

Intermolecular and intramolecular $V \rightarrow V$ transfer in the vibrational predissociation of some polyatomic van der Waals molecules

J. A. Beswick

Laboratoire de Photophysique Moléculaire du CNRS, Université de Paris Sud, 91405 Orsay, France

Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel

(Received 4 April 1980; accepted 8 May 1980)

In this paper we present a theoretical study of vibrational predissociation (VP) on the ground state potential surface of van der Waals complexes consisting of polyatomic molecules. The intermolecular interaction was represented by separate contributions of atom-atom interactions, which were expressed in terms of Morse potentials. The VP process was handled utilizing the distorted wave approximation to describe a zero-order Hamiltonian, which is separable in the intramolecular and in the intermolecular motion, while the residual interaction, which induces the reactive process, corresponds to the deviations of the intermolecular interaction from its value at the frozen intramolecular equilibrium configurations of the two constituents. Model calculations of the VP dynamics were performed for the $\text{He}\cdots\text{N}_2\text{O}$ complex and for the $(\text{N}_2\text{O})_2$ dimer, where the N_2O unit is initially excited to the (001) vibrational state. These calculations were performed for the linear configuration as well as for the T -shaped configuration of the complexes. We have considered three VP channels; (1) the $V \rightarrow T$ process, (2) the intramolecular $V \rightarrow V + T$ process and (3) the intermolecular $V \rightarrow V + T$ process. For $\text{He}\cdots\text{N}_2\text{O}$ channels (1) and (2) prevail, while for $(\text{N}_2\text{O})_2$ all three channels are open. For collinear $\text{He}\cdots\text{N}_2\text{O}$ a second-order process of type (2) dominates the VP, while for the T -shaped $\text{He}\cdots\text{N}_2\text{O}$ complex the first-order process (1) is not efficient. In both cases the VP lifetimes, τ is $\tau \sim 10^{-5}$ – 10^{-6} sec. For the collinear $(\text{N}_2\text{O})_2$ dimer a $V \rightarrow V + T$ process of type (2) dominates, with $\tau \sim 10^{-2}$ – 10^{-3} sec, the inefficiency of this process being attributed to a large mass effect. For the T -shaped $(\text{N}_2\text{O})_2$ dimer the most effective VP channel involves simultaneous intermolecular and intramolecular $V \rightarrow V + T$ process with low $\Delta E = 355 \text{ cm}^{-1}$ translational energy, which is characterized by $\tau \sim 10^{-5}$ – 10^{-6} sec. These results provide guidelines for the analysis of the infrared spectra of the $(\text{N}_2\text{O})_2$ complex.

I. INTRODUCTION

Experimental¹⁻⁷ and theoretical⁸⁻¹⁹ studies of vibrational predissociation (VP) of van der Waals (vdW) molecules provide important information regarding the basic problem of intramolecular vibrational energy flow and vibrational energy redistribution in polyatomic molecules. In this context the following basic VP processes will be exhibited with increasing complexity of the molecular constituents of the vdW complex:

(i) For a triatomic $X\text{-AB}$ vdW molecule, where AB is a conventional diatomic molecule and X represents a rare-gas atom, the VP process involves the conversion of vibrational energy of AB to translational energy of the AB and X fragments, i. e., a $V \rightarrow T$ process.^{9-11,13,14,16,19} The VP of the HeI_2 vdW molecule^{1-3,13,14,16} can be semiquantitatively accounted for in terms of the $V \rightarrow T$ process.²⁰

(ii) For a vdW dimer AB-CD , where AB and CD are both normal diatomic molecules, the VP channels involve the $V \rightarrow T$ process as well as the conversion of the vibrational energy of one molecule to vibrational energy of the other, while the energy balance is made up by translational energy. The $V \rightarrow T$ process determines the VP mechanism of a homodimer such as $\text{Cl}_2\text{-Cl}_2$.¹⁷ Intermolecular vibrational energy exchange, constituting an intermolecular $V \rightarrow V + T$ process may considerably enhance the VP rate of some vdW heterodimers.^{17,19}

(iii) For a vdW molecule $X\text{-A}$, where X is a rare-

gas atom and A is a polyatomic molecule, two VP channels should be considered. First, the conventional $V \rightarrow T$ process prevails. Second, one should consider the intramolecular degradation of a vibrational quantum of A to a lower frequency vibration of the same molecule, the energy balance being made up by translation. This process involves an intramolecular $V \rightarrow V + T$ exchange. This intramolecular process bears a close analogy to collision-induced vibrational energy redistribution in polyatomic molecules.²¹

(iv) In the case of a vdW complex A-B , consisting of a pair of polyatomic molecules A and B, the VP process can involve conventional $V \rightarrow T$ as well as additional channels which correspond to vibrational energy exchange. Two types of such VP decay mechanisms accompanied by vibrational energy exchange should be considered. First, in complete analogy to the case of the heterodimer,^{17b} we can consider the intermolecular conversion of the vibrational energy of A to the vibrational energy of B, i. e., an intermolecular $V \rightarrow V + T$ process. This intermolecular process bears a close analogy to $V \rightarrow V$ transfer in collisions²² and was considered also in relation to the broadening of infrared absorption bands in liquids.²³ Second, we can envisage the intramolecular energy exchange within the initially excited molecule A, resulting in the degradation of a vibrational quantum of A to a vibration of a lower frequency of the same A molecule, i. e., an intramolecular equivalent to the $V \rightarrow V + T$ exchange in the VP of $X\text{-A}$ considered in point (iii).

In this paper we consider the problem of the interplay between intermolecular $V \rightarrow V+T$ and intramolecular $V \rightarrow V+T$ in the vibrational predissociation of vdW complexes, consisting of polyatomic molecules, in an attempt to assess the relative importance of these decay channels. The problem of intermolecular and intramolecular vibrational energy exchange in such systems is of interest because of the following reasons:

(a) The fragmentation of the vdW bond provides a unique example for VP on a single electronic potential surface. A complete understanding of the role of vibrational energy exchange in VP will elucidate the nature of a basic molecular relaxation process.

(b) The understanding of VP of polyatomic vdW molecules is relevant for establishing the general features of bond-breaking processes in chemical systems.

(c) These processes will determine the VP mechanism and the internal energy content of the polyatomic fragments $A+B$, resulting from the fragmentation of a vibrationally excited vdW complex interrogated in a supersonic beam.¹⁻⁷

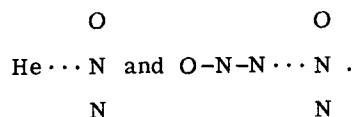
(d) Vibrational energy exchange in vdW complexes is central for the understanding of the mechanism of collision-induced vibrational relaxation, particularly at low translational temperatures. Recent studies of such^{24,25} atom-diatom vibrational relaxation should be extended to low-energy collision of polyatomic molecules.

(e) The problem of vibrational relaxation of guest polyatomic molecules in host matrices may also benefit from the understanding of vibrational energy exchange. Specific chemical interactions of the vdW type have a profound effect on the vibrational relaxation of some diatomic radicals in mixed rare-gas solids.²⁶ The role of $V \rightarrow V+T$ transfer in the VP of vdW complexes may be important for the elucidation of vibrational relaxation of polyatomic molecules in a monoatomic or polyatomic host matrix.

(f) It was suggested 30 years ago²⁷ that VP of hydrogen-bonded complexes may result in the line broadening of the infrared (IR) absorption bands of such complexes. Several workers have considered^{9-11,19} the $V \rightarrow T$ decay channel, concluding that the inefficiency of the latter process precludes any appreciable line broadening. Intramolecular and intermolecular vibrational energy exchange will be crucial for the understanding of the intramolecular dynamics of hydrogen-bonded complexes and may be important for the broadening of their IR absorption bands.

In what follows we present the results of model calculations for VP of two model systems on their ground potential surface. We shall consider the VP of the $\text{He} \cdots \text{N}_2\text{O}$ complex as well as the VP of $(\text{N}_2\text{O})_2$ dimer, which consists of a vdW molecule containing two linear triatomic molecules. The major goal of the present study is to explore the relative efficiency of the three VP channels, (1) $V \rightarrow T$, (2) intermolecular $V \rightarrow V+T$, and (3) intramolecular $V \rightarrow V+T$. For the $\text{He} \cdots \text{N}_2\text{O}$ complex, channels (1) and (2) prevail, while for the $(\text{N}_2\text{O})_2$ dimer, which was experimentally investigated,⁶

all three channels are open. In our model calculations we have considered both the linear $\text{He} \cdots \text{O}-\text{N}-\text{N}$ and $\text{N}-\text{N}-\text{O} \cdots \text{O}-\text{N}-\text{N}$ complexes, as well as the T -shaped complexes



The choice of these linear and T -shaped structures was motivated by two kinds of reasoning. First, from the practical point of view the structure of the $(\text{N}_2\text{O})_2$ complex is as yet unknown. Second, from the point of view of general methodology, the comparison of the results of the model calculations for the linear and the T -shaped vdW complexes will provide information concerning the role of low frequency out-of-plane vibration of the linear triatomic in the process of vibrational energy redistribution. In the first part of the calculation the N_2O molecule is treated in the harmonic approximation. Subsequently, the role of anharmonicity of the N_2O molecule in the dynamics of VP will be considered.

II VIBRATIONAL PREDISSOCIATION OF A POLYATOMIC VAN DER WAALS MOLECULE

We consider a vdW molecule $A \cdots B$, where A and B represent two polyatomic molecules. We shall denote by $|R|$ the distance between the centers of mass of the two molecules (Fig. 1). The total Hamiltonian of the system, after separation of the motion of the center of mass of the entire system, is

$$H = -(\hbar^2/2\mu)\nabla_{\mathbf{R}}^2 + H_A + H_B + U_{AB}, \quad (1)$$

where H_A and H_B are the internal Hamiltonians for the "free" molecules A and B , respectively, while U_{AB} is the intermolecular interaction. Finally, $\mu = M_A M_B / (M_A + M_B)$ is the reduced mass for the relative motion of A and B . We now invoke the dumbbell model for the intermolecular interaction, representing U_{AB} in terms of a sum of atom-atom interactions

$$U_{AB} = \sum_{\alpha, \alpha'} U_{\alpha\alpha'}(|\mathbf{r}_{\alpha\alpha'}|), \quad (2)$$

where $|\mathbf{r}_{\alpha\alpha'}|$ is the distance between atom α on molecule A and atom α' on molecule B . In general we have

$$\mathbf{r}_{\alpha\alpha'} = \mathbf{R} - \boldsymbol{\rho}_\alpha + \boldsymbol{\rho}_{\alpha'}, \quad (3)$$

where $\boldsymbol{\rho}_\alpha$ and $\boldsymbol{\rho}_{\alpha'}$ are distances of the atoms α and α' from the centers of mass of the molecules A and B , respectively. Denoting by $\bar{\rho}_\alpha$ and $\bar{\rho}_{\alpha'}$ the corresponding equilibrium distances, we then have

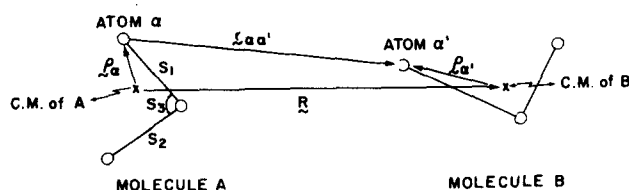


FIG. 1. Coordinate system used to describe the motion of two triatomic molecules A and B coupled through a van der Waals interaction.

$$|\mathbf{r}_{\alpha\alpha'}| = \left[|\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}|^2 + |\Delta\rho_\alpha - \Delta\rho_{\alpha'}|^2 - 2(\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}) \cdot (\Delta\rho_\alpha - \Delta\rho_{\alpha'}) \right]^{1/2}, \quad (4)$$

where $\Delta\rho_\alpha$ and $\Delta\rho_{\alpha'}$ are the displacements of atoms α and α' from their respective equilibrium positions. Expanding Eq. (4) and retaining only up to the linear terms in $\Delta\rho_\alpha$ and $\Delta\rho_{\alpha'}$, we obtain²⁸

$$|\mathbf{r}_{\alpha\alpha'}| \equiv |\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}| - \hat{\mathbf{r}}_{\alpha\alpha'} \cdot (\Delta\rho_\alpha - \Delta\rho_{\alpha'}), \quad (5)$$

where the unit vector $\hat{\mathbf{r}}_{\alpha\alpha'}$ is defined by

$$\hat{\mathbf{r}}_{\alpha\alpha'} = (\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}) / |\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}|. \quad (6)$$

In general, we can express the displacements $\Delta\rho_\alpha$ and $\Delta\rho_{\alpha'}$ in terms of two sets of internal coordinates²⁹ $\{s_i\}$ and $\{s'_i\}$ for molecules A and B, respectively,

$$\begin{aligned} \Delta\rho_\alpha &= \sum_i (a_{\alpha i} \hat{x} + b_{\alpha i} \hat{y} + c_{\alpha i} \hat{z}) s_i, \\ \Delta\rho_{\alpha'} &= \sum_{i'} (a'_{\alpha' i'} \hat{x}' + b'_{\alpha' i'} \hat{y}' + c'_{\alpha' i'} \hat{z}') s'_{i'}, \end{aligned} \quad (7)$$

where $a_{\alpha i}$, $b_{\alpha i}$, and $c_{\alpha i}$, as well as $a'_{\alpha' i'}$, $b'_{\alpha' i'}$, and $c'_{\alpha' i'}$ represent the elements of the appropriate transformations. Equation (2), together with Eqs. (5) and (7), specify the intermolecular interactions in terms of the intermolecular distance \mathbf{R} and the internal coordinates $\{s_i\}$ and $\{s'_i\}$.

To proceed with the description of the intermolecular dynamics we have to define an appropriate zero-order Hamiltonian. To accomplish this goal we use the distorted wave treatment where the zero-order Hamiltonian is

$$H_0 = -(\hbar^2/2\mu) \nabla_{\mathbf{R}}^2 + H_A + H_B + U_{AB}(|\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}|), \quad (8)$$

where the intermolecular interaction U_{AB} corresponds to the two molecules frozen at their equilibrium nuclear configurations. The residual interaction

$$V = H - H_0 = U_{AB}(|\mathbf{r}_{\alpha\alpha'}|) - U_{AB}(|\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}|) \quad (9)$$

induces the nonradiative intramolecular VP transitions. The zero-order Hamiltonian, Eq. (8), is separable and its eigenstates correspond to the discrete states

$$\psi_{v_A, v_B, l}(\{s_i\}, \{s'_i\}, |\mathbf{R}|) = \chi_{v_A}(\{s_i\}) \chi_{v_B}(\{s'_i\}) \phi_l(|\mathbf{R}|) \quad (10)$$

and to the continuum states

$$\psi_{v_A, v_B, \epsilon}(\{s_i\}, \{s'_i\}, |\mathbf{R}|) = \chi_{v_A}(\{s_i\}) \chi_{v_B}(\{s'_i\}) \phi_\epsilon(|\mathbf{R}|). \quad (11)$$

Here the rotational degrees of freedom are not considered so that Eqs. (10) and (11) represent vibrational wave functions for a fixed angular configuration. The functions $\chi_{v_A}(\{s_i\})$ and $\chi_{v_B}(\{s'_i\})$ represent general vibrational eigenstates of the molecules A and B, respectively. These nuclear eigenstates are characterized by the collection of nuclear vibrational quantum numbers v_A and v_B , and by the energies E_{v_A} and E_{v_B} , so that

$$\begin{aligned} H_A |\chi_{v_A}\rangle &= E_{v_A} |\chi_{v_A}\rangle, \\ H_B |\chi_{v_B}\rangle &= E_{v_B} |\chi_{v_B}\rangle. \end{aligned} \quad (12)$$

The eigenstates $\phi_l(|\mathbf{R}|)$ and $\phi_\epsilon(|\mathbf{R}|)$ correspond to a bound state and to a continuum state of the vdW bond, respectively, l is a discrete quantum number characterizing bound states of the vdW bond with energies E_l ,

while ϵ is the relative kinetic energy of A and B. The VP dynamics on the ground state potential surface can be adequately described¹⁴ by defining a "preparation" process, where a single $\psi_{v_A v_B l}$ discrete state is amenable to infrared optical excitation or to collisional excitation.¹⁷ The VP rate is essentially dominated by discrete-continuum (d-c) resonance interaction, while the effect of continuum-continuum coupling terms is relatively small. Accordingly, the decay rate $\Gamma_{v_A v_B l}$ of the metastable state $\psi_{v_A v_B l}$ is given by the Golden Rule

$$\Gamma_{v_A v_B l} = \pi \sum_{v_A} \sum_{v_B} |\langle \psi_{v_A v_B l} | V | \psi_{v_A' v_B' \epsilon} \rangle|^2, \quad (13)$$

where the relative kinetic energy ϵ is now taken on the energy shell

$$\epsilon = E_{v_A} + E_{v_B} + E_l - E_{v_A'} - E_{v_B'}, \quad (14)$$

while the interaction V , Eq. (9), which induces the VP process, can be expressed with the help of Eq. (2) in the form

$$V = \sum_{\alpha, \alpha'} [U_{\alpha\alpha'}(|\mathbf{r}_{\alpha\alpha'}|) - U_{\alpha\alpha'}(|\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}|)]. \quad (15)$$

Equations (13)–(15), together with Eq. (5), constitute a comprehensive and quite complete theory of VP of polyatomic vdW complexes. What remains to be done is to specify explicitly the atom-atom interaction potentials appearing in Eq. (15). These will be represented in terms of Morse potentials

$$\begin{aligned} U_{\alpha\alpha'}(|\Delta\mathbf{r}_{\alpha\alpha'}|) &= D_{\alpha\alpha'} \{ \exp(-2\beta_{\alpha\alpha'} [|\mathbf{r}_{\alpha\alpha'}| - |\bar{\mathbf{r}}_{\alpha\alpha'}|]) \\ &\quad - 2 \exp(-\beta_{\alpha\alpha'} [|\mathbf{r}_{\alpha\alpha'}| - |\bar{\mathbf{r}}_{\alpha\alpha'}|]) \}, \end{aligned} \quad (16)$$

where $D_{\alpha\alpha'}$ is an effective dissociation energy, while $\beta_{\alpha\alpha'}$ denotes a characteristic inverse length. The use of a superposition of Morse potentials, Eq. (16), to represent the intermolecular interaction is quite adequate as our previous model calculations for the HeI₂ vdW molecule¹⁸ have indicated that the VP dynamics are dominated by the short-range part of the intermolecular interaction potential. In particular, the discrete-continuum coupling terms are essentially determined by the details of the potential in the region of the minimum $\mathbf{R} = \bar{\mathbf{R}}$. We therefore expand

$$|\mathbf{R} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}| \approx |\bar{\mathbf{R}} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}| + \hat{\mathbf{r}}_{\alpha\alpha'} \cdot \Delta\mathbf{R}, \quad (17)$$

where $\Delta\mathbf{R}$ is the displacement of the intermolecular distance \mathbf{R} from the equilibrium distance $\bar{\mathbf{R}}$, and $\hat{\mathbf{r}}_{\alpha\alpha'}$ is the unit vector defined in Eq. (6) evaluated at the equilibrium configuration. Using Eqs. (5)–(7), (10), and (11), together with Eqs. (15)–(17), the discrete-continuum coupling can be written in terms of products of intramolecular contributions and of intermolecular terms

$$\begin{aligned} \langle \psi_{v_A v_B l} | V | \psi_{v_A' v_B' \epsilon} \rangle &= \sum_{\alpha, \alpha'} D_{\alpha\alpha'} [A_{\alpha\alpha'}^{(2)}(v_A, v_B, v_A', v_B', \alpha, \alpha') B_{l\epsilon}^{(2)}(\alpha, \alpha') \\ &\quad - 2 A_{\alpha\alpha'}^{(1)}(v_A, v_B, v_A', v_B', \alpha, \alpha') B_{l\epsilon}^{(1)}(\alpha, \alpha')], \end{aligned} \quad (18)$$

where the intramolecular contributions are

$$\begin{aligned} A_{\alpha\alpha'}^{(j)} &= \langle \chi_{v_A v_B} | \{ \exp[j\beta_{\alpha\alpha'} \hat{\mathbf{r}}_{\alpha\alpha'} \cdot (\Delta\rho_\alpha - \rho_{\alpha'})] - 1 \} | \chi_{v_A' v_B'} \rangle, \\ j &= 1, 2, \end{aligned} \quad (19a)$$

with $\Delta\rho_\alpha$ and $\Delta\rho_{\alpha'}$ given by Eq. (7), while the intermo-

lecular contributions are given by

$$B_{(\alpha, \alpha'), j}^{(j)} = \exp[-j\beta_{\alpha\alpha'}(|\bar{\mathbf{R}} - \bar{\rho}_\alpha + \bar{\rho}_{\alpha'}| - |\bar{\mathbf{r}}_{\alpha\alpha'}|)] \\ \times \langle \phi_j | \exp[-j\beta_{\alpha\alpha'} \hat{\mathbf{r}}_{\alpha\alpha'} \cdot \Delta \mathbf{R}] | \phi_e \rangle, \quad j=1, 2. \quad (19b)$$

The eigenfunctions $\phi_j(|\mathbf{R}|)$ and $\phi_e(|\mathbf{R}|)$ of the vdW bond can be obtained by fitting the potential $U_{AB}(|\mathbf{R}|)$ in Eq. (8) to the Morse form

$$U_{AB}(|\mathbf{R}|) = D (\exp[-2\beta(|\mathbf{R}| - |\bar{\mathbf{R}}|)] - 2 \exp[-\beta(|\mathbf{R}| - |\bar{\mathbf{R}}|)]). \quad (20)$$

The explicit expressions for the intermolecular matrix elements $\langle \phi_j | \exp[-\eta(|\mathbf{R}| - |\bar{\mathbf{R}}|)] | \phi_e \rangle$ have already been provided⁸

$$\langle \phi_j | \exp[-\eta(|\mathbf{R}| - |\bar{\mathbf{R}}|)] | \phi_e \rangle = (\alpha \pi \hbar)^{-1} \left(\frac{l! (2K - 2l - 1)!}{\Gamma(2K - l)} \right)^{1/2} \\ \times (-1)^l [\mu \sinh(2\pi\theta)]^{1/2} |\Gamma(\frac{1}{2} - K - i\theta)| (2K)^{-n/\alpha} \\ \times \sum_{n=0}^l \frac{\Gamma(2K - l) (-1)^{n-l} |\Gamma(K + i\theta - n + \eta/\alpha - \frac{1}{2})|^2}{n! (l-n)! \Gamma(2K - l - n) \Gamma(-n + \eta/\alpha)}, \quad (21a)$$

with the definitions

$$K = (\hbar\beta)^{-1} (2\mu D)^{1/2} \equiv 2D/\hbar\omega, \quad (21b)$$

$$\theta = (\hbar\beta)^{-1} (2\mu\epsilon)^{1/2} \equiv 2(D\epsilon)^{1/2}/\hbar\omega. \quad (21c)$$

Equations (13) and (17) constitute a comprehensive, quite complete, and practical theory of VP of polyatomic vdW molecules. It should be emphasized at this point that all the approximations introduced up to the present stage essentially pertain only to the description of the intermolecular interaction, while the intramolecular vibrational states $\chi_{v_A v_B}$ and $\chi_{v_A' v_B'}$ of the individual molecules are retained in a general form without alluding to any specific approximation. An approximate description of the intramolecular potential in terms of a harmonic potential will considerably simplify the analysis for specific model system which will now be considered.

III. MODEL SYSTEMS

We have considered four model systems corresponding to the collinear and perpendicular VP of atom-linear triatomic and of linear triatomic-linear triatomic vdW molecules. The relevant schemes are portrayed in Fig. 2. The internal coordinates for the linear triatomic molecules (see Fig. 2) are s_1 and s_2 , corresponding to the displacements from equilibrium of the distances between atoms 1 and 2, and 2 and 3, respectively, and s_3 which corresponds to the variation of the bending angle. The coefficients $a_{\alpha t}$, $b_{\alpha t}$, and $c_{\alpha t}$ of Eq. (7), relating the internal coordinates to the displacements $\Delta\rho_\alpha$ from the center of the mass are given by (choosing the z axis along the molecular axis)

$$b_{13} = a_{13} = -m_2 m_3 l_2 / N, \\ b_{23} = a_{23} = m_1 m_3 (l_1 + l_2) / N, \\ b_{33} = a_{33} = -m_1 m_2 l_1 / N, \\ c_{11} = -(m_2 + m_3) / M, \quad c_{12} = -m_3 / M = c_{22}, \\ c_{21} = m_1 / M = c_{31}, \quad c_{32} = (m_1 + m_2) / M, \quad (22)$$

where m_1 , m_2 , and m_3 are the masses of the atoms, l_1 and l_2 are the equilibrium distances of the two bonds,

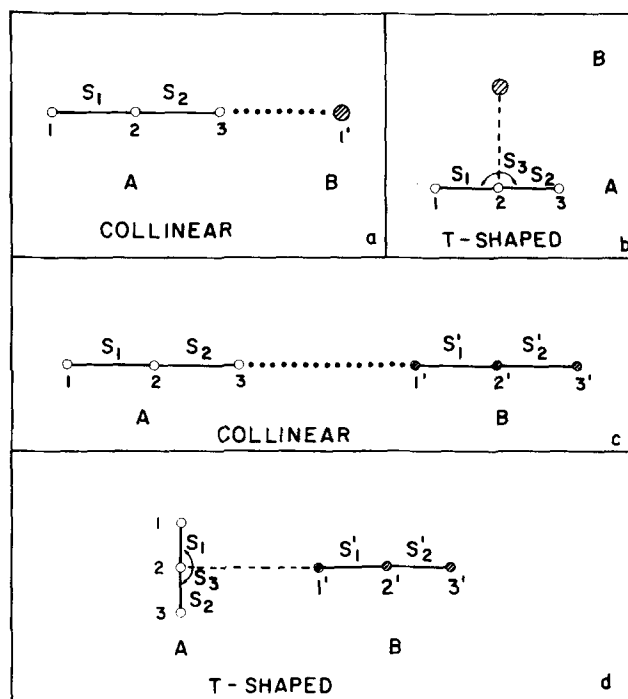


FIG. 2. Model systems of linear and T-shaped van der Waals molecule of atom-linear triatomic complex and a dimer of two triatomic molecules.

M is the total mass of the triatomic molecule, and

$$N = (m_1 m_2 l_1^2 + m_1 m_3 (l_1 + l_2)^2 + m_2 m_3 l_2^2 + m_2 m_3 l_2^2) / l_1 l_2. \quad (22a)$$

All other coefficients are zero. We now have to specify the vibrational eigenstates of the fragments. In the model calculations presented in this section we have adopted the harmonic approximation for the intramolecular motion. The eigenstates are thus products of normal mode wavefunctions, i. e.,

$$|\chi_{v_A}\rangle = |v_A^{(1)}\rangle_{Q_1} |v_A^{(2)}\rangle_{Q_2} \cdots |v_A^{(k)}\rangle_{Q_k} \cdots, \quad (23)$$

where Q_1, Q_2, \dots , etc., are the normal coordinates. The relation between the internal coordinates s_t and the normal coordinates Q_k is given by the linear transformation²⁹

$$s_t = \sum_k L_{tk} Q_k. \quad (24)$$

For the case of linear triatomic molecules, expressing the intramolecular potential as

$$W = \frac{1}{2} (f_{11} s_1^2 + f_{12} s_1 s_2 + f_{22} s_2^2 + f_{33} s_3^2), \quad (25)$$

results in the normal frequencies ν_1 , ν_2 , and ν_3 , with

$$4\pi^2(\nu_1^2 + \nu_3^2) = \frac{f_{11}}{\mu_{12}} + \frac{f_{22}}{\mu_{23}} - 2 \frac{f_{12}}{m_2}, \\ 16\pi^4 \nu_1^2 \nu_3^2 = (f_{11} f_{22} - f_{12}^2) M / m_1 m_2 m_3, \\ 4\pi^2 \nu_2^2 = \frac{f_{33} [l_1^2/m_3 + l_2^2/m_1 + (l_1 + l_2)^2/m_2]}{l_1^2 l_2^2}, \quad (26)$$

where $\mu_{12} = m_1 m_2 / (m_1 + m_2)$ and $\mu_{23} = m_2 m_3 / (m_2 + m_3)$ are reduced masses. The coefficients L_{tk} for the transformation between normal modes and internal coordinates,

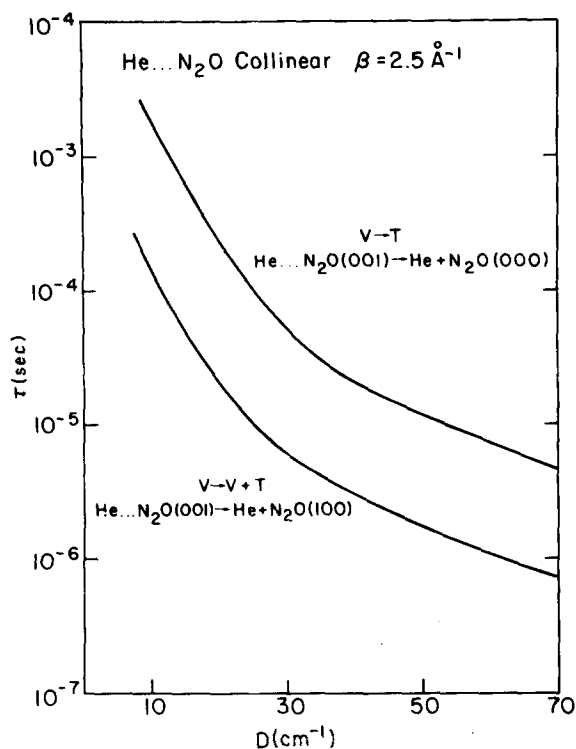


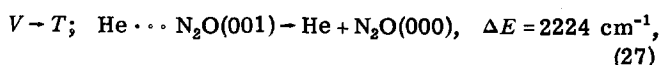
FIG. 3. Lifetimes for VP of a collinear $\text{He} \cdots \text{N}_2\text{O}$ complex initially excited at (001) of the N_2O constituent. The potential parameters for the van der Waals bond, Eq. (20), are $\beta = 2.5 \text{ \AA}^{-1}$, while the dissociation energy is varied in the range 10–70 cm^{-1} . Calculations were performed for the channels (27) and (28).

Eq. (24), are given by standard methods.²⁹ We have considered the linear molecule N_2O with force constants and equilibrium distances taken from the literature.^{30,31} We shall now proceed to discuss the different model systems portrayed in Fig. 2.

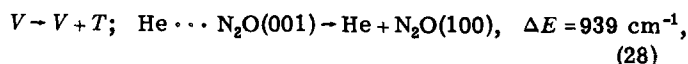
A. Collinear $\text{He} \cdots \text{N}_2\text{O}$

The intermolecular interaction, Eq. (2), is represented in this case by a simple atom–atom interaction between the nearest atoms of the two molecules, i.e., between atoms 3 and 1 (see Fig. 2). This is sufficient for the understanding of the general qualitative behavior of the VP dynamics, in view of our poor knowledge of the details of the interaction potential. In the normal mode description of N_2O there will then be no coupling between the bending mode and the other degrees of freedom. We consider an initial state after photon absorption corresponding to the excitation of N_2O , the other two modes being in their ground states. This state will be denoted by (001); i.e., $\nu_1 = 0$, $\nu_2 = 0$, and $\nu_3 = 1$.

Two VP processes are then possible:



involving the conversion of vibrational energy in mode 3 to translational energy of the fragments, and



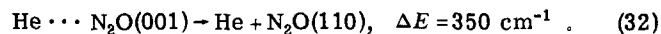
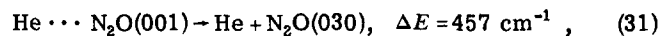
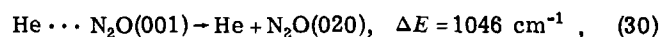
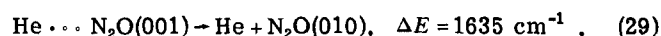
corresponding to the intramolecular degradation of the

vibrational quantum in mode 3 to the lower frequency vibration ν_1 , the excess energy being transformed into translational kinetic energy. Reaction (28) corresponds to a second-order process and, therefore, the intramolecular coefficients $A^{(j)}$ [see Eq. (19a)] will be smaller. On the other hand the excess energy ΔE being smaller, in this case the intermolecular terms $B^{(j)}$ [see Eq. (20)] will be larger according to the energy gap law.^{14,32} The competition between these two opposite effects will finally determine which one of the two processes, (27) or (28) will provide the most efficient decay channel.

We have calculated the lifetimes τ for processes (27) and (28), evaluating the VP rate, Eq. (13), and using the relationship $\tau = \hbar/2\Gamma$. The results for some typical intermolecular potential parameters are presented in Fig. 3. From the calculations two conclusions emerge. First, we note that the intramolecular $V \rightarrow V + T$ process, Eq. (28), is about an order of magnitude more efficient than the simple first order $V \rightarrow T$ process, Eq. (27). Second, for reasonable parameters of the vdW bond the calculated VP lifetime for the more efficient $V \rightarrow V + T$ process is $\tau \sim 10^{-15} - 10^{-8}$ sec.

B. T-shaped $\text{He} \cdots \text{N}_2\text{O}$ molecule

In this case we cannot get away by considering only the nearest-neighbor interatomic interaction. If we only consider the interaction between nearest atoms, i.e., the two atoms 2 and 1' in Fig. 2(b), there will be no coupling between the intermolecular vibration and the Q_3 mode (in the harmonic approximation for N_2O). We have therefore considered both the interaction between nearest atoms as well as the interaction between the helium atom and the two end atoms of N_2O . We assume the same parameters β and D for all the pairwise Morse potentials. Now, we will have in addition to the $V \rightarrow T$ process (27) and the intramolecular $V \rightarrow V + T$ process (28) the following additional intramolecular $V \rightarrow V + T$ channels:



All of these new intramolecular $V \rightarrow V + T$ channels involve the bending excitation of the N_2O fragment. Process (29) is a second-order process similar to the one considered before in Eq. (28), the only difference being that the final state of N_2O involves bending rather than symmetric stretch vibration. Processes (30) and (32) are third-order processes in which two quanta are created, while process (31) is a fourth-order process in which three quanta of the bending vibrational mode are excited. The lifetimes for all these processes as a function of the dissociation energy parameter D are plotted in Fig. 4. The following features of the numerical results should be noted. Firstly, for the T-shape vdW molecule the first-order $V \rightarrow T$ process, Eq. (27), is more efficient than any of the second-order $V \rightarrow V + T$ processes, Eqs. (28)–(32). The efficiency of the $V \rightarrow T$ channel for the T-shaped configuration is in contrast with the characteristics of the linear molecule where

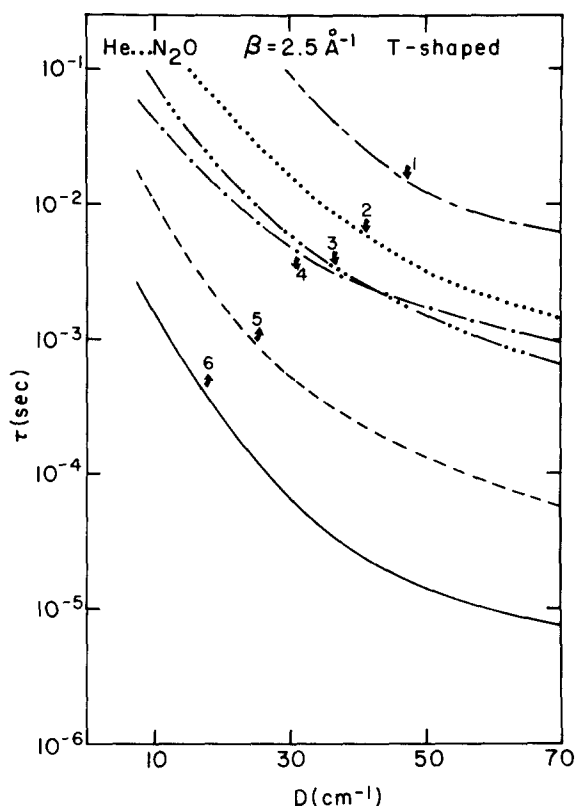


FIG. 4. Lifetimes for VP of a T -shaped $\text{He}\cdots\text{N}_2\text{O}$ complex initially excited at (001) of the N_2O constituent. The potential parameters are identical to those of Fig. 1. Calculations were performed for the channels (27)–(32). The curves correspond to the following processes: (1) $V \rightarrow V+T$: $\text{He}\cdots\text{N}_2\text{O}(001) \rightarrow \text{He} + \text{N}_2\text{O}(030)$; (2) $V \rightarrow V+T$: $\text{He}\cdots\text{N}_2\text{O}(001) \rightarrow \text{He} + \text{N}_2\text{O}(020)$; (3) $V \rightarrow V+T$: $\text{He}\cdots\text{N}_2\text{O}(001) \rightarrow \text{He} + \text{N}_2\text{O}(100)$; (4) $V \rightarrow V+T$: $\text{He}\cdots\text{N}_2\text{O}(001) \rightarrow \text{He} + \text{N}_2\text{O}(110)$; (5) $V \rightarrow V+T$: $\text{He}\cdots\text{N}_2\text{O}(001) \rightarrow \text{He} + \text{N}_2\text{O}(010)$; (6) $V \rightarrow T$: $\text{He}\cdots\text{N}_2\text{O}(001) \rightarrow \text{He} + \text{N}_2\text{O}(000)$.

the $V \rightarrow V+T$ process, Eq. (28), dominates the VP dynamics. Secondly, the VP lifetimes for the $V \rightarrow T$ channels of the T -shaped and of the linear configurations of the $\text{He}\cdots\text{N}_2\text{O}$ are very similar. Accordingly, the VP process of the T -shaped vdW molecule is less efficient by about one order of magnitude than that of the linear molecule.

C. Collinear $(\text{N}_2\text{O})_2$ dimer

In complete analogy with the $\text{He}\cdots\text{N}_2\text{O}$ case, we have the $V \rightarrow T$ process, Eq. (27), and the $V \rightarrow V+T$ process, Eq. (28), with the He atom being replaced by another N_2O molecule in its ground state. However, the intermolecular dissociation energy parameter D is much larger in this case. Also, the reduced mass for intermolecular relative motion is larger. These two changes affect the VP lifetimes in opposite ways. While the increase of D usually decreases the VP lifetimes,¹⁴ the increase of the reduced mass results in an increase of the VP lifetimes.^{14,32} In Fig. 5 we have presented the two processes, the $V \rightarrow T$ process $(000)\cdots(001) \rightarrow (000) + (000)$ and the $V \rightarrow V+T$ process $(000)\cdots(001) \rightarrow (000) + (100)$, as a function of the dissociation energy parameter D . We note that the $V \rightarrow V+T$ process is faster than $V \rightarrow T$ predissociation in complete analogy with the situa-

tion for the collinear $\text{He}\cdots\text{N}_2\text{O}$ molecule. On the other hand, the absolute values of the lifetimes for $(\text{N}_2\text{O})_2$ collinear dimers are much larger than the corresponding values for collinear $\text{He}\cdots\text{N}_2\text{O}$, demonstrating the strong effect of the reduced mass^{14,32} on the VP dynamics.

D. T -shape $(\text{N}_2\text{O})_2$ dimer

In this case we have the following VP processes:

$$(000)\cdots(001) \rightarrow (000) + (000), \quad \Delta E = 2224 \text{ cm}^{-1}, \quad (33)$$

$$(000)\cdots(001) \rightarrow (010) + (000), \quad \Delta E = 1635 \text{ cm}^{-1}, \quad (34)$$

$$(000)\cdots(001) \rightarrow (020) + (000), \quad \Delta E = 1046 \text{ cm}^{-1}, \quad (35)$$

$$(000)\cdots(001) \rightarrow (030) + (000), \quad \Delta E = 457 \text{ cm}^{-1}, \quad (36)$$

$$(000)\cdots(001) \rightarrow (000) + (100), \quad \Delta E = 939 \text{ cm}^{-1}, \quad (37)$$

$$(000)\cdots(001) \rightarrow (010) + (100), \quad \Delta E = 350 \text{ cm}^{-1}. \quad (38)$$

Equation (33) corresponds to the usual $V \rightarrow T$ process, while Eqs. (34)–(36), correspond to intermolecular $V \rightarrow V+T$ processes in which vibrational energy in one molecule is converted in vibrational energy of the other molecule forming the dimer. Equation (37) corresponds to an intramolecular $V \rightarrow V+T$ process. Finally, Eq. (38) describes a mixed $V \rightarrow V+T$ process in which the initial vibrational quantum in the mode ν_3 is converted into one vibrational quantum in the mode ν_1 of the same

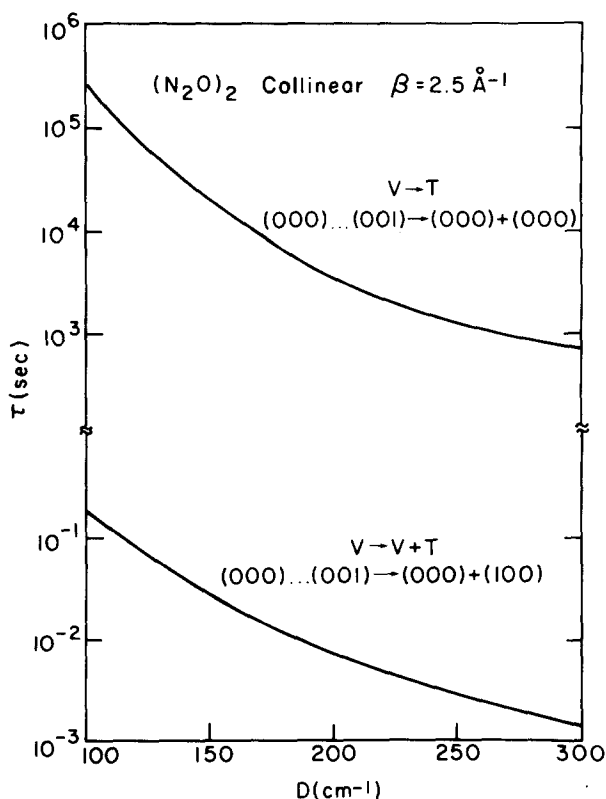


FIG. 5. Lifetimes for VP of the collinear $(\text{N}_2\text{O})_2$ dimer initially excited at the (001) state of N_2O . The atom–atom potential parameters, Eq. (20), are $\beta = 2.5 \text{ \AA}^{-1}$, while the dissociation energy of the van der Waals bond was varied in the range $D = 100\text{--}300 \text{ cm}^{-1}$. Calculations were performed for the $V \rightarrow T$ channel and for the intramolecular $V \rightarrow V+T$ channel.

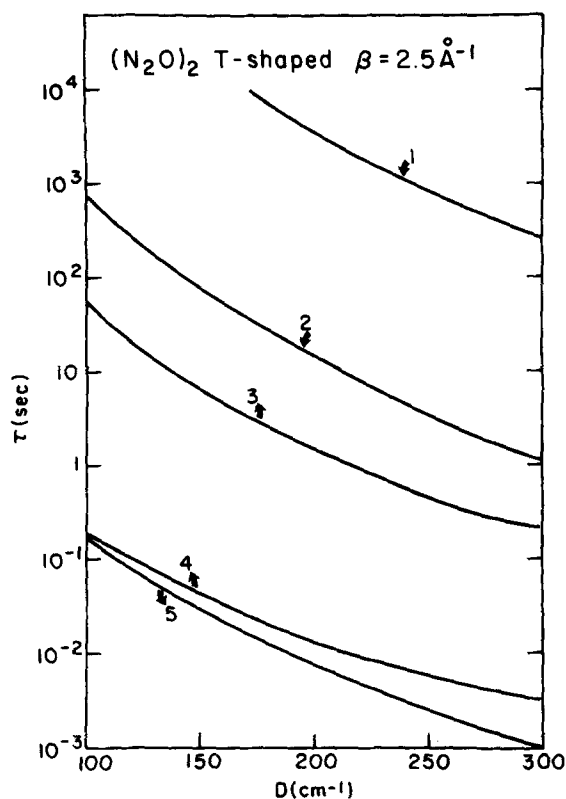


FIG. 6. Lifetimes for VP of the T -shaped $(\text{N}_2\text{O})_2$ dimer initially excited at the (001) state of N_2O . The intermolecular potential was constructed from three atom-atom Morse functions, each of which being given by Eq. (20) with $\beta = 2.5 \text{ \AA}^{-1}$ and $D = 100\text{--}300 \text{ cm}^{-1}$. Calculations were performed for the channels (33)–(37). The curves correspond to the following processes: (1) $V \rightarrow T$: $(000) \cdots (001) \rightarrow (000) + (000)$; (2) $V \rightarrow V+T$: $(000) \cdots (001) \rightarrow (010) + (000)$; (3) $V \rightarrow V+T$: $(000) \cdots (001) \rightarrow (020) + (000)$; (4) $V \rightarrow V+T$: $(000) \cdots (001) \rightarrow (030) + (000)$; (5) $V \rightarrow V+T$: $(000) \cdots (001) \rightarrow (000) + (100)$.

molecule and in an additional vibrational quantum in mode ν_2 of the second N_2O molecule.

In Figs. 6 and 7 are presented the results of model calculations of the VP lifetimes for processes (33)–(38) for different intermolecular potential parameters. We see that, in general, the processes with smaller excess translational energy ΔE are characterized by shorter lifetimes. One exception, however, is the second-order process (37), which is faster than the fourth-order process (36), although it has a value of ΔE which is twice as large. The most efficient VP channel involves the mixed process (38) which is characterized by the smallest of ΔE . From a cursory examination of the results of the model calculations presented in Figs. 5–7, we conclude that for a wide range of reasonable potential parameters, which specify the vdW bond, the predicted features of the VP dynamics of the $(\text{N}_2\text{O})_2$ dimer are as follows:

(i) The major decay channel involves the third-order process (38), which involves simultaneous intermolecular and intramolecular vibrational energy exchange and is characterized by the lowest translational energy, in accordance with the energy gap law.

(ii) All other decay channels (33)–(37) are considerably less efficient than the dominating channel (38). The branching ratio between the two most efficient channels (37) and (38) is 10^{-3} ,

(iii) The VP lifetime of the T -shaped $(\text{N}_2\text{O})_2$ vdW complex is $10^{-5}\text{--}10^{-6}$ sec.

IV. COMPARISON WITH EXPERIMENT

We now turn to the confrontation of our theoretical results with the experimental evidence. The $(\text{N}_2\text{O})_2$ dimer excited to the $\text{N}_2\text{O}(001) \cdots \text{N}_2\text{O}(000)$ state exhibits VP on the ground state potential surface.⁸ Gough, Miller, and Scoles have measured the infrared spectrum of N_2O dimers in a beam at low temperatures.⁶ The VP lifetime of the complex was estimated to be in the range $10^{-12} \leq \tau \leq 10^{-4}$ sec, and the lower limit was obtained from the assignment of the entire width of the infrared absorption band to lifetime broadening, while the upper limit was estimated from a time of flight experiment. Recently, Bernstein and Kolb³³ have performed a detailed analysis of the inhomogeneously broadened absorption line shapes, showing that there are $10^4\text{--}10^5$ lines/ cm^{-1} at the beam temperature. Bernstein and Kolb³³ have attributed the continuous absorption spectrum⁶ to arise from thermal broadening rather than from lifetime broadening, and

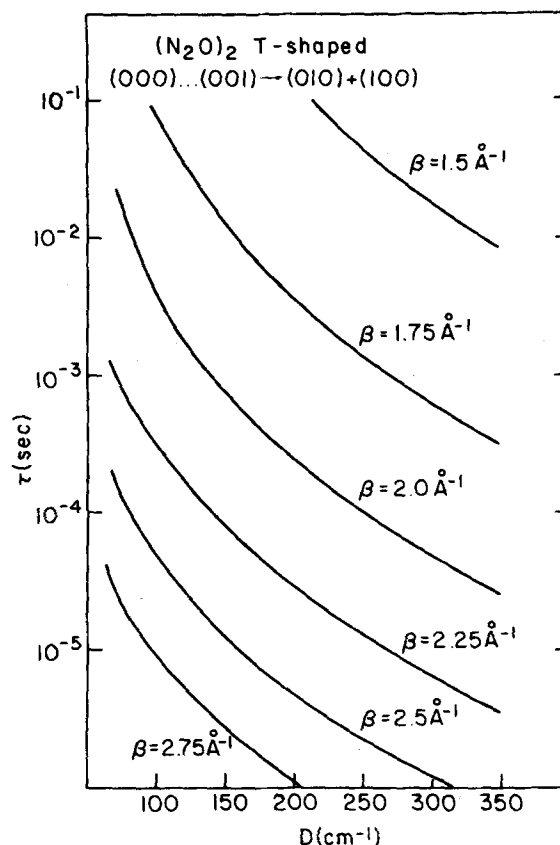


FIG. 7. VP lifetimes for channel (38) of the T -shaped $(\text{N}_2\text{O})_2$ dimer initially excited to the (001) state of N_2O . The intermolecular van der Waals potential was constructed as a superposition of three atom-atom Morse potentials, each of which being given by Eq. (20). The reciprocal length was varied in the range $\beta = 1.5\text{--}2.75 \text{ \AA}^{-1}$, while the dissociative energy was varied in the range $D = 100\text{--}300 \text{ cm}^{-1}$.

have estimated the VP lifetimes to be in the range 10^{-4} – 10^{-6} sec. It is apparent that at the present stage of development of this interesting area theory will be extremely useful in providing general outlines for the understanding of the VP dynamics of such vdW complexes. The structure of the $(\text{N}_2\text{O})_2$ dimer has not yet been determined, however, Bernstein and Kolb³³ favor the T-shaped configuration on the basis of spectroscopic evidence. The numerical model calculations for the VP of the T-shaped vdW complex provide a theoretical estimate of $\tau = 10^{-5}$ – 10^{-6} sec for the VP lifetime. This theoretical result is close to the lower limit of τ set by Gough *et al.*,⁶ being in accord with the recent analysis of the available experimental data.³³ We would like to conclude this discussion of the VP dynamics of the $(\text{N}_2\text{O})_2$ dimer by pointing out that our model calculations provide evidence for the efficiency of the simultaneous intramolecular and intermolecular vibrational energy redistribution accompanying the VP process and result in explicit predictions regarding the vibrational energy of the products, which can be subjected to an experimental test.

Finally, we would like to comment briefly on the VP dynamics of the $\text{He} \cdots \text{N}_2\text{O}$ complex and its relation to the VP of the $\text{He} \cdots \text{NO}_2$ molecule in the 2B electronically excited state of NO_2 . While our model calculations for the VP of the linear $\text{He} \cdots \text{N}_2\text{O}$ complex on the ground state potential surface result in $\tau = 10^{-5}$ – 10^{-6} sec, the VP lifetime of the electronically excited $\text{He} \cdots \text{NO}_2({}^2B)$ is $\tau \sim 10^{-11}$ sec.³⁴ We would like to argue that our results for the ground state $\text{He} \cdots \text{N}_2\text{O}$ are inapplicable to VP in an electronically excited state of a polyatomic vdW complex, where new mechanisms set in.^{34,35} The $\text{He} \cdots \text{NO}_2({}^2B)$ vdW complex is expected to be characterized by a moderately high density of vibronic levels, resulting from interstate scrambling within the NO_2 molecule with one state per 10 – 20 cm^{-1} . Now, the restrictions imposed by the energy gap law on the efficiency of the VP process can easily be relaxed. Near-resonance VP can occur as, in view of the congested level structure of the molecular eigenstates, degradation of vibrational energy will occur between closely lying states and the kinetic energy of the fragments will be very low, i.e., of the order of level spacing between molecular eigenstates. The description of this process involving induced vibrational energy exchange between molecular eigenstates requires the incorporation of intramolecular anharmonicity effects. These effects will be considered in the next section.

V. DISCUSSION

We have presented in this paper model calculations for VP lifetimes of the vdW complexes, $\text{He} \cdots \text{N}_2\text{O}$ and $\text{N}_2\text{O} \cdots \text{N}_2\text{O}$, when the initial state corresponds to the excitation of a ν_3 vibrational quantum of a N_2O subunit. These calculations rest on the following assumptions: (i) we disregard rotational effects; (ii) we use a dumb-bell model potential, the total vdW interaction being represented by separate contributions of atom–atom interactions; (iii) the atom–atom interactions are represented by Morse potentials; and (iv) the intramolecular

potential (i.e., the N_2O potential) is represented in the harmonic approximation.

Assumption (i) is a reasonable approximation for vdW molecules containing N_2O . If the VP process is rotationally assisted, such process will be efficient only if a substantial amount of the excess energy ΔE is transformed to rotational energy of the fragments. This will imply high rotational states of the N_2O molecule whose rotational constant is small. As the initial temperature is low, this can be obtained only provided that the intermolecular vdW potential is highly anisotropic, which is certainly not the case. We conclude that, although rotational effects may change fine details of the VP dynamics, for molecules involving N_2O or heavier molecules they cannot provide a faster decay channel for VP. In systems like $(\text{HF})_2$, for example, the situations may be drastically different.¹⁹

Assumption (ii) is likely to be a good approximation for vdW molecules. We have already discussed the validity of assumption (iii) in relation with our previous results,¹⁸ demonstrating that the VP rates are essentially determined by the details of the potential surface in the region of the minimum where the Morse functional form is adequate.

Assumption (iv) has to be examined in detail. If the intramolecular anharmonic terms of the potential are included, the vibrational wave functions χ_{v_A} and χ_{v_B} will be given by linear combinations of the normal mode wave functions, Eq. (23), i.e.,

$$|\chi_{v_A}\rangle = \sum_{v_A^{(1)}v_A^{(2)}v_A^{(3)}\dots} C_{v_A^{(1)}v_A^{(2)}v_A^{(3)}\dots} |v_A^{(1)}\rangle_{Q_1} |v_A^{(2)}\rangle_{Q_2} |v_A^{(3)}\rangle_{Q_3} \dots \quad (39)$$

and similarly for $|\chi_{v_B}\rangle$. Equation (39) implies that a VP process involving $V \rightarrow V+T$, which in the harmonic approximation will be of third order in the intermolecular coupling constant β , may now be second order or first order. However, in order that such reduction of the order of the $V \rightarrow V+T$ process be effective, the mixing coefficient $C_{v_A^{(1)}v_A^{(2)}v_A^{(3)}\dots}$ should not be too small. We expect that for low vibrational excitation, which is the case considered here, these coefficients will be rather small and, therefore, the VP rates are determined mainly by the intermolecular anharmonicity rather than by the intramolecular anharmonicity. For example, for the most strongly coupled level to the initial state (001) in the N_2O molecule [which is the (200) level located at ~ 350 cm^{-1} above the (001) level], the mixing coefficient is of the order of 0.1. If we compare the rates of the direct second-order process, in the harmonic approximation

$$(001) - (000) - (100), \quad (40)$$

with the first-order process in the anharmonic N_2O molecule

$$[(001) + C(200)] - (100), \quad (41)$$

we find that the latter process may be comparable in some cases (depending on the intermolecular potential parameter β) to the former but is never expected to be much faster. We conclude that for low vibrational excitation intramolecular anharmonicity may contribute to

the VP rates but will not provide the rate determining mechanism. For higher excited vibrational states this situation will be altered and intramolecular anharmonicity effects will dominate the VP dynamics.

ACKNOWLEDGMENT

One of Us (J. A. B.) is grateful to the Department of Chemistry, University of California, Los Angeles, for their kind hospitality while completing this work.

- ¹R. E. Smalley, D. H. Levy, and L. Wharton, *J. Chem. Phys.* **64**, 3266 (1976).
- ²M. S. Kim, R. E. Smalley, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **65**, 1216 (1976).
- ³K. E. Johnson, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **69**, 2719 (1978).
- ⁴R. E. Smalley, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **66**, 2750 (1977).
- ⁵G. Kubiak, P. S. H. Fitch, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **68**, 4477 (1978).
- ⁶T. F. Gough, R. E. Miller, and G. Scoles, *J. Chem. Phys.* **69**, 1588 (1978).
- ⁷M. A. Hoffbauer, W. R. Gentry, and C. F. Giese, in *Laser Induced Processes in Molecules*, edited by K. Kompa and S. D. Smith, Springer Ser. Chem. Phys. Vol. 6 (Springer, Berlin, 1978).
- ⁸N. Rosen, *J. Chem. Phys.* **1**, 319 (1933).
- ⁹C. A. Coulson and G. N. Robertson, *Proc. R. Soc. London Ser. A* **337**, 167 (1974).
- ¹⁰C. A. Coulson and G. N. Robertson, *Proc. R. Soc. London Ser. A* **342**, 289 (1975).
- ¹¹G. N. Robertson, *J. Chem. Soc. Faraday Trans. 2* **72**, 1153 (1976).
- ¹²C. J. Ashton and M. Child, *Faraday Discuss. Chem. Soc.* **62**, 307 (1977).
- ¹³J. A. Beswick and J. Jortner, *Chem. Phys. Lett.* **49**, 13 (1977).
- ¹⁴J. A. Beswick and J. Jortner, *J. Chem. Phys.* **68**, 2277 (1978).
- ¹⁵J. A. Beswick and J. Jortner, *J. Chem. Phys.* **68**, 4453 (1978).
- ¹⁶J. A. Beswick and J. Jortner, *J. Chem. Phys.* **69**, 512 (1978).
- ¹⁷(a) J. A. Beswick and J. Jortner, *J. Chem. Phys.* **71**, 4737 (1979); (b) J. A. Beswick and J. Jortner, *Chem. Phys. Lett.* **65**, 240 (1979).
- ¹⁸J. A. Beswick, G. Delgado Barrio, and J. Jortner, *Chem. Phys.* **70**, 3895 (1979).
- ¹⁹G. Ewing, *J. Chem. Phys.* **72**, 2096 (1980).
- ²⁰In the present discussion of VP of linear and of T-shaped vdW molecules we shall disregard the effects of vibrational-rotational energy conversion. Such $V \rightarrow R + T$ processes may be important in some cases, e.g., in the VP of the ArHCl complex.
- ²¹C. S. Parmenter and K. Y. Tang, *Chem. Phys.* **27**, 127 (1978).
- ²²E. Weitz and G. Flynn, *Ann. Rev. Phys. Chem.* **25**, 275 (1974).
- ²³W. G. Rothschild, *J. Chem. Phys.* **65**, 455 (1976).
- ²⁴E. E. Nikitin, *Opt. Spectrosc.* **9**, 8 (1960).
- ²⁵G. Ewing, *Chem. Phys.* **29**, 253 (1978).
- ²⁶J. Goodman and L. E. Brus, *J. Chem. Phys.* **67**, 4858 (1977).
- ²⁷B. I. Stepanov, *Nature (London)* **157**, 808 (1946).
- ²⁸A. Miklavc and S. Fisher, *Chem. Phys. Lett.* **44**, 209 (1976).
- ²⁹E. Wilson, J. C. Decius, and P. Cross, in *Molecular Vibrations* (McGraw-Hill, New York, 1955).
- ³⁰J. Vulovic, in *Critical Evaluation of Chemical and Physical Structural Information* (Natl. Acad. Sci., Washington, D. C., 1974).
- ³¹J. C. Armiot, thèse d'Etat (Université Pierre et Marie Curie, Paris, 1976).
- ³²G. Ewing, *J. Chem. Phys.* **71**, 3143 (1979).
- ³³L. Bernstein and C. Kolb, *J. Chem. Phys.* **71**, 2818 (1979).
- ³⁴D. H. Levy, *J. Chem. Phys.* **68**, 1454 (1968).
- ³⁵J. A. Beswick and J. Jortner, *J. Chem. Phys.* **68**, 1455 (1978).