{11}\text{BCl}_3$

Before applying the theoretical analysis of the previous section, one must choose appropriate potential energy functions for both the strongly bound BCl_3 moiety and the van der Waals bond. We assume that to a first approximation the potential description *apropos* of an isolated BCl_3 molecule provides an adequate functional form for the corresponding bound species, implying that the weak van der Waals bonding does not significant-

TABLE I. ¹¹BCl₃ potential parameters.

Force constants ^a (mdyn Å ⁻¹)	
$k_R = 2.66$	
$k_\theta/l^2 = 0.277$	
$k_\Delta/l^2 = 0.418$	
Normal mode frequencies ^b (cm ⁻¹)	
$\nu_1 = 357$ (471)	Symmetric stretch, A_1'
$\nu_2 = 462$ (462)	Out-of-plane bend, A_2''
$\nu_3 = 957$ (958)	Doubly degenerate asymmetric stretch, E'
$\nu_4 = 243$ (243)	Doubly degenerate asymmetric stretch, E'

^aIn order to express k_θ and k_Δ in the same units as k_R , they must be divided by the square of the B-Cl bond length $l = 1.75$ Å.

^bThe values in parentheses are the corresponding experimental frequencies from Ref. 21.

ly perturb the intramolecular interactions (or geometry, for that matter).²⁰ Having made this assumption, we adopt the simple potential form given by Herzberg²¹ for molecules of the type XY_3 having D_{3h} symmetry,

$$2V = k_R(R_1^2 + R_2^2 + R_3^2) + k_\theta(\delta_{12}^2 + \delta_{23}^2 + \delta_{31}^2) + k_\Delta(\Delta_1^2 + \Delta_2^2 + \Delta_3^2).$$

In this equation R_i represents the displacement away from its equilibrium value of the length of the bond connecting atoms X and Y_i , δ_{ij} is a distortion of the angle between two Y atoms (i. e., the angle Y_iXY_j), and Δ_i describes the deviation of the line XY_i from the plane defined by the three Y atoms (i. e., the out-of-plane distortion). The force constants used in this calculation as well as the resulting normal mode frequencies are given in Table I. One sees immediately that the functional form above cannot, since it only involves three constants, be expected to yield accurate values for all four of the fundamental frequencies. In fact, one finds that force constants can be chosen such that either the symmetric stretch frequency (ν_1) matches the experimentally observed result but the asymmetric ones do not, or the asymmetric stretches (ν_3 and ν_4) are of the correct frequency while the symmetric stretch is not. For the present work the latter set of constants was selected (calculated using the equations given by Herzberg²¹), inasmuch as it is the ν_3 mode which was excited in the single experimental study of Ar · BCl₃ predissociation. Normal coordinate vectors deriving from the above analysis were also calculated²² for use in assigning the initial conditions.

The selection of potential parameters appropriate to the van der Waals interaction represents a somewhat more difficult task. We begin by assuming that a pairwise additive potential model provides a realistic representation of the bonding and take the two-body potentials to be Morse functions. Then, in the absence of other information, we make the rather gross approximation that the interactions between rare gas atoms and chemically bound atoms are identical to those between rare gas atoms themselves. In the present work, this approximation leads to the use of Ar₂ and ArNe potential parameters²³ (describing, respectively, ArCl and ArB)

in order to model the Ar · BCl₃ bonding (the actual values used being listed in Table II). Admittedly, one should not expect this potential correlation to be quantitative; nonetheless, until more detailed structural measurements or calculations become available, such assumptions provide at least a starting point for characterizing van der Waals forces in more complex systems.

One may now proceed to the assignment of the total system energy and hence to the specification of the shell upon which the sampling walk is to be taken. A determination of the proper internal energy of the BCl₃ moiety is, of course, a trivial exercise given the above assumptions concerning the potential interactions. The process is begun by choosing a random configuration of the fragment consistent with the assumed excitation, a particularly convenient starting point being just the equilibrium (undistorted) structure for which all the internal energy appears as kinetic energy of the four atoms. Following the usual quasiclassical prescription,²⁴ the initial action variables are identified with their (integral) quantum number analogs; thus, in order that the calculation may mimic the experimental investigation, the action variables are set to zero for all normal modes other than the excited ν_3 mode, for which one quantum of vibrational energy is included. However, this assignment *per se* does not reproduce exactly the "experimental" energy as a result of the incorrect value of ν_1 being used in the calculation. A correction must therefore be made so as to produce the correct energy content of BCl₃; accordingly, the action variable associated with ν_1 is taken to have a value of 0.160. Having made this choice of action variables (the conjugate angle variables are automatically determined when the molecule is fixed in its equilibrium geometry), one constructs the velocities conjugate to the normal mode coordinates Q via the equations

$$\dot{Q}_i = \pm [(2n_i + 1) h \nu_i]^{1/2},$$

n_i denoting the i th action variable. These velocities are then transformed into the Cartesian momenta of the four atoms by the relation

$$p = M^{1/2} L \dot{Q},$$

where L is the matrix of eigenvectors obtained from the force constant matrix diagonalization mentioned previously, and M is a diagonal matrix having elements equal to the atomic masses.²⁵

The initial energy of the van der Waals bond is set

TABLE II. van der Waals Morse potential parameters.

	Ar-B ^a	Ar-Cl ^b
D (eV)	0.006 03	0.012 34
α (a. u. ⁻¹)	0.926	0.844
r_0 (a. u.)	6.48	7.11

^aAr-B parameters are adapted from ArNe data (Ref. 23).

^bAr-Cl parameters are adapted from Ar₂ data (Ref. 23).

equal to the zero point energy. Recognize, first, that the basic structure of the molecule is determined by the fact that the minimum in the potential function described above corresponds to the argon atom lying along the threefold rotational axis of BCl₃ (i.e., C_{3v} symmetry), a result which agrees with the structure determined for the analogous Ar·BF₃ molecule.⁹ If one then freezes the BCl₃ fragment in its equilibrium configuration, application of the Bohr-Sommerfeld quantum condition yields the energy of the desired Ar·BCl₃ vibrational level E_0 :

$$\frac{1}{2} = \frac{2}{h} \int_{r_-}^{r_+} dr [2\mu(E_0 - V(r))]^{1/2},$$

where μ is the reduced mass for Ar-BCl₃ oscillation and r is the (perpendicular) distance of the argon atom from the BCl₃ center of mass (here located at the boron atom), the integral being evaluated numerically between the classical turning points. For the potential parameters of Table II and the assumed geometry, the E_0 level is thus found to be bound by 0.0404 eV (326 cm⁻¹), with the potential minimum occurring at an argon-boron separation of approximately 6.35 a.u. (3.36 Å) and the classical turning points for this lowest level appearing at 6.06 and 6.69 a.u. Note that the position of the energy minimum is reasonable in light of the corresponding value of 3.325 Å reported by Klemperer and co-workers⁹ for Ar·BF₃.

Having calculated all contributions to the total energy of the nonrotating system, we then adjust the coordinates and momenta of the atoms such that the overall center of mass remains fixed at the origin and begin the Monte Carlo walk from this initial configuration. Of course, the initial sets of configurations generated according to the Metropolis sampling scheme need to be omitted from the actual rate determination; these first steps merely allow the system to move away from the arbitrarily chosen starting geometry and permit energy redistribution in accordance with the RRKM assumptions. After performing these preliminary moves, one may proceed to the calculation of a rate constant on the basis of a number (typically 25 to 50) of sets of 5×10^4 – 2×10^5 Monte Carlo moves. (Two atoms are displaced for each attempted move, with an acceptance probability of 40%–50% being obtained through the adjustment of the maximum displacement length.) From an average rate constant and standard deviation computed for these sets of moves, one easily calculates the predissociation lifetime,

$$\tau = k^{-1}(E).$$

One will note that there are still a few parameters appearing in the calculation which cannot be determined by any of the above means. These remaining quantities r_d , ϵ , and ΔE either represent the position of the "counting surface" for dissociation or are associated with the approximation introduced for the delta functions. Consider first the delta function parameters. In the single previous application of the Monte Carlo-RRKM approach,^{14(b)} the width of the energy shell was taken to be a few percent of the total system energy. However, one must remember in the present

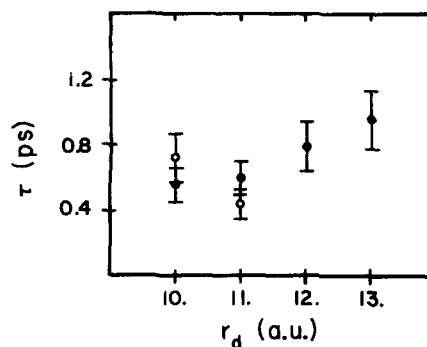


FIG. 1. Variation of Ar·BCl₃ predissociation lifetime with choice of counting surface position. The open and solid circles refer to the different choices for ΔE and ϵ indicated in the text. Error bars correspond to one standard deviation.

case that the van der Waals bond itself is but a small fraction of the total energy; the width must not be so great that *any* displacement of the argon atom will yield an energy which falls on the shell. Fortunately, the calculated lifetimes do not appear to depend very strongly upon ΔE . Results are shown in Fig. 1 for two different choices of ΔE and ϵ (with ϵ in each case being 40% of ΔE .) The open circles correspond to lifetimes calculated using $\Delta E = 0.005$ eV, which is roughly 12% of the van der Waals bond energy, while the solid circles reflect the use of a shell width which is twice as large. Inasmuch as the two sets of results cannot be distinguished within the statistical accuracy of the calculations, we assume that the width need not be reduced further. (One would like to adopt as large a ΔE as possible in order to maximize the computational efficiency.)

The final parameter to be specified, the critical separation distance r_d , defines the distance beyond which the complex may be presumed dissociated. Since for a system having no potential saddle point the choice of this dividing surface is somewhat arbitrary, one need only insure that there be no significant contribution to the counting function [i.e., the prelimit form of $\delta(r - r_d)$] from bound Ar-BCl₃ vibrational motion. In Fig. 1 one will find results for a series of r_d choices ranging from 10 to 13 a.u., all of which are well beyond the outer turning point of the van der Waals oscillator having only zero point energy (e.g., at $r_d = 12$ a.u., the residual Ar-BCl₃ interaction is only about 2% of the well depth). Although one observes a weak dependence on r_d over this range of values, the lifetime variation is clearly not as large as the uncertainty in the measured τ values, namely a picosecond or so. Thus, we feel that the calculated lifetimes are sufficiently well-characterized to be of use in an analysis of the experimental findings.

DISCUSSION

We have shown in this study that an RRKM (microcanonical transition state theory) calculation performed within the Monte Carlo framework yields vibrational predissociation lifetimes for Ar·BCl₃ which are comparable with those obtained in the recent CO₂ laser photolysis

experiment of Casassa *et al.*⁷ This agreement implies that rapid internal energy redistribution provides a reasonable explanation for the unexpectedly rapid rate of breakup of the van der Waals molecule. More specifically, one concludes that rapid predissociation need not arise solely as a consequence of efficient, direct coupling of the single excited vibrational mode to the van der Waals bond (the direct coupling mechanism appears to be ruled out for reasonable $\text{Ar} \cdot \text{BCl}_3$ structures); one should not rule out an indirect pathway for energy transfer whereby internal coupling leads first to the excitation of one or more of the other nondissociative modes and then to energy flow from these low-frequency modes to the fragile bond.

One should also note that the applicability of an RRKM calculation is compatible with another of the experimental observations, namely that the product fragments separate with very low relative translational energy. (The product translational energy distribution is not particularly well-characterized experimentally in recent molecular beam studies, inasmuch as the products are scattered very near the forward direction.⁸ This forward peaking does, however, suggest a low final relative velocity.) Recall that implicit in the theory is the assumption that once enough energy flows into the van der Waals bond to overcome the small binding energy, dissociation proceeds immediately. Also note that the statistical nature of the energy exchange among the oscillators presumably favors the transfer of small amounts of energy into the bond. Thus, the most probable dissociative event will be one in which just barely enough energy is made available for bond rupture, thereby leaving little to be released as fragment translation.²⁶

It is, admittedly, always possible that a classical model will fail to reproduce correctly the observed energy redistribution by permitting the transfer of arbitrary amounts of energy rather than discrete quanta. In the corresponding quantum mechanical formulation, the leakage of small amounts of energy from one mode to another can occur only when a fairly dense manifold of internal states (here, rotational) is accessible to the product fragment. For many practical systems, this restriction on the allowed transitions does not appear to represent a particularly severe limitation on the analysis^{12,26,27}; e.g., the presence of a number of low-frequency modes in BCl_3 suggests that the states are indeed available in the case considered here. However, one should be particularly cautious in applying such a model to a predissociative event proceeding via the excitation of a low-energy vibration, since the available product states are likely to be more widely spaced.

In this study no attempt has been made to optimize the agreement with experiment by adjusting either the form of the assumed interaction potentials or the parameters describing those potentials. Any significant revision must necessarily incorporate more detailed structural and energetic data than is currently available, and hence seems unproductive at present. An obvious consequence of this lack of refinement of the po-

tential energy function is that a dynamical study of $\text{Ar} \cdot \text{BCl}_3$ predissociative via classical trajectories is not likely to reflect the extent of energy randomization presumed in the RRKM calculations. In the Monte Carlo approach described here, the sampling walk necessarily couples the internal modes of the molecule whether or not mode-mode coupling terms appear in the potential. Without a rather detailed knowledge of these terms, one should not, however, expect to observe fast energy flow in the exact dynamics. A few sample trajectories generated for the present system in fact testify to the unsuitability of the potential description for use in that sort of study of intramolecular energy randomization.

As a concluding point, we cannot help but be somewhat amazed that the computational methods described herein have not been heretofore adopted as a means for performing calculations of unimolecular decomposition rates, even though the basic formulas are well known. The one previous application^{14(b)} was to the dissociation of quasibound argon clusters, for which the potential interactions are particularly simple and well characterized and for which there is little doubt about the validity of the rapid energy redistribution assumption. Clearly, the method may be easily extended to any system, regardless of the complexity of the potential energy function involved (recall that the calculation of forces is not required in the Monte Carlo formalism, and hence the functional form need not even be conveniently differentiable). Aside from shedding light on the specific question of the mechanism of vibrational predissociation in a specific van der Waals molecule, we hope that the present work recommends the use of Monte Carlo techniques as a convenient means for evaluating RRKM expressions appropriate to "real" unimolecular problems.

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- ²²See, for example, S. Califano, *Vibrational States* (Wiley, New York, 1976), p. 23.
- ²³G. Scoles, *Annu. Rev. Phys. Chem.* **31**, 81 (1980).
- ²⁴See, for example, R. N. Porter and L. M. Raff in *Modern Theoretical Chemistry*, edited by W. H. Miller (Plenum, New York, 1976), Vol. I.
- ²⁵Although the boron mass was taken to be that of the ^{11}B isotope, the relative natural abundance average value was used for the chlorine mass.
- ²⁶The low product relative translational energy predicted by RRKM theory has been noted previously; see, for example, W. L. Hase, R. J. Wolf, and C. S. Sloane, *J. Chem. Phys.* **71**, 2911 (1979).
- ²⁷See, for example, D. L. Bunker and W. L. Hase, *J. Chem. Phys.* **59**, 4621 (1973); C. A. Parr, A. Kuppermann, and R. N. Porter, *ibid.* **66**, 2914 (1977).