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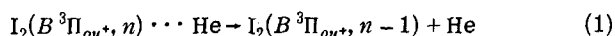
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The dynamics of van der Waals molecules (VDWM's) has attracted considerable attention in recent years.¹ A number of such molecules have been formed by a variety of methods² and several of their properties, e.g., geometry³ and dissociative lifetimes,⁴ have been experimentally determined. Theoretical analyses of VDWM's have included quantum mechanical⁵ and quasiclassical treatments.⁶ In principle, the total dynamics of any VDWM can be derived from the full close-coupled treatment of the nuclear motion⁷; in practice, the lack of knowledge about the VDW "bond" potential combined with the extreme sensitivity of dissociation lifetimes to this potential⁸ leads to the inability of theory to match experiment quantitatively.

In this Communication, we present an analysis of the vibrational predissociation process,^{4,9}



The experimental configuration, which determines the internal states of both reactants and products,^{4,9} allows the assignment of the vibrational quantum levels as n and $n-1$ in the above process. The present theoretical treatment, which is based upon the recently developed energy corrected sudden (ECS) scaling theory for inelastic collision processes,¹⁰ does not depend upon the VDW potential but instead focuses on the variation of the (experimentally measured) vibrational dissociation lifetimes with n . From this variation, we are able to extract dynamical information about the dissociation of VDWM's. For example, the half-collision model interpretation¹¹ is shown to be consistent with the experimental data on Process (1).

The scaling relationship appropriate for a vibration-translation ($V-T$) de-excitation rate^{10,12} can be written as

$$K(n-n-1)/K(1-0) = |I_1^{n,n-1}|^2 \left(\frac{6 + (\omega_{1,0}\tau_c/2)^2}{6 + (\omega_{n,n-1}\tau_c/2)^2} \right)^2 \quad (2)$$

In Eq. (2), $\omega_{n,n-1}$ is the transition frequency for the $n \rightarrow n-1$ transition, τ_c is the average collision time and

$$I_1^{n,n-1} \equiv \int \psi_n^*(r) \phi_{n-1}(r) \phi_1(r) / \phi_0(r) dr, \quad (3)$$

where $\phi_n(r)$ is the vibrational part of the wave function for $I_2(B^3\Pi_{ou^+}, n)$. Two important properties of Eq. (2) are used in the analysis: (1) the ratio of any two rates $K(n_1-n_1-1)/K(n_2-n_2-1)$ can be calculated by eliminating $K(1-0)$ first; and (2) the values of $\omega_{n,n-1}$ and $I_1^{n,n-1}$ can be determined¹³ from the vibrational constants of

the I_2^* molecule,¹⁴ $\omega_e = 125.273 \text{ cm}^{-1}$ and $\omega_e x_e = 0.7016 \text{ cm}^{-1}$. An additional point of interest concerns the bounded nature of Eq. (2); the quantity $K(n-n-1)/[K(1-0)|I_1^{n,n-1}|^2]$ is restricted to lie between 1 which is the sudden limit (i.e., $\omega_{n,n-1}\tau_c \ll 1$), and $(\omega_{1,0}/\omega_{n,n-1})^4$ which is the adiabatic limit (i.e., $\omega_{n,n-1}\tau_c \gg 1$). Finally, we note that Eq. (2) accurately describes the full three dimensional dynamics for systems with small rotational spacings.¹⁵

The analysis of vibrational predissociation lifetimes⁴ is accomplished in two steps:

(i) The rates, which are associated with the inverse of a lifetime, are normalized to $K(12-11)$.

(ii) The value of $\tau_c/2$ is determined by fitting Eq. (2), which is rewritten for $K(n-n-1)/K(12-11)$, to the results of (i).

Figure 1 clearly demonstrates the accuracy of the $V-T$ scaling relationship, Eq. (2), in the correlation of the experimental data. Furthermore, the value of the "half-collision" time is well determined by the data as

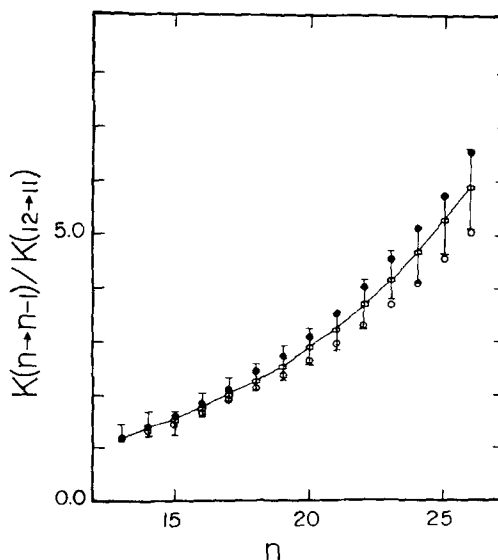


FIG. 1. The relative rates for the dissociation of the VDWM I_2^*He . The experimental data is shown by the vertical bars. The scaling predictions using Eq. (2) are shown for $\tau_c/2 = 1.3, 1.0,$ and 0.6×10^{-13} sec which correspond to the symbols $\bullet, \square,$ and \circ respectively. The solid line segments connect the scaling predictions with $\tau_c/2 = 1.0 \times 10^{-13}$ sec and are shown for the purpose of clarity.

$\tau_c/2 = 1.0^{+0.3}_{-0.4} \times 10^{-13}$ sec. Since a typical vibrational period is $\sim 2.6 \times 10^{-13}$ sec, these results indicate that the actual dissociation process occurs in less than a single vibration. With this value of $\tau_c/2$ the ratio of lifetimes for any two sets of vibrational states can be predicted. For example, $K(27-26)/K(7-6)$ is predicted to be ~ 15 which is in very good accord with the experimentally measured value of Smalley, Levy and Wharton,^{9a} $K(27-26)/K(7-6) > 10$.

The above observations lend support to the view of VDW dissociation as a simple $V-T$ process.¹¹ In addition, the VDW bond potential is unimportant for the scaling of rates, and we thus bypass the most serious difficulty in an *ab initio* calculation of predissociation lifetimes.^{5,6} Indeed, it is becoming increasingly clear that representations of the Morse or Lennard-Jones type are inadequate in describing the nature of VDW bonds, and in simple diatomic systems, a rather different potential function has been used.¹⁶

The success of the $V-T$ scaling theory for the present system is attributable to two facts. Firstly, the $\text{He} \cdots \text{I}_2$ bond supports at most one bound level, and thus, each quantum of I_2^* transferred leads to dissociation. (This is consistent with the observation¹⁷ in He_mI_2^* systems that m vibrational quanta are necessary to remove all He atoms.) For systems with stronger VDW bonds, the depth of the potential could have a significant effect due to the occurrence of near-resonant energy transfer processes.¹⁸ The stronger bond can also necessitate the transfer of several vibrational quanta into translation before the VDWM dissociates. A scaling theoretical analysis of such systems would necessarily include $V-V$ energy transfer considerations. Secondly, in He_mI_2^* VDWM's intramolecular energy transfer is relatively unimportant,¹⁷ whereas in heavier rare-gas systems, there are indications of energy disposal through modes other than purely dissociative ones.¹⁷ In such cases, then, a scaling theoretical analysis would yield valuable information on the extent of internal energy randomization (sharing) in the dynamics of van der Waals molecules.

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^{a)} Contribution No. 6109.

¹See, e.g., Sec. V of *Advances in Laser Chemistry*, edited by A. H. Zewail (Springer-Verlag, New York, 1978).

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¹²For deexcitation processes, the scaling relationship for rates and cross sections is the same. See Eqs. (5.5), (5.10) and (5.18) in Ref. 10. Note that Eq. (5.18) is restricted to $\bar{j} = 0$, $\bar{n} = 1$, $n' = n - 1$.

¹³It is shown in Ref. 10 that $I_1^{n,n-1}$ only depends upon χ_e for a Morse oscillator.

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An exact relation for the reactivity dependence of the recombination probability

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In this Communication we report the new finding¹ of an exact relation for the reactivity dependence of the recombination probability for diffusional systems with or without scavengers. It is found that the recombination probability for an arbitrary system can be expressed in terms of the recombination probability for a diffusion controlled system.

It is well known² that the recombination probability in

the presence of a scavenger is equal to the Laplace transform of the recombination rate in the absence of a scavenger. The rate of recombination of a pair of particles with initial separation r may, in the absence of scavenger, be defined as

$$R(t, r) = -\frac{\partial}{\partial t} \int d^3r' P(r', t | r), \quad (1)$$

where $P(r', t | r)$ is the conditional probability density,