

## A SEMICLASSICAL TREATMENT OF COLLISION INDUCED DISSOCIATION \*

L. L. JOHNSON and R. E. ROBERTS

Indiana University, Bloomington, Indiana 47401, USA

Received 25 September 1970

Transition probabilities for the collision induced dissociation reaction,  $A + BC \rightarrow A + B + C$ , are calculated for a harmonic oscillator model using a semiclassical approximation. One of the unique features of this investigation is the appearance of quantum oscillations in the dissociation probability as a function of collision energy. The number of oscillations is correlated to the number of bound states of the BC molecule.

Recent investigations of vibrationally inelastic encounters have pointed out the advantages of treating inelastic problems semiclassically \*\*. For example, simple and accurate expressions have been derived for the model problem of the collision of an atom with a harmonic oscillator [2]. The following communication presents a related preliminary study of the molecular dissociation process  $A + BC \rightarrow A + B + C$ . If one can accurately estimate the set of inelastic and elastic transition probabilities for the  $A + BC$  collision, then by the conservation of probability it is possible to calculate the dissociation probability from a given initial state  $i$  from

$$P_{\text{diss}} = 1 - \sum_f P_{i \rightarrow f} \quad (1)$$

where  $f$  refers to all other elastic and inelastic channels of the BC molecule. The problem of calculating  $P_{\text{diss}}$  is then reduced to the calculation of  $P_{i \rightarrow f}$ . It is important to note that any approximation used to find  $P_{i \rightarrow f}$ , and subsequently  $P_{\text{diss}}$ , must be accurate for multiple quantum excitations as well as direct excitations, and it must also be unitary in order for eq. (1) to be meaningful. Since a semiclassical theory has been developed which meets these requirements it is possible to determine  $P_{\text{diss}}$  for a model system corresponding to a vibrational dissociation mechanism.

\* Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

\*\* See for example the comprehensive review article by Rapp and Kassal [1]. Several investigations scheduled for publication have been carried out independently by Roberts [2], Heidrich et al. [3], Miller [4] and Marcus [5].

The infinite order semiclassical approximation [6] leads to an expression for  $P_{i \rightarrow f}$  of the form

$$P_{i \rightarrow f} = |\langle i | \exp\{-iG\} | f \rangle|^2 \quad (2)$$

where  $|n\rangle$  represents the internal molecular states and  $G$  is an operator which depends upon the time dependent molecular interaction. Recent approximate theories using eq. (2) have given promising results for both vibrational and rotational inelastic collisions [2, 7].

In order to investigate vibrational dissociation, the following simple model due to Montroll and Shuler [8] has been introduced. The BC molecule is approximated by a truncated harmonic oscillator potential as depicted in fig. 1. Furthermore, the collisions are restricted to collinear trajectories with the molecule-atom interaction being of the exponential form:

$$V(x, y) = C[1 + m_C y / L(m_B + m_C)] \exp(-x/L) \quad (3)$$

where  $x$  is the relative motion coordinate,  $y$  is the displacement of the oscillator from its equilibrium position,  $L$  is the effective range parameter, and  $m_i$  refers to the mass of the subscripted atom. Treating the relative molecular motion classically [1] leads to a time dependent perturbation  $V(t, y)$  which is linear in  $y$ . Using eq. (2), Pechukas and Light [6] have derived an analytical expression for  $P_{i \rightarrow f}$  corresponding to this model system:

$$P_{i \rightarrow f} = \exp(-p) i! f! (p)^{f-i} \times \left[ \sum_{j=0}^i \frac{(-1)^j p^j}{j!(f-i+j)!(i-j)!} \right]^2 \quad (4)$$

for  $f \geq i$ . If  $f < i$ , the roles of  $i$  and  $f$  in the right side of eq. (4) are interchanged.  $p$  is the simple perturbation theory result for the  $0 \rightarrow 1$  excitation

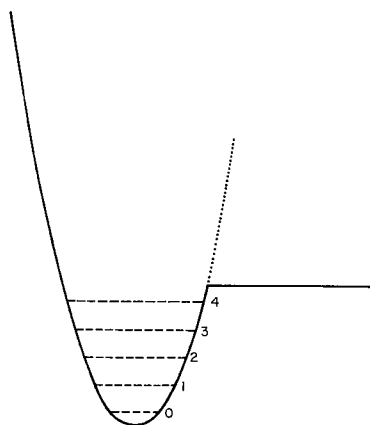


Fig. 1. Model used for diatomic molecule. In this case  $\epsilon = 5$  and the energy levels range from 0 to 4. Any excitation to a state greater than 4 is considered to be dissociated.

of a harmonic oscillator [1]. Calculations were carried out using eqs. (1) and (4) for different values of the reduced parameters [9]:

$$m = m_A m_C / (m_A + m_B + m_C) m_B,$$

$$\alpha = [m_C \hbar \omega / \omega m_B (m_B + m_C)]^{1/2} / L,$$

$E$  = relative kinetic energy of the system in units of  $\hbar\omega$ ,

and

$\epsilon$  = number of bound states in the harmonic well (also the well depth) in units of  $\hbar\omega$ ,

where  $\omega$  is the vibrational frequency of the molecule BC.

Since a forthcoming paper will present detailed results for the truncated harmonic oscillator model as well as results for more realistic systems, we have chosen to outline only the more important features of this calculation. The effect on  $P_{\text{diss}}(E)$  due to changes in the mass parameter  $m$  and the potential range parameter  $\alpha$  are indicated in fig. 2. For a fixed mass one finds that a larger value of  $\alpha$  (or smaller value for  $L$ ) leads to a less adiabatic collision and hence a more efficient transfer of translational energy into the dissociative channel. The mass effect is also demonstrated in fig. 2. For smaller  $m$  values (lighter incident atoms) the probability of dissociation is enhanced at lower kinetic energies; however,  $P_{\text{diss}}$  does not approach its maximum value of unity as rapidly as does  $P_{\text{diss}}$

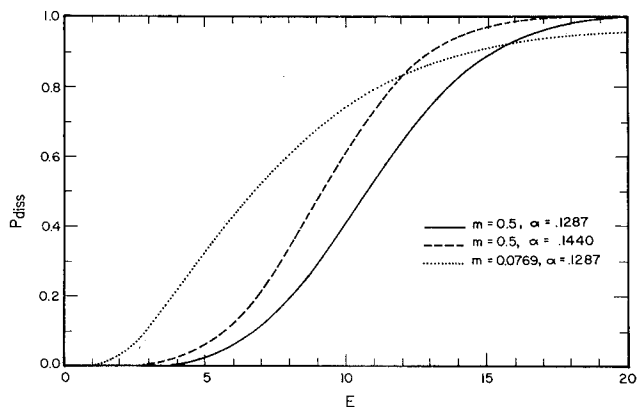


Fig. 2. Probabilities of dissociation versus kinetic energy for  $i = 0$ ,  $\epsilon = 1$ , varying  $m$  and  $\alpha$ .

for larger  $m$ . This is in accordance with the trend for vibrational excitation transition probabilities as computed exactly by Secrest and Johnson [9], since a high efficiency for vibrational excitation would coincide with a more efficient dissociation in our model. The effects of varying the well depth ( $\epsilon \hbar\omega$ ) as well as the initial vibrational state of the harmonic oscillator are shown in fig. 3. As expected, an increase in the well depth lowers  $P_{\text{diss}}$ . A particularly interesting feature is the occurrence of oscillatory behavior of  $P_{\text{diss}}$  as a function of  $E$ . It can be shown that the oscillations are a direct consequence of the individual deexcitation probabilities from a given state  $i$ . Furthermore, the number of maxima is equivalent to the number of bound states for the BC molecule below the initial  $i$ th level. This property of  $P_{\text{diss}}$  versus  $E$  is ex-

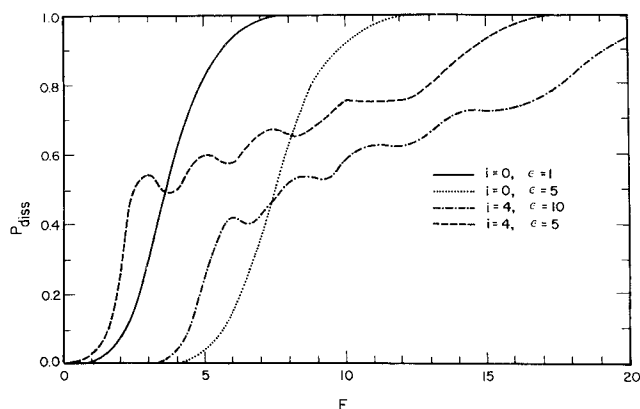


Fig. 3. Probabilities of dissociation for  $m = 0.6667$  and  $\alpha = 0.3000$ , varying  $i$  and  $\epsilon$ .

pected to persist for more realistic models of dissociation and hence could provide a measure of the number of bound levels for the dissociating molecule.

A discussion of the validity of the present model and a more detailed account of the method used to calculate  $P_{i \rightarrow f}$  will appear in a later publication. Future plans include the use of more realistic interactions such as an "untruncated" anharmonic oscillator which can be directly compared with the classical calculation of Benson and Berend [10] as well as the extension to three dimensions with the subsequent onset of rotational transitions. It is expected, however, that the qualitative features of this work will remain valid.

#### REFERENCES

- [1] D. Rapp and T. Kassal, *Chem. Rev.* 69 (1969) 61.
- [2] R. Roberts, to be published.
- [3] F. Heidrich, K. Wilson and D. Rapp, to be published.
- [4] W. Miller, to be published.
- [5] R. Marcus, to be published.
- [6] P. Pechukas and J. Light, *J. Chem. Phys.* 44 (1966) 3897.
- [7] R. B. Bernstein and K. H. Kramer, *J. Chem. Phys.* 44 (1966) 4473;  
R. D. Levine and G. Balint-Kurti, *Chem. Phys. Letters* 6 (1970) 101.
- [8] R. Montroll and K. Shuler, in: *Advances in chemical physics*, Vol. 1, ed. I. Prigogine (Interscience, New York, 1958).
- [9] D. Secrest and B. R. Johnson, *J. Chem. Phys.* 45 (1966) 4556.
- [10] S. W. Benson and G. C. Berend, *J. Chem. Phys.* 40 (1964) 1289.